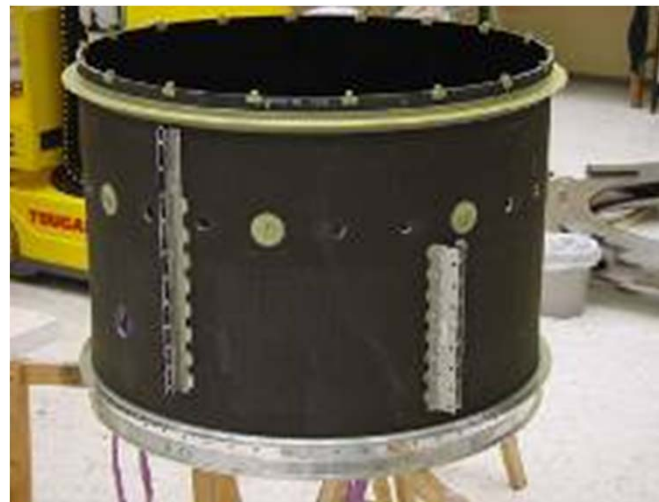
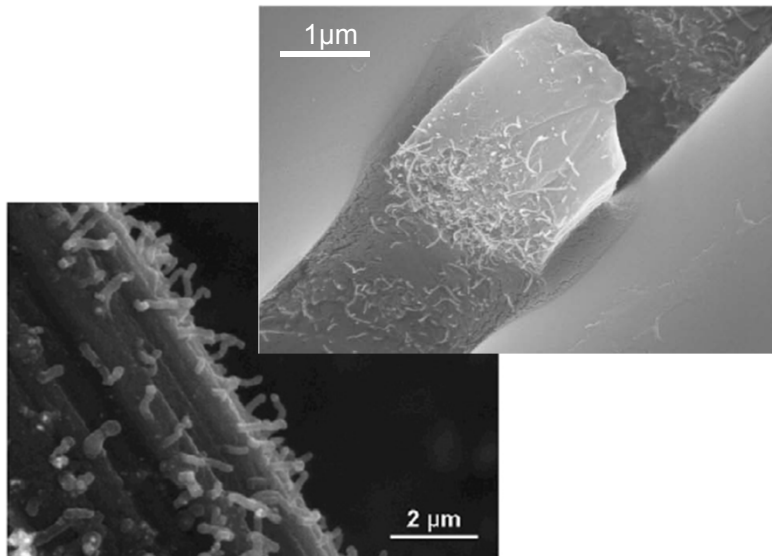


NANOTECHNOLOGIES FOR STRUCTURAL COMPOSITE MATERIALS

Review of latest research developments and open challenges towards application

*V. Kostopoulos**, *A. Vavouliotis*, *G. Sotiriadis*, *A. Baltopoulos*,
E. Fiamegkou, *C. Kostagiannakopoulou*, *A. Masouras*

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Starting point

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

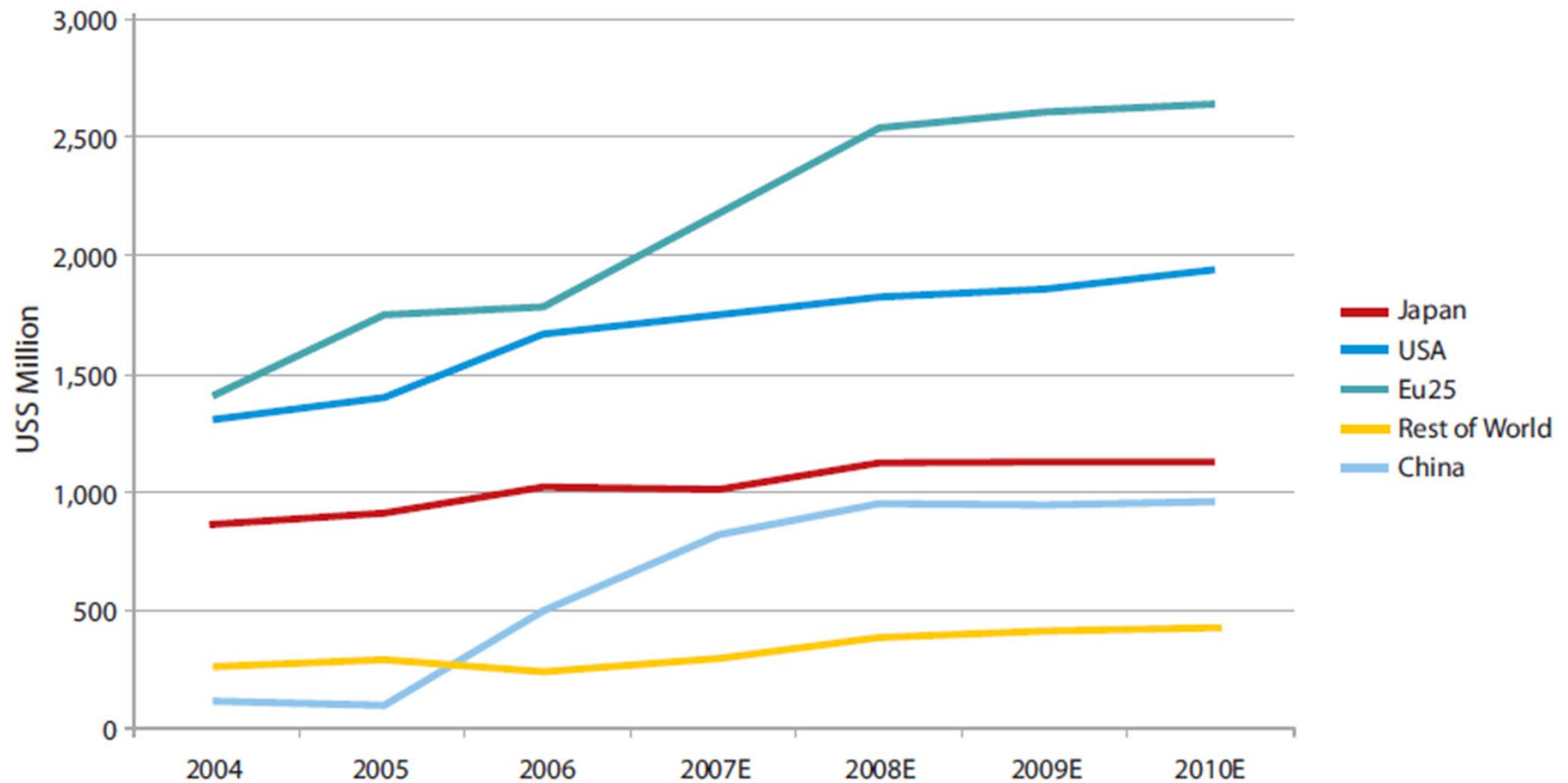
The tipping point

Nano-modification of FRP matrix for hybrid fibrous composite materials

Multi-scale reinforcement

- Initial works related to structural composites:
 - **EU-FP6-AEROSPACE-NOESIS**: Aerospace nanotube hybrid composite structures with sensing and actuating capabilities, 2004-2009

Since then... *Nanotechnology*



Source: Tekes Programme Report 2006 (FI)

Background

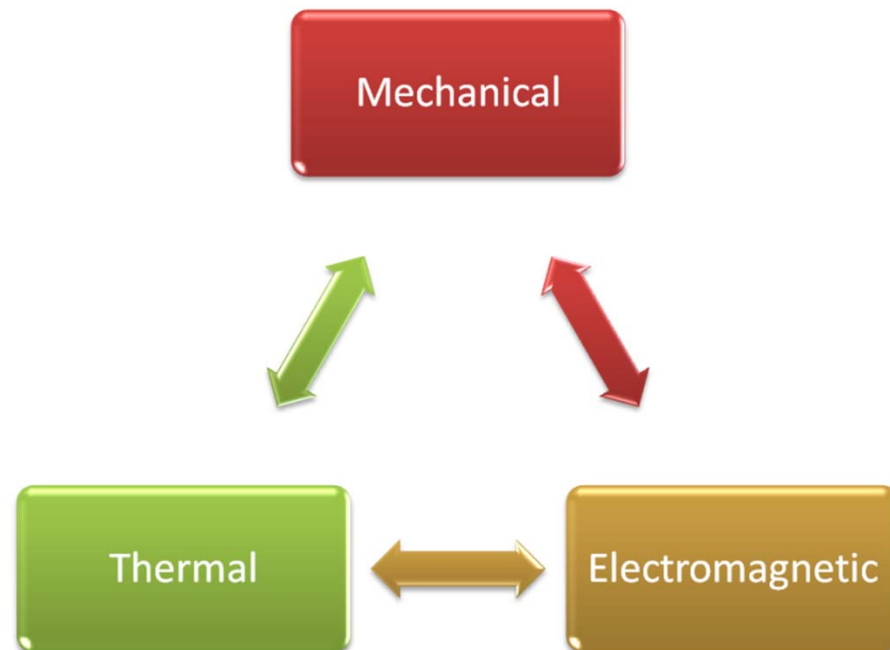
- During the past decade:
 - A lot of money (>1b€) (specific to nano-composites)
 - A lot of people (>100 research groups in EU)...have been “invested” to investigate nanotechnology for materials
- Progress has been made, but where do we stand after >10 years?
- What do the end-users see and say?
- Our focus is on structural nano-composites

Introduction

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

Framework

- Structural Composites: $E > 50\text{GPa}$, $\sigma > 100\text{MPa}$
- Fibrous composites \rightarrow Manufacturing methods
- Multi-functional performance
- Novel functionalities

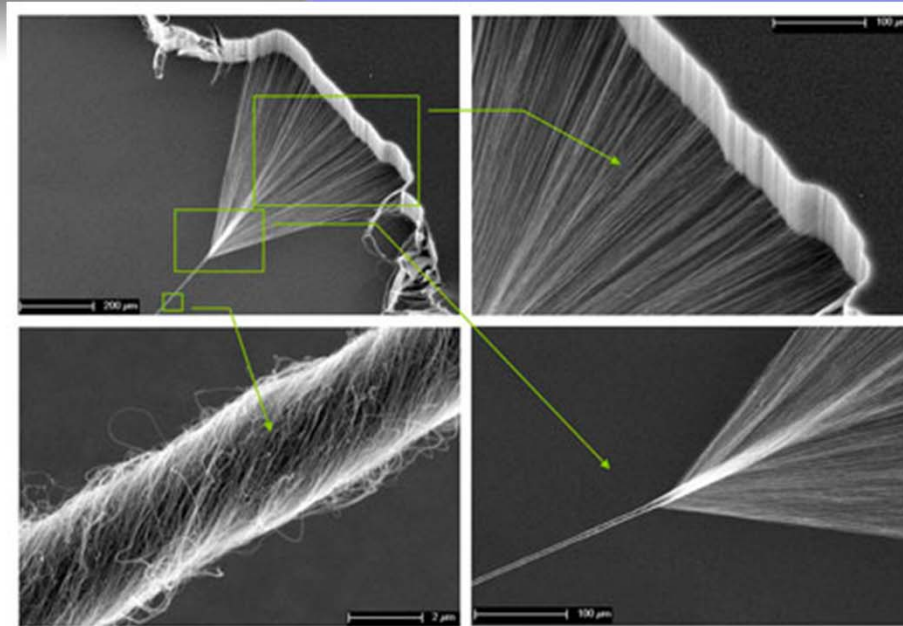
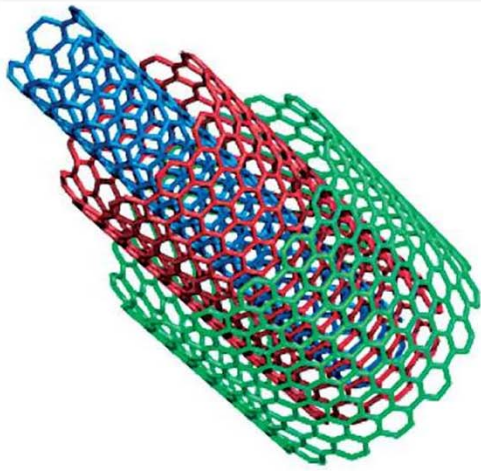


Approaches

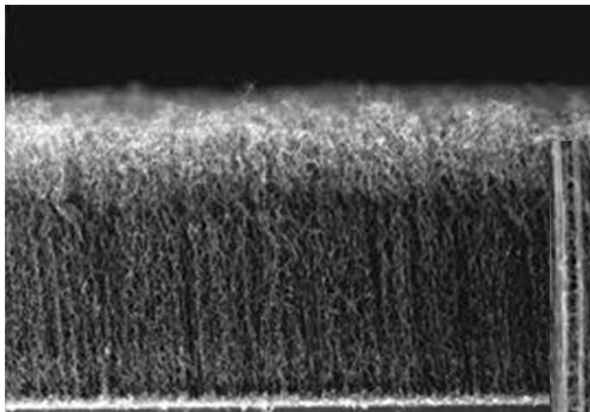
Concepts of utilizing nanotechnology in composites

<u>Nano-Augmenting</u>	<u>Nano-Engineering</u>	<u>Nano-Design</u>
<ul style="list-style-type: none">• Multifunctional materials• Hybrid nanocomposites• Enhancement of Mechanical, Electrical and Thermal Properties• Sensing properties (Damage monitoring, SHM)	<ul style="list-style-type: none">• Organized structures of nano-reinforcements (continuous nanofibers, bucky papers, aligned 2D structures, CNT forests)• Multifunctional materials• Hybrid nanocomposites• Enhancement of Mechanical, Electrical and Thermal Properties• Sensing properties (Damage monitoring, SHM)• Actuating capabilities in various scales and various forms	<ul style="list-style-type: none">• Organized structures of nano-reinforcements (continuous nanofibers, bucky papers, aligned 2D structures, CNT forests)• Multifunctional materials• Hybrid nanocomposites• Optimization of the enhancement of Mechanical, Electrical and Thermal Properties• Sensing properties (Damage monitoring, SHM)• Actuating capabilities in various scales and various forms

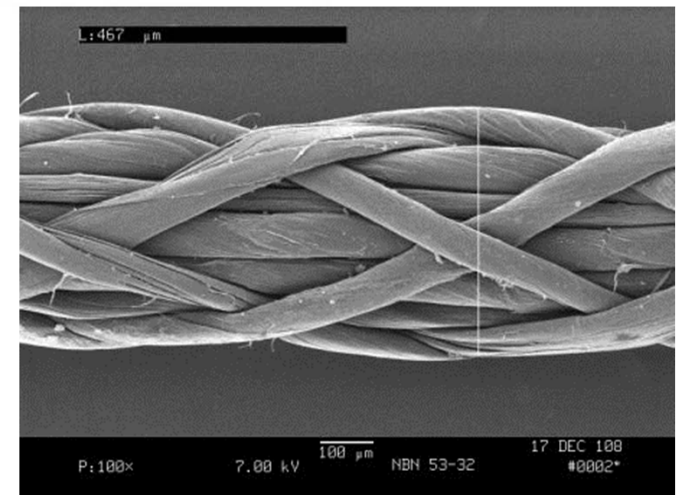
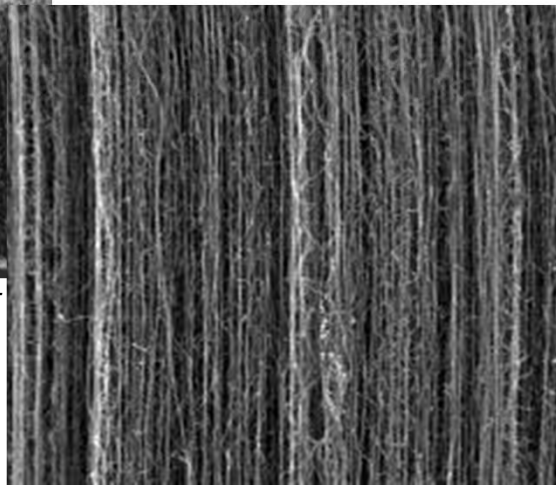
Snapshots I *Grown CNT forests and ropes*



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



Riccardo Signorelli/MIT

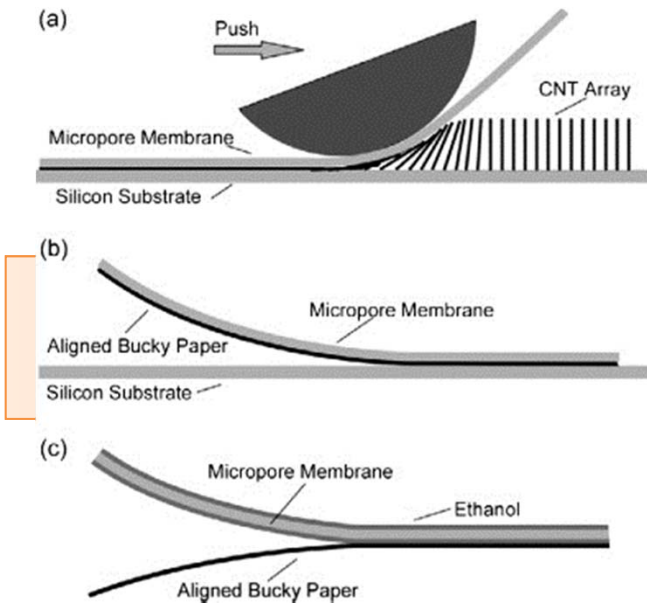
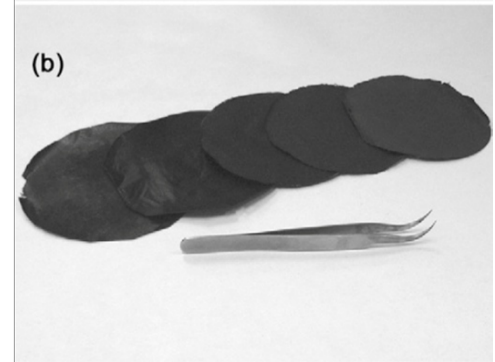
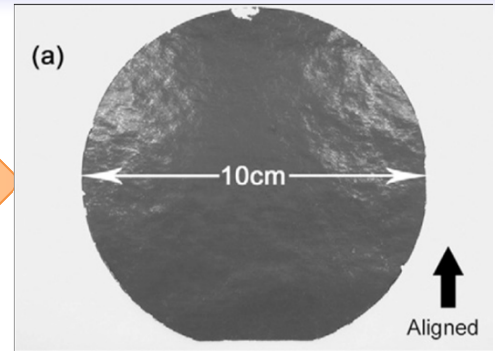


CNT yarn (Nanocomp, USA)

Snapshots II *CNT Buckypaper preforms*



Kostopoulos et al. 14th European Conference on Composite Materials, Budapest, Hungary, June 2010



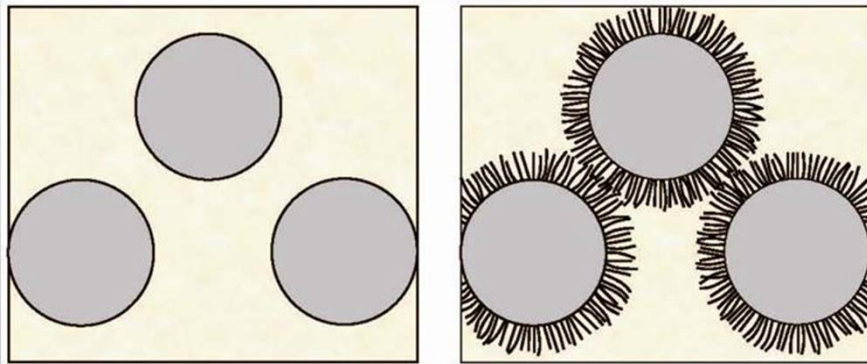
Florida State University

Wang et al. Nanotechnology 2008;19(7):075609

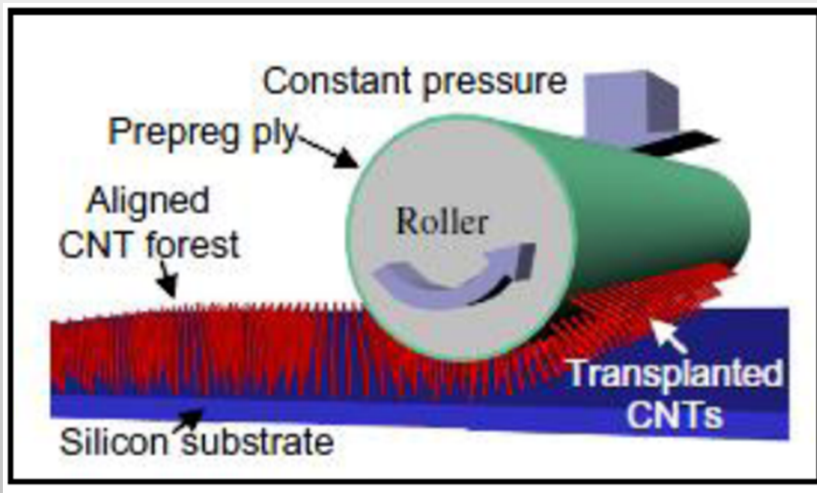
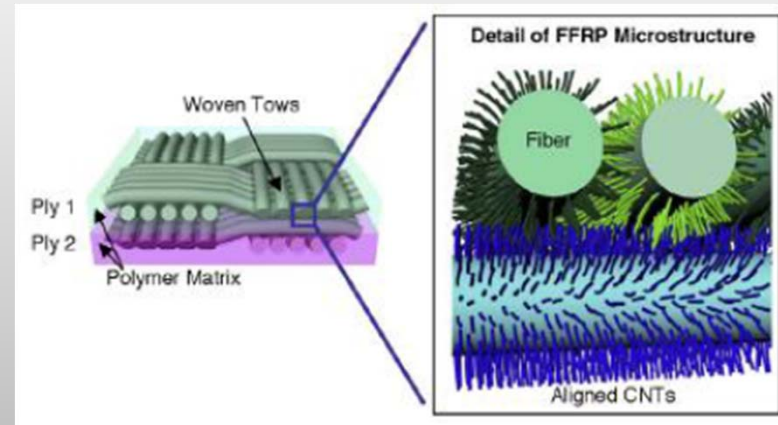
Wang et al. Nanotechnology 2008;19(7):075609

Snapshots III

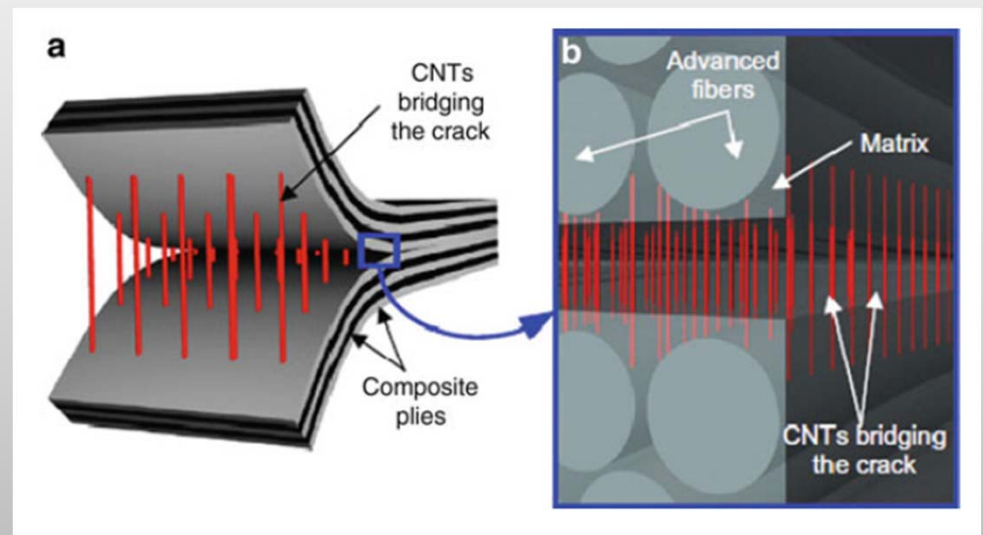
Growth on fibres and transferred forests



Wicks et al. *Composites Science and Technology* 70 1 (2010) pp. 20-28.

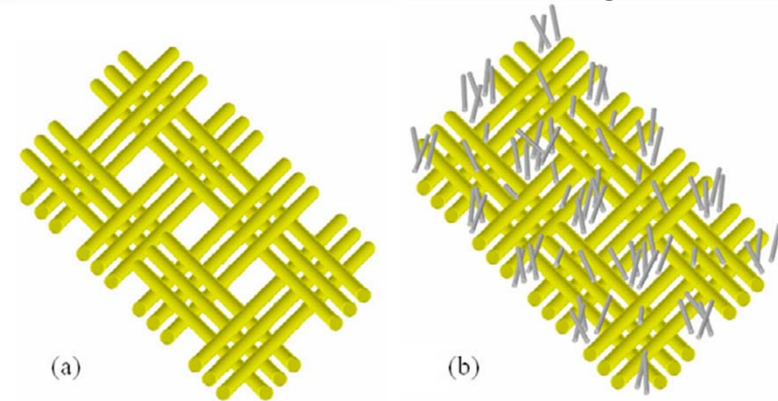
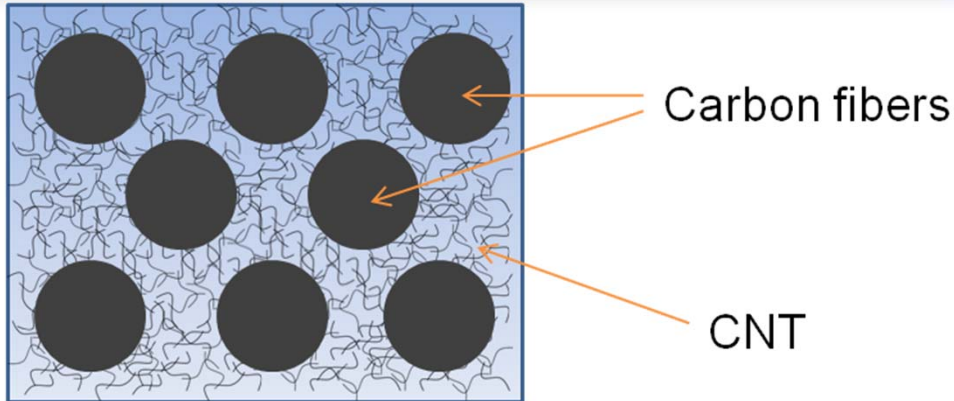


Garcia et al. *Compos. Part A: Appl. Sci. Manuf.* 39(6), 1065–1070 (2008).

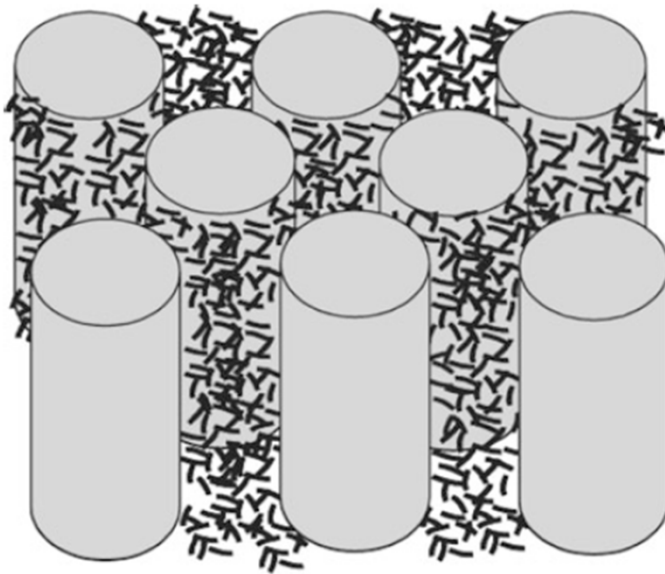


Snapshots IV *CNT doped matrix*

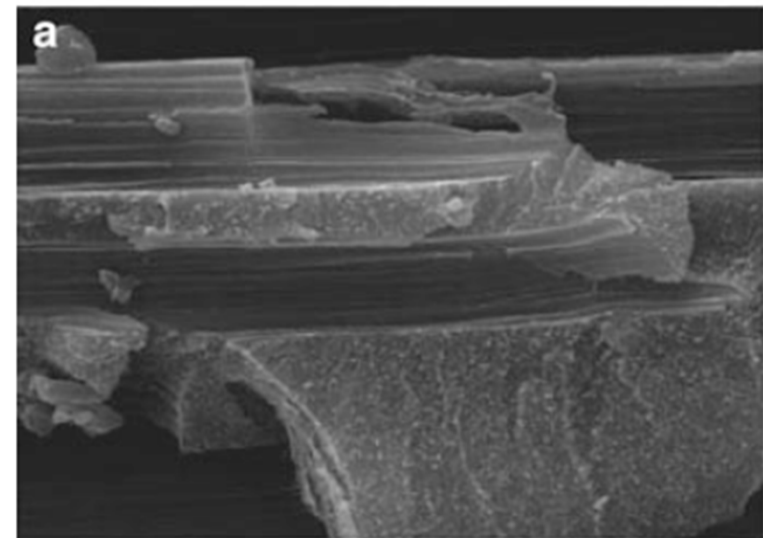
Preferential orientation through thickness



Qiu et al. *Nanotechnology* 18 (2007) 275708



Vlasveld et al. *Polymer* 46(23), 10269–10278 (2005)



Karapappas et al. *J. Compos. Mater.* 43(9), 977–985 (2009)

Performance enhancement *CNT doped matrix*

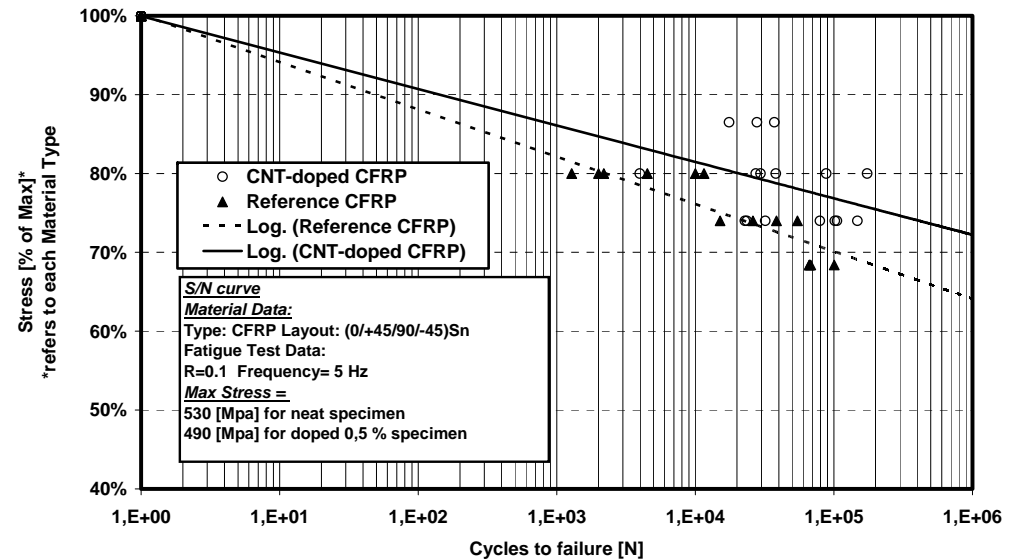
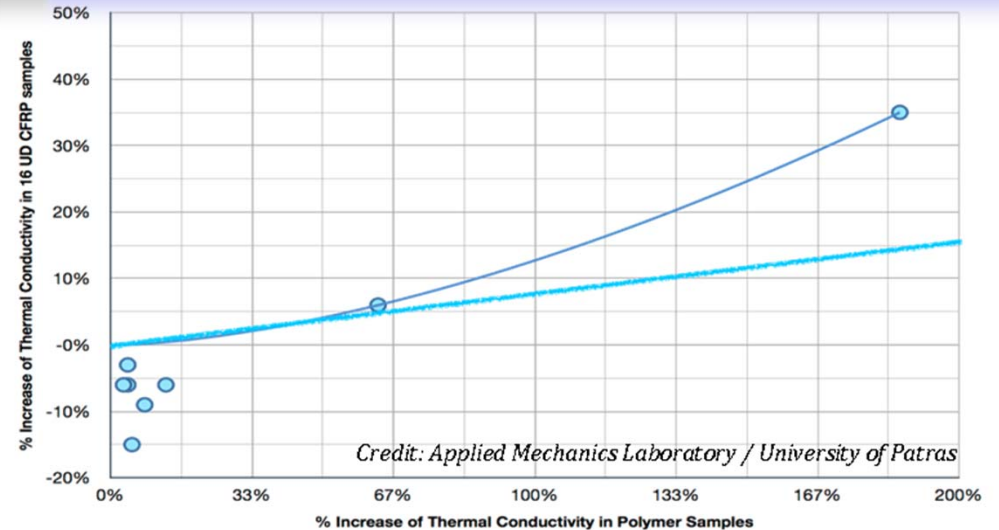
Novel aerospace structures via:

- Improved Fracture Toughness
- Improved Fatigue Life
- Increased electrical conductivity
- Increased thermal conductivity
- Damage Sensing Capabilities

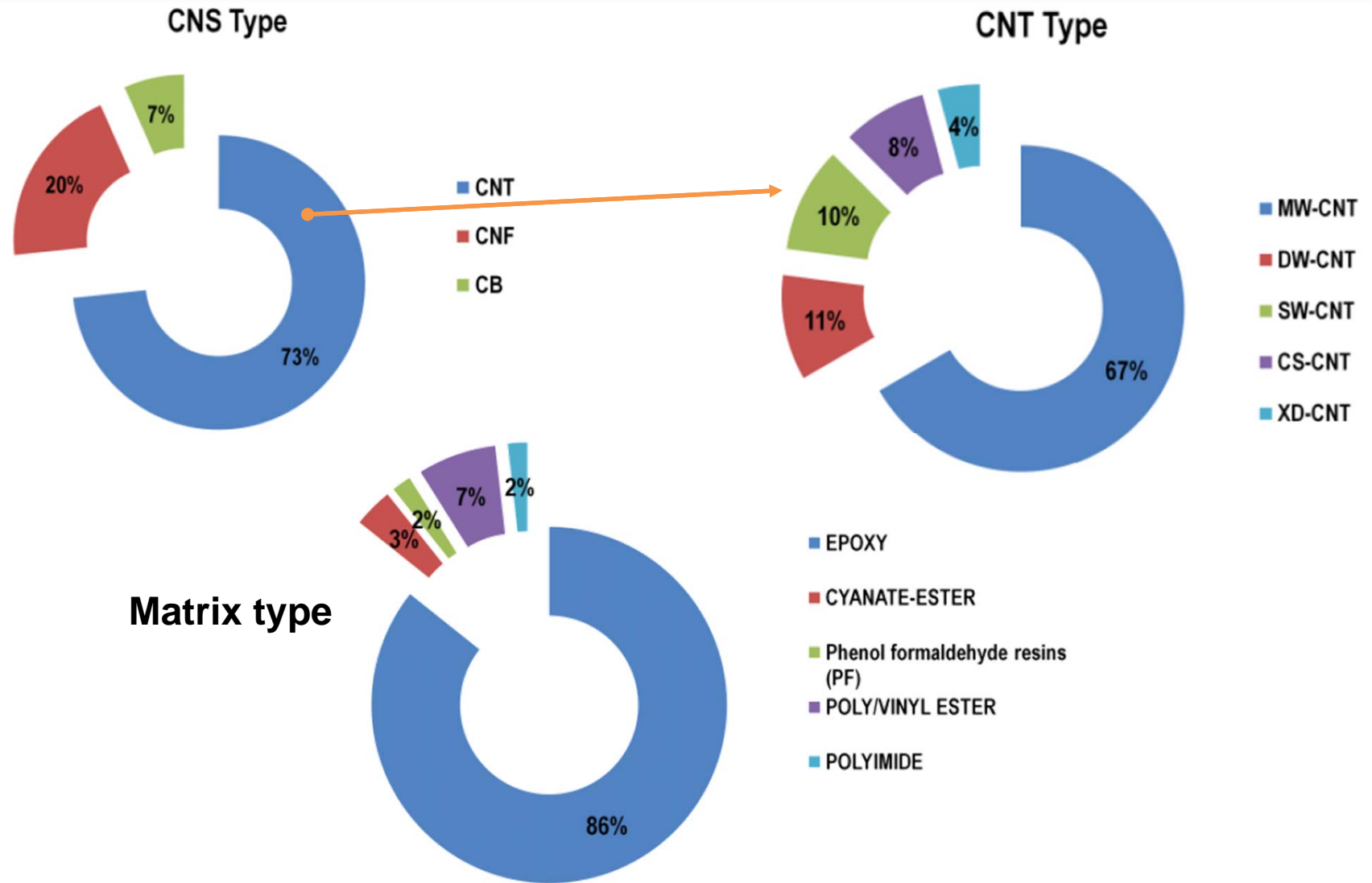
Specific interest for space applications

- Stiffness to density
- Thermal Conductivity
- Electrical Conductivity
- CTE

Thermal Conductivity Relationship between CNS Matrix and CNS-CFRP

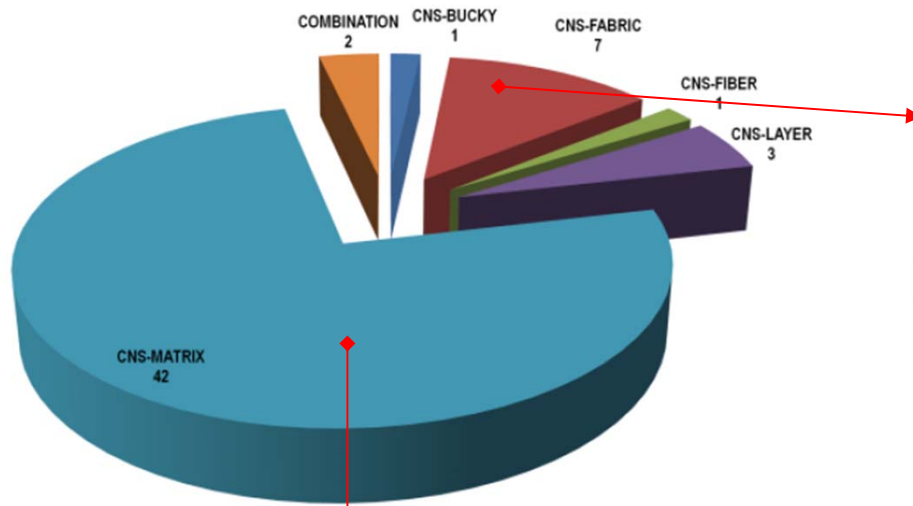


ESA Projects *NAREMA survey*

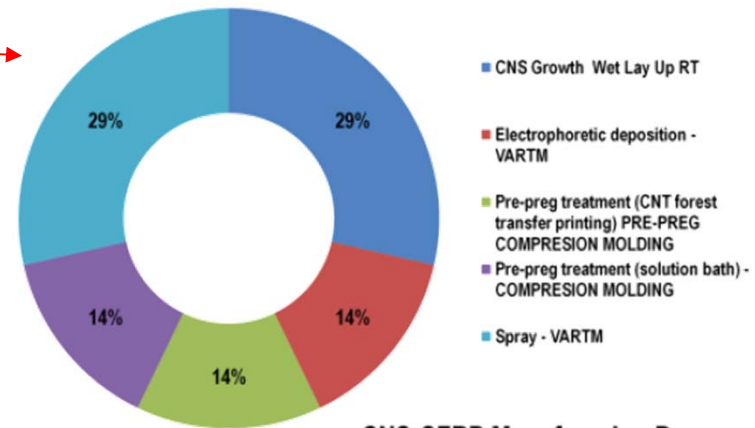


ESA Projects *NAREMA survey*

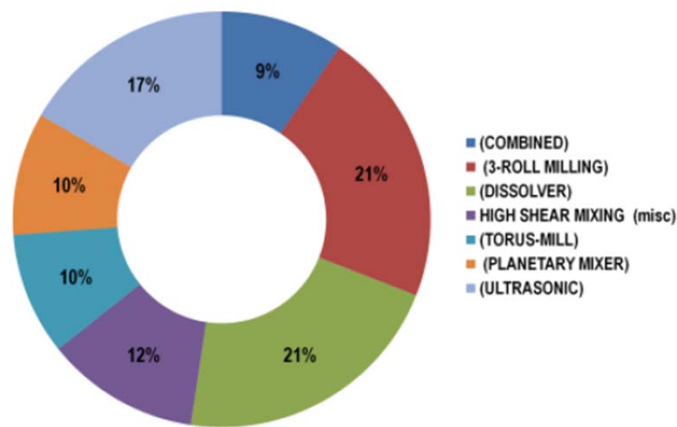
Type of CNS introduction in CNS-CFRP



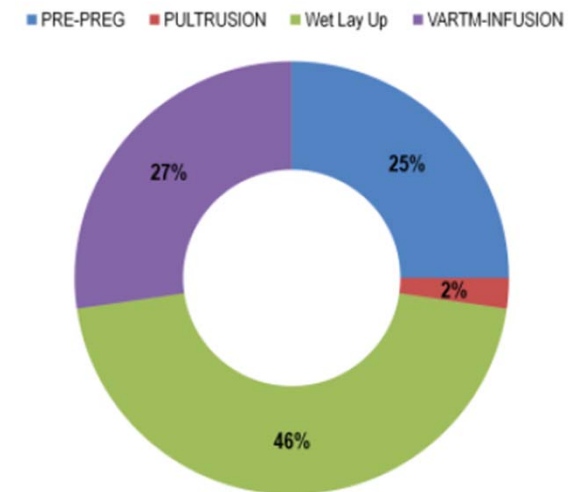
(CNS-FABRIC) CNS incorporation and CNS-CFRP Manufacturing Process (Lamination+ Curing)



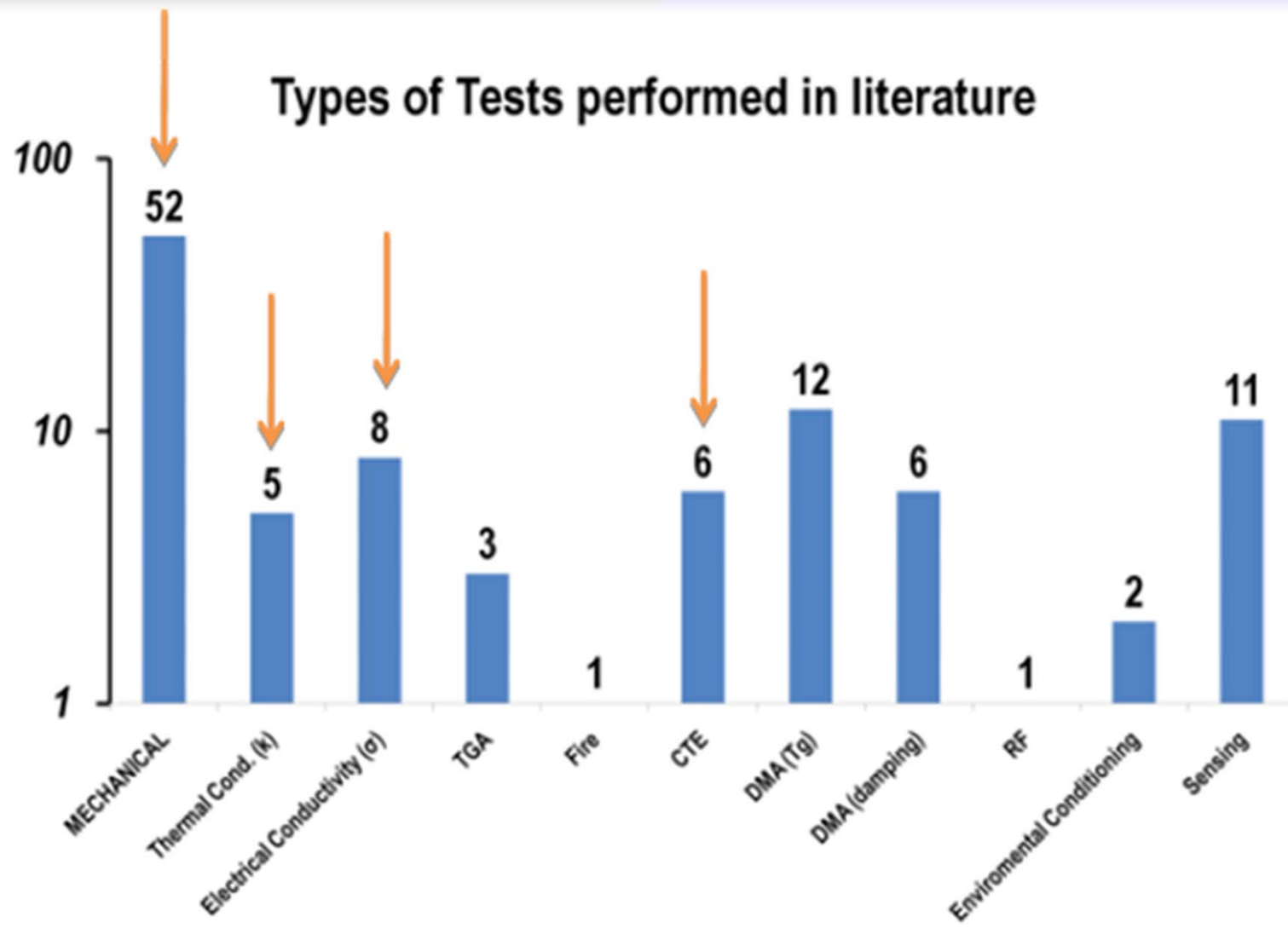
(CNS-Matrix) CNS Major Dispersion Technique






































CNS-CFRP Manufacturing Process (Lamination)



ESA Projects *NAREMA survey*



Trade-off *Routes Vs. Applicability*

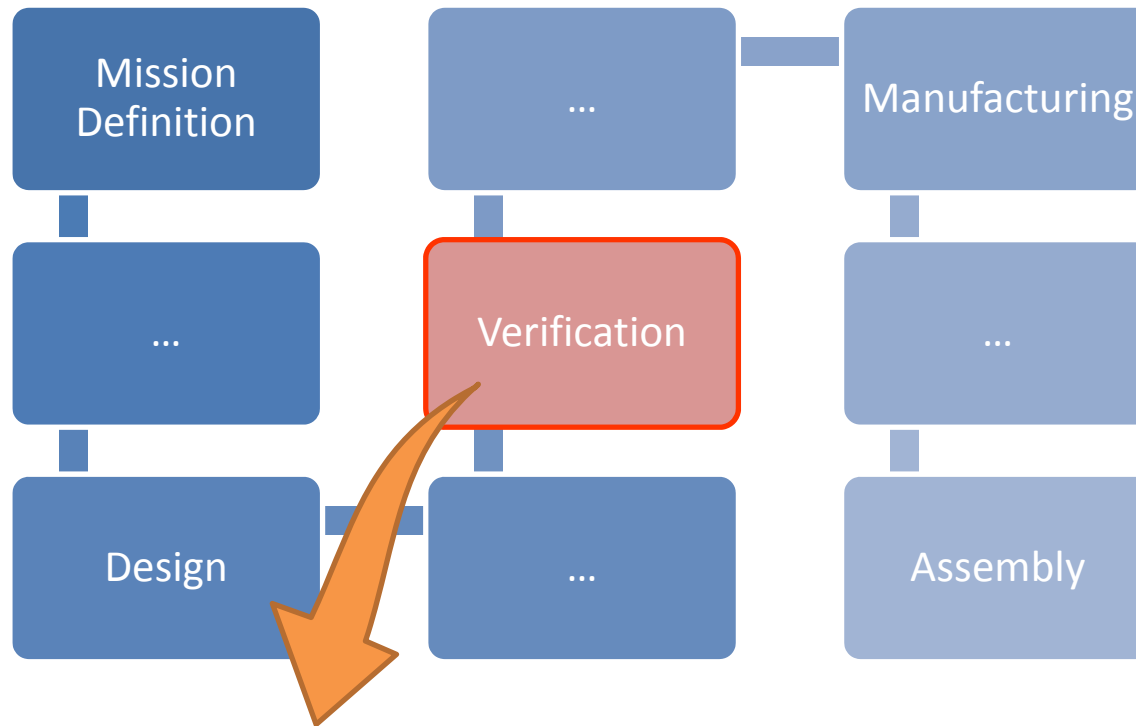
	Nano-integration Process			Manufacturing Process		
	Safety	Handling	Scalability	Resin Infusion	Autoclave	Quality Control
Resin Doping	 			 		 
Growth	 					 
Buckypaper preform		 	 		 	 
Prepreg		 	 	N.A.	 	

- Agglomerations
 - Effective use of nano-species
- High nano-phase content may be needed
 - Depending on the process different levels can be achieved
- Modification routes may alter the host material
 - It is usual to employ solvents in such processes
- IP Rights

Why modeling?

Importance of modelling @NANO-scale

- The road to the launch



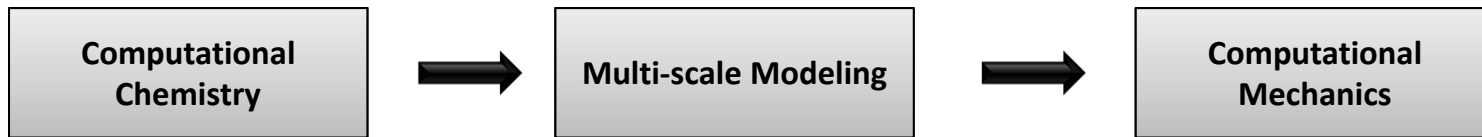
Modeling

"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*

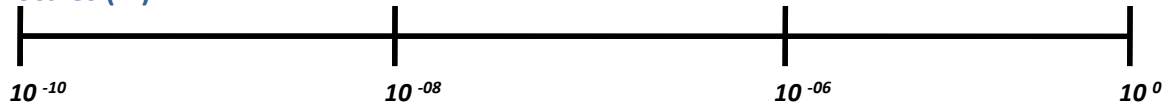
Modeling Methods



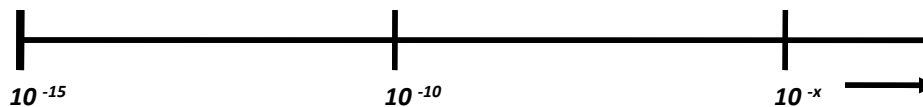
Modeling Tools



Spatial Scales (m)

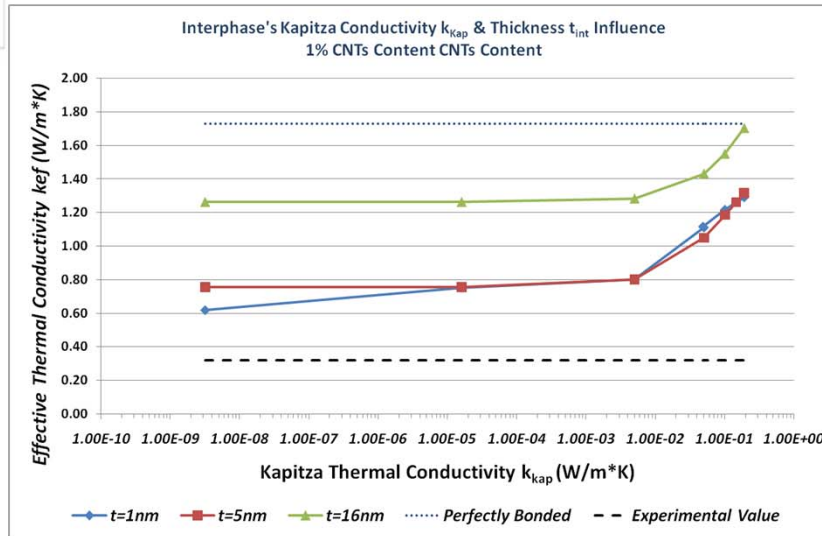
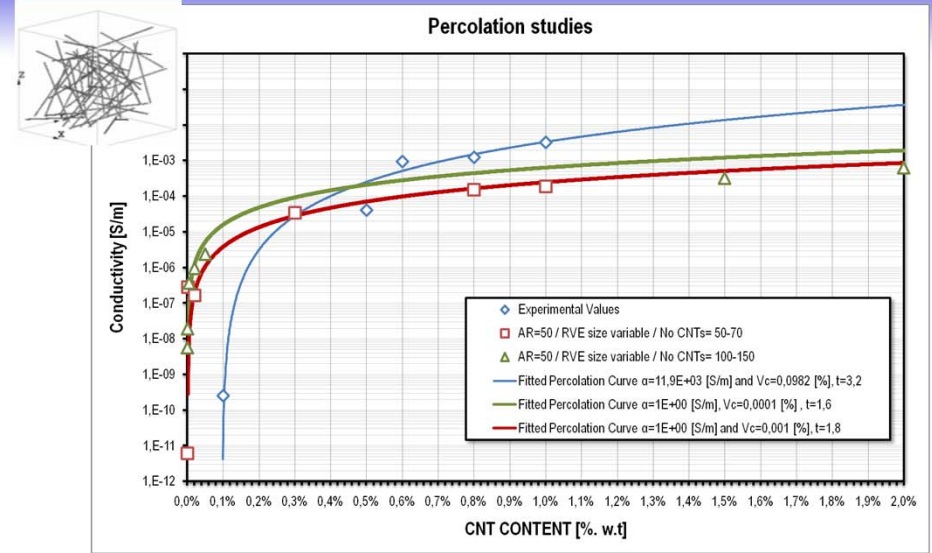
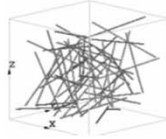
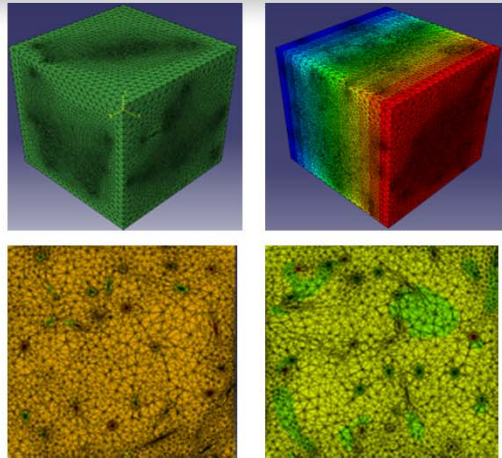
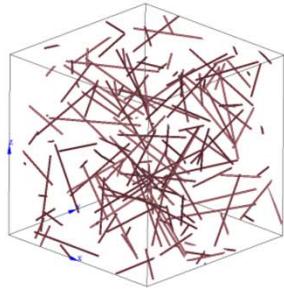


Time Scales (sec)



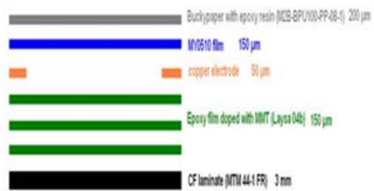
Nano-modeling capabilities

Electrical and Thermal properties



Nano-modeling capabilities *Multi-physics problems*

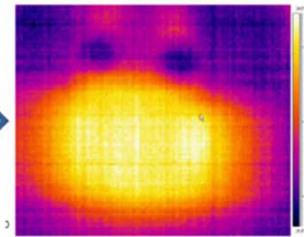
Experiment



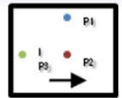
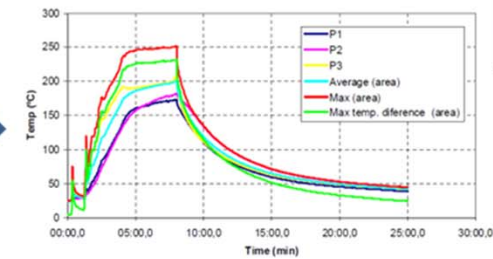
Experimental Layer Set Up



Application of Electrical Power P_e At RT



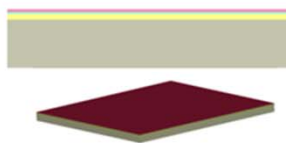
Heat of Top Specimen Surface due to Joule Phenomenon



1st Modelling Approach

FEA Model

- LAYER_1_BP/EPOXY_Electro-Thermal Conductive
- LAYER_2_MY OS10 FILM_Electrical & Thermal Insulator
- LAYER_3_EPOXY/MMT_Electrical & Thermal Insulator
- LAYER_4_CF LAMINATE



Computational Layer Set Up

Material Model Variables

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

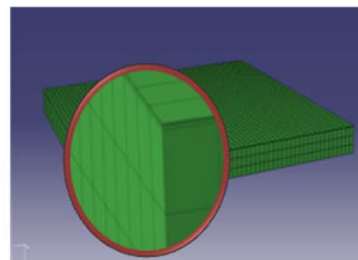
Where:

$\sigma \rightarrow$ derived by the NrPM_RVE

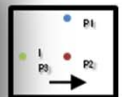
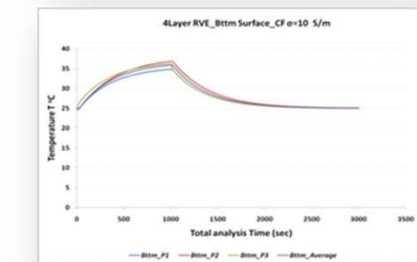
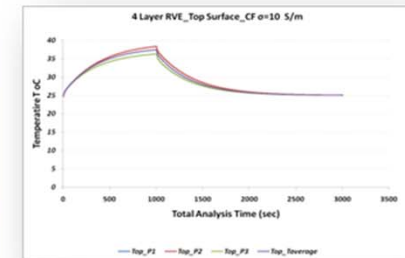
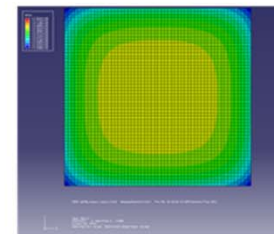
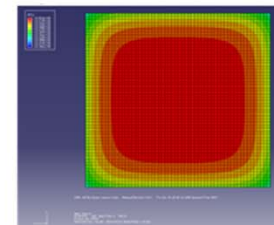
developed for the Electrical Analysis

$k, c_p \rightarrow$ derived by the NrPM_RVE

developed for the Thermal Analysis



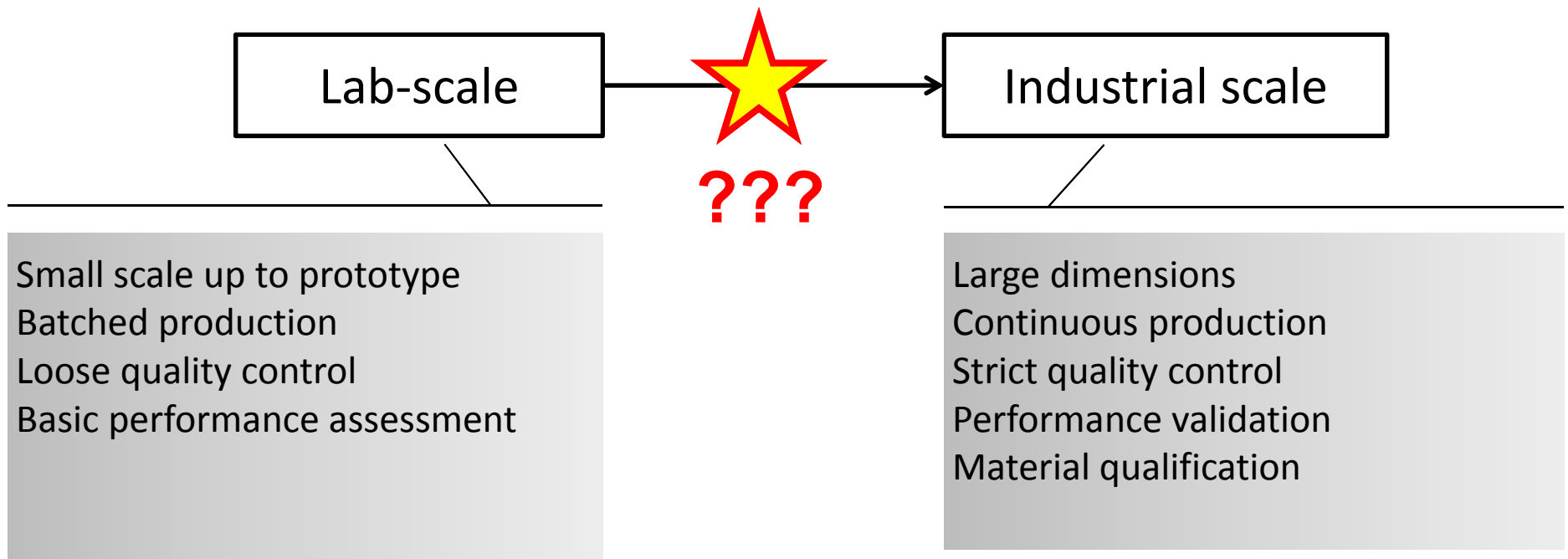
Application of Electrical Power P_e At RT



....the other side

Large scale applications *The scale gap*

- When it comes to real and large structures, what is the strategy there?



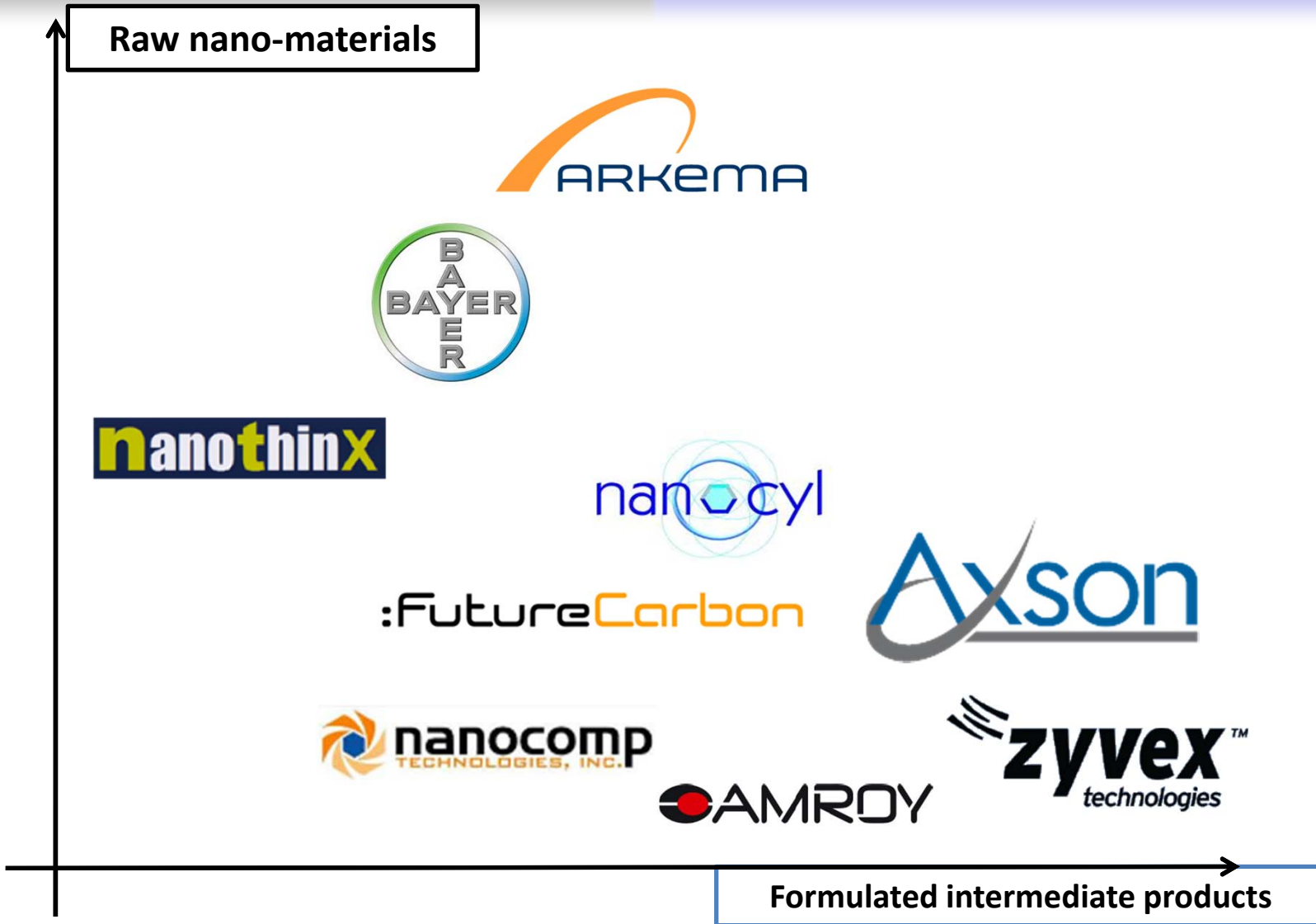
Large scale applications

- Quality Control System
 - Performance validation (...B-values?)
 - Quantity requirement
 - Continuous processes
 - Safety issues in production (*"The European Commission envisages modifications in some of the REACH Annexes and encourages ECHA to further develop guidance for registrations after 2013."*)
 - *European Commission, Press release 3-10-2012, IP/12/1050*
- Interest from major players pushes viable scenarios to the surface
 - Alternative routes for adoption of nanotechnologies in existing production lines
 - **IP rights and availability of materials & formulations****

Standardization of Nanotechnology *Latest addition...*

- ISO/TS 27687:2008
 - Nanotechnologies -- Terminology and definitions for nano-objects -- Nanoparticle, nanofibre and nanoplate
- ISO/TS 80004-1:2010
 - Nanotechnologies -- Vocabulary -- Part 1: Core terms
- ISO/TS 80004-3:2010
 - Nanotechnologies -- Vocabulary -- Part 3: Carbon nano-objects
- ISO/TS 12805:2011
 - Nanotechnologies -- Materials specifications -- Guidance on specifying nano-objects
- ISO/TS 80004-4:2011
 - Nanotechnologies -- Vocabulary -- Part 4: Nanostructured materials
- ISO/TR 11360:2010
 - Nanotechnologies -- Methodology for the classification and categorization of nanomaterials
- ISO/TR 10929:2012
 - Nanotechnologies -- Characterization of multiwall carbon nanotube (MWCNT) samples
- ...

The Market *Commercial products*



Products

Indicative nano-enabled products for composites



Baytubes (Bayer Materialscience, D)



BuckyShield (Buckeye Composites, USA)

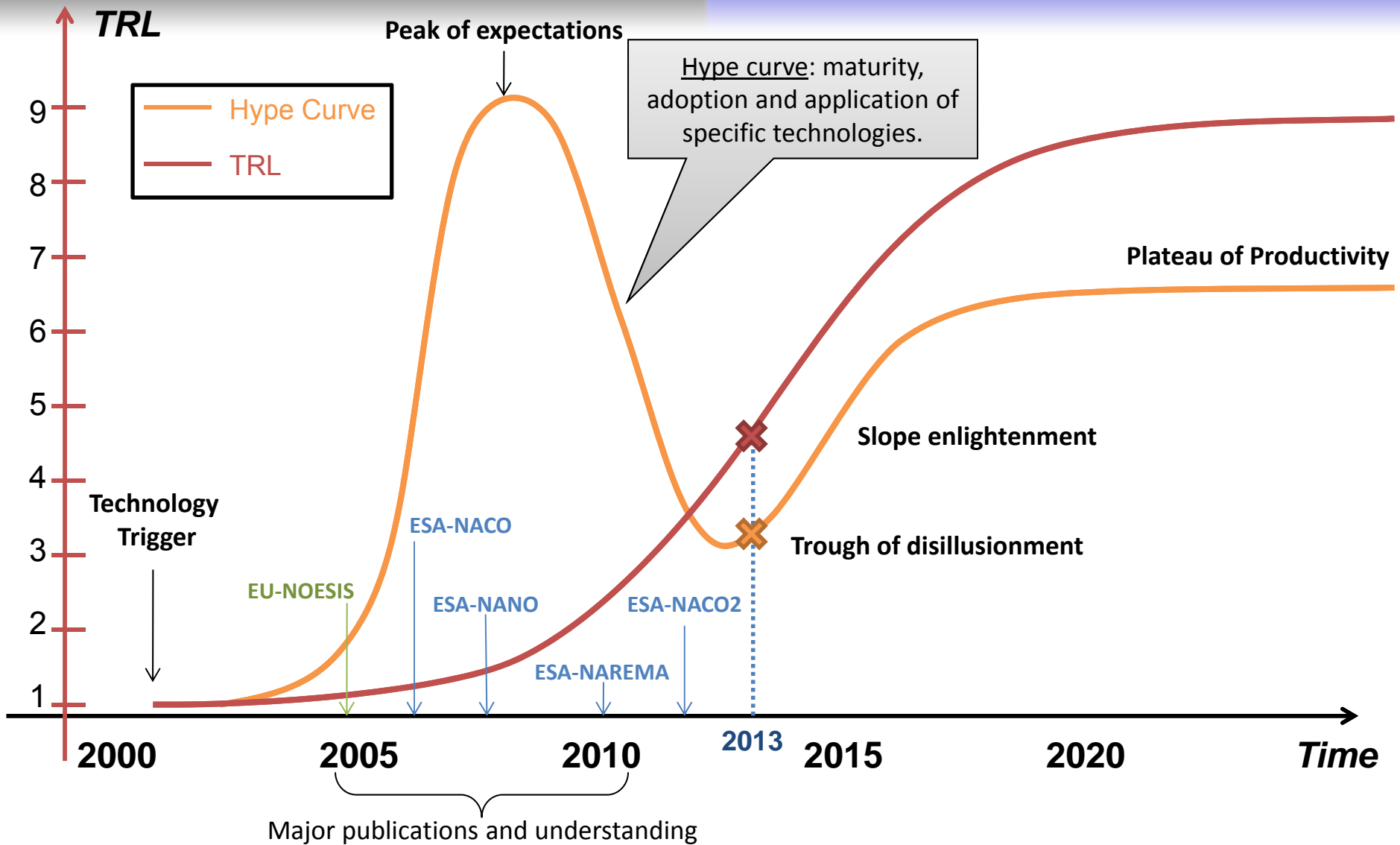


Raw MWCNT & Epocyl (Nanocyl, BE)



TRL & Gartner chart

Structural nano-composites: Hype curve



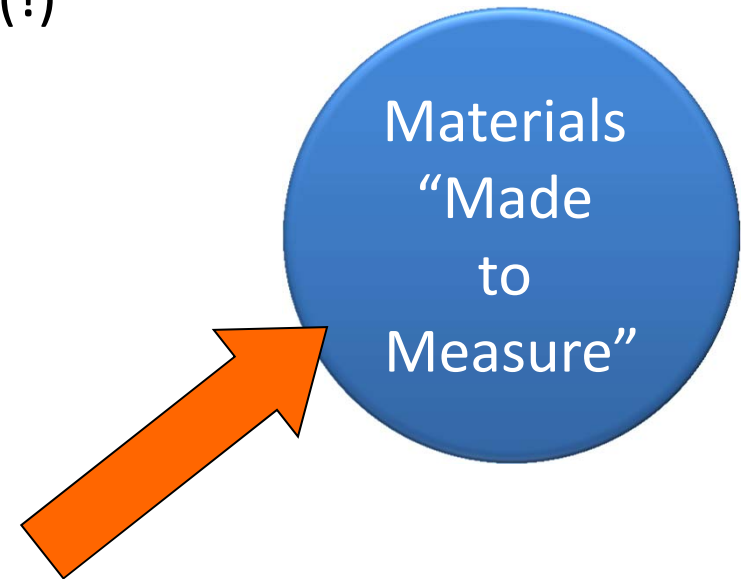
- Nano-materials is a key enabling technology
- The global market for nano-materials is estimated at 11 million tons at a market value of €20 billion
- 300,000 to 400,000 employed in Europe
- Presently dominated by carbon black, amorphous silica etc.
- Products underpinned by nanotechnology are forecast to grow from a global volume of €200 billion in 2009 to €2 trillion by 2015

**European Commission, Press release 3-10-2012, IP/12/1050*

- ...nano-materials for Structural applications is a rather small piece of the pie

Conclusions

- Targets to be achieved still remain:
 - Reduce mass and improve stiffness (!)
- Steps to reach the target:
 - Processing
 - Tune specific properties
 - Thermal conductivity
 - Electrical conductivity
 - EM compatibility
 - Tune combination of properties
- What should be expected the coming years?
 - Integration of nano-enabled products in commercial portfolios



Acknowledgements

The presented information were gathered, summarized and/or developed under the framework of the following projects. Their support is greatly acknowledged.

ESA-NAREMA

ESA-NANO

EU-FP6-NOESIS Project

ESA-NACO1 & NACO2

EU-FP7-ELECTRICAL Project

EU-FP7-LAYSA Project

EU-FP7-SARISTU Project

EU-FP7-IAPETUS Project

Applied Mechanics Laboratory Internal Projects

