HPS High Performance Space Structure Systems GmbH GERMANY

Improvement of CFRP Polymer Matrix Composites by adding Nano-Materials or creating Composites by using Infiltrated Bucky Paper Layers

General Overview of Research and Development of Nano-Composites at HPS GMBH in cooperation with several European Partners

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Part 1: Motivation

Why using Nano-particles,

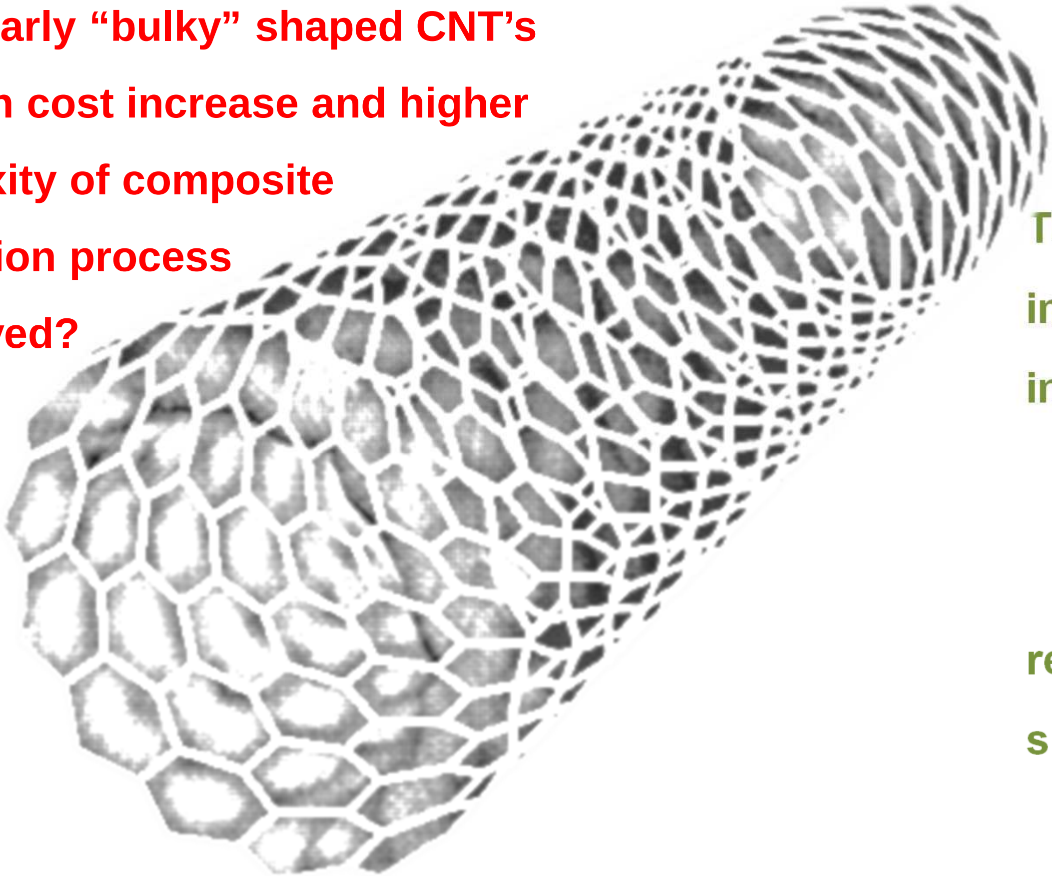
particularly "bulky" shaped CNT's

although cost increase and higher

complexity of composite

production process

is involved?



The aim is to :

improve material behaviour

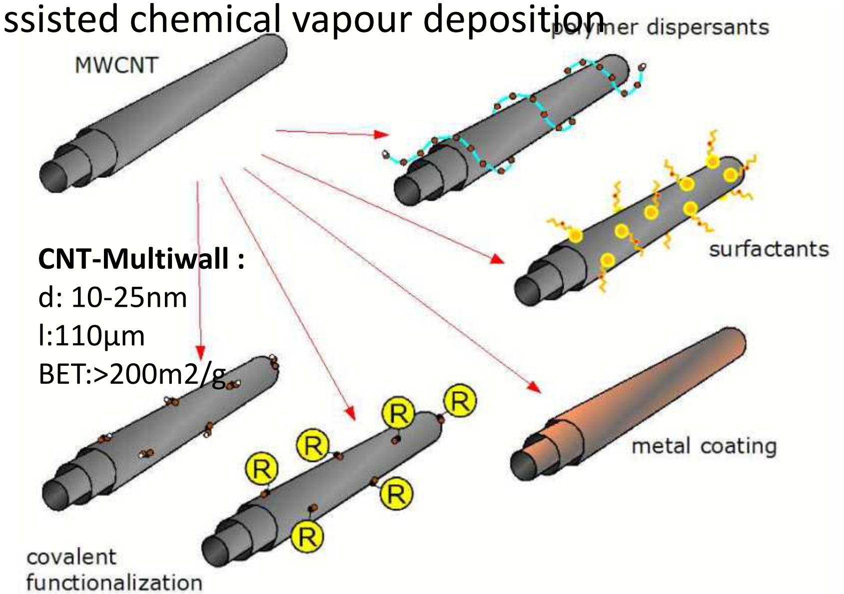
increase functional performance, e.g.:
- electrical properties
- thermal properties
- mechanical strength

reduce mass for more payload

substitute parts that are currently made from metals and other materials

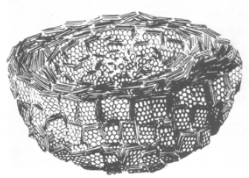
Part 1: Nano-Materials

Nanotubes produced by **FutureCarbon** using catalytic assisted chemical vapour deposition



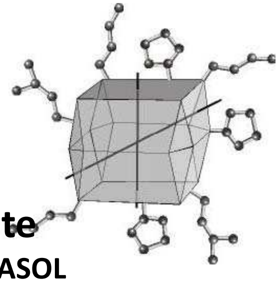
CNT-Multiwall :
d: 10-25nm
l:110µm
BET:>200m2/g

Burghard, M.; Balasubramanian K. Chem. Unserer Zeit, **2005**, *39*, 16



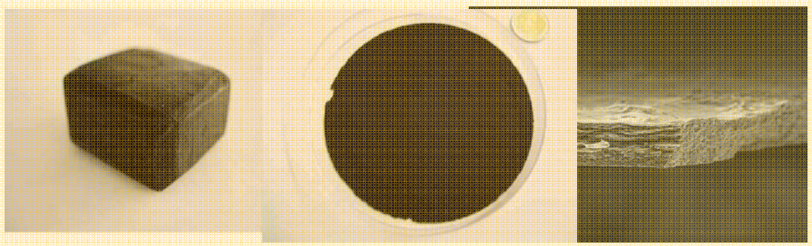
Carbon Black produced by **FutureCabon** Model of Primary Particle

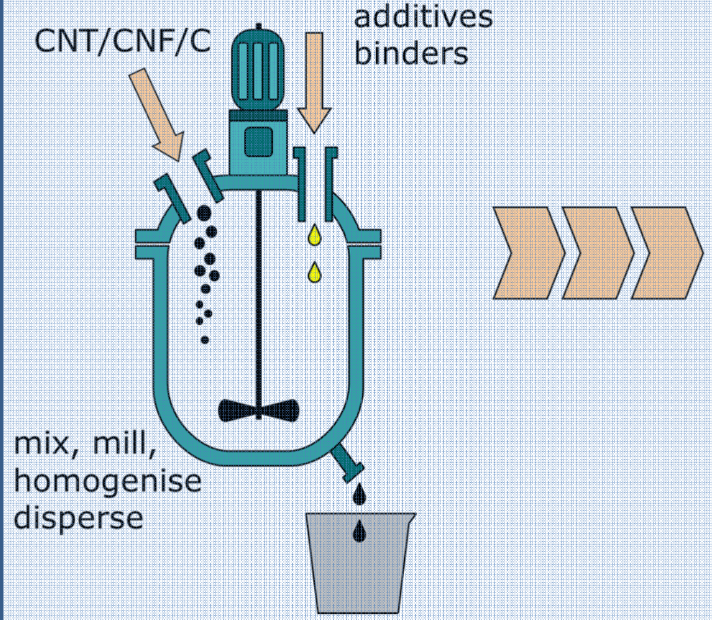
http://duepublico.uni-duisburg-essen.de/servlets/DerivateServlet/Derivate-5431/02Carbon_Black.pdf



Boehmite
Provider **SASOL** GermanyUsed by partner **DLR**In ESA project **NAREMA**

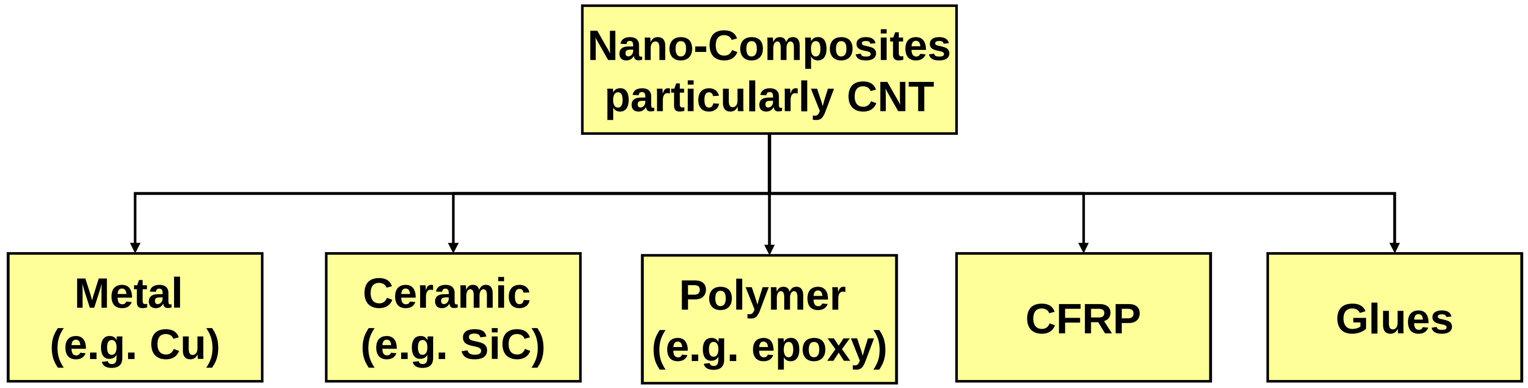
Skeletons by FutureCarbon:Bucky papers and felts by filtration, slip and tape casting



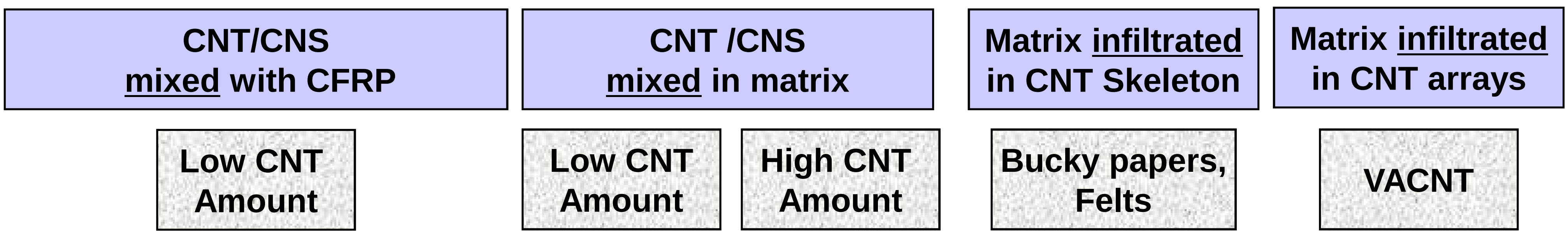


- purification
- homogenization
- functionalisation
- water and solvent based dispersions and pastes
- metallization
- CNT and CNF felts

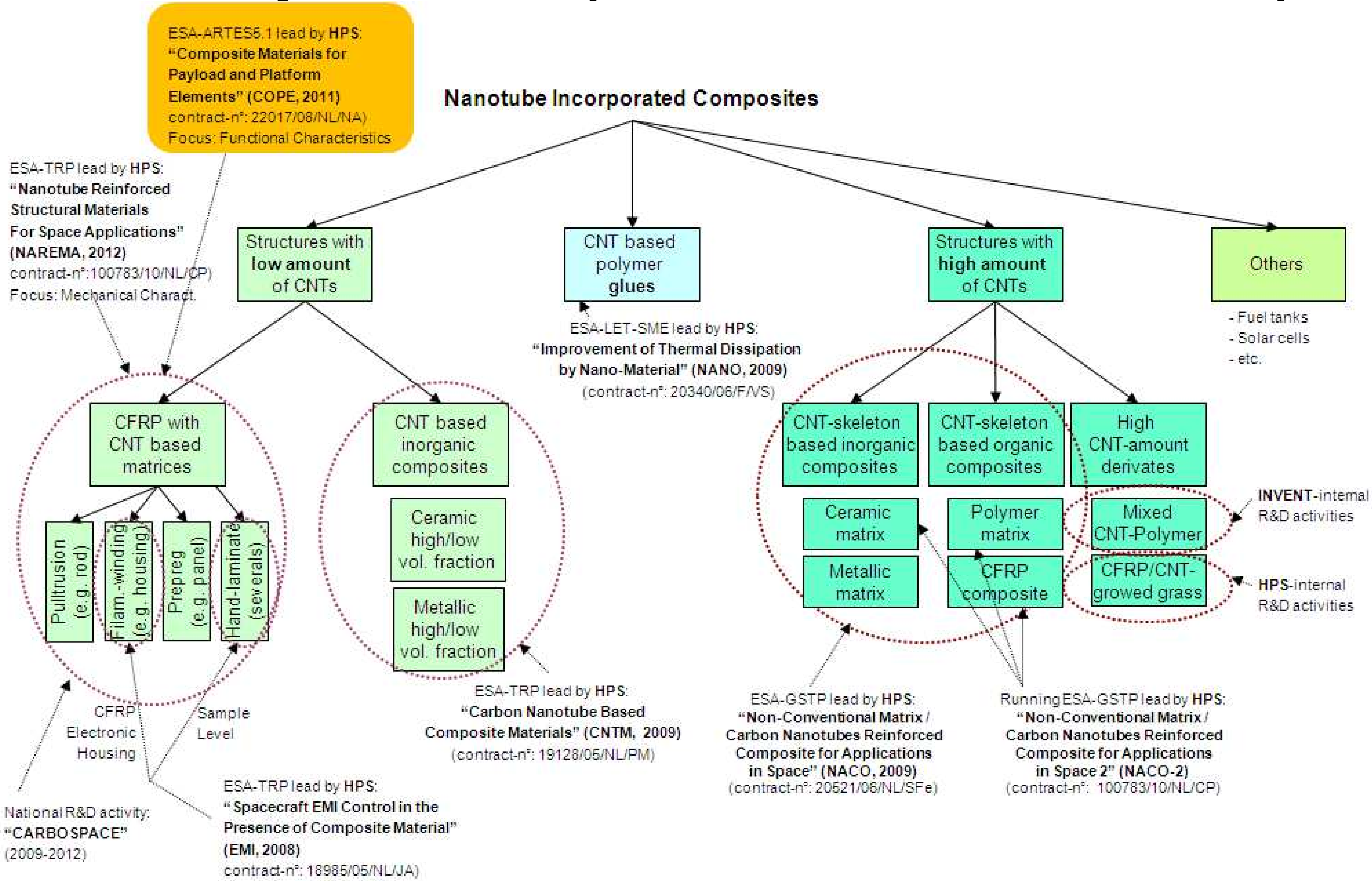
Different materials for different applications



Different Classes and Production Principles (combinations possible):



Nanotube-Projects at HPS (Classification via CNT-share)



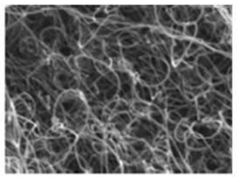
Part 2:

Improvement of CFRP Polymer Matrix Com-posites by adding Nano-Materials: Summary of ESA Projects COPE and NAREMA and of BMBF funded Project CARBOSPACE

NAREMA/COPE/CARBOSPACE

Project outlines

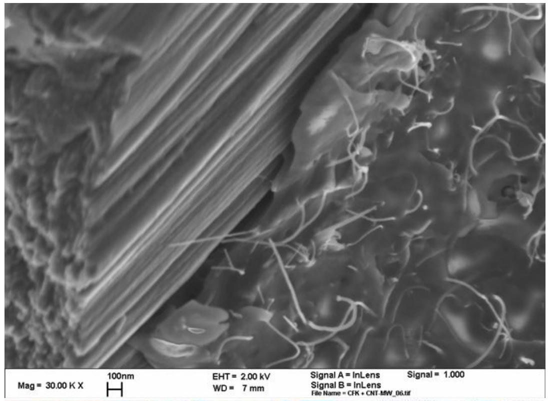
- **COPE Composite Materials for Payload and Platform Elements** (ESA ARTES Contract No. 22017/08/NL/NA), 2009 – 2012 (Prime HPS, Partners FC, TUHH, Ubay, INVENT, INEGI, ASTRIUM)
- **NAREMA Nanotube Reinforced Structural Materials for Spacecraft Applications (**ESA TRP Contract No.: 4000 100783/10/NL/CP), 2010 – 2012 (Prime HPS, Partners; DLR, INVENT, INEGI, UOP, ICOTEC, OHB, KT, Arianespace) Project complementary to COPE, incl. Literature Survey
- **CARBOSPACE** (BMBF funded), 2009 -2012 (Prime ASTRIUM, Partners FC, DLR, INVENT, HPS



- Matrices
  - Epoxy , LY556
  - Cyanate-Ester, PT30 and others
  - PEEK
  - Phenolic
- Fibres
  - HT PAN based fibres, T300, HTA, T700
  - UHM pitch based fibres, K13C2U

- Nano species
  - MW-CNTs
    - As-produced
    - Purified
    - Processed
  - CNF
  - Boehmites
  - Nano graphite platelets (graphene)

→ Countless variations



Hand lamination (e.g. UOP)

Filament winding (e.g. INEGI)

Rating of most important properties (NAREMA/COPE/CARBOSPACE)

NAREMA/COPE/CARBOSPACE

Property (NAREMA/COPE/CARBOSPACE)	Influence of Nano-Filling
Through thickness thermal conductivity max. by factor 2 (nano-filled CFRP, recent results by UOP Bucky paper interleaved CFRP composite), in-plane TC could not be iimproved	↑
Thermal-optical properties: minor increase in solar absorption but increase of 10 – 20% infrared emissivity (ε)	↗
CTE in CNT/CFRP samples slightly decreased/increasing dispersion of results at temperatures higher 75°C	↙
Through thickness electrical conductivity by factor 2 – 4 (nano-filled CFRP, CNT-filled CF/PEEK)	↑
In-plane electrical conductivity could not be improved (nano-filled CFRP)	→
radio frequency properties	→
Tensile strength/modulus (all NAREMA composites)	→
Bending strength (CNT filled CF/PEEK)	↗
Interlaminar fracture toughness (nano-filled CFRP)	↑
ILSS (nano-filled CFRP samples) selected as mechanical reference test testing of fibre-matrix bond, slight influence on NAREMA samples, increase of max. 30% for CARBOSRACE samples	→
Storage modulus (nano-filled CFRP samples)	→
Glass transition temperature (nano-filled CFRP samples)	→

↑ increase

↗ slight increase

→ no changes

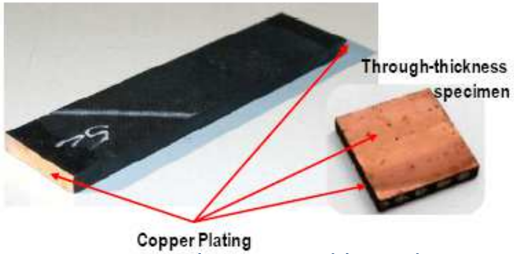
↙ slight decrease

Please note that the results presented were achieved with specific composite set-ups and that the outcome depends on the soundness of the selected process production route

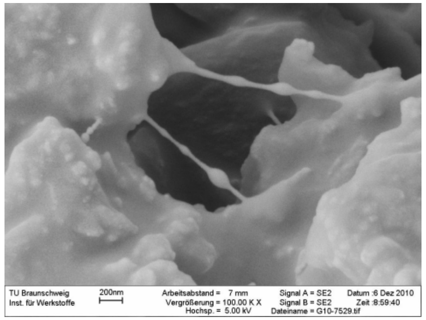
Lessons learned

Invent (hand lamination)

Inegi (pultrusion)



Fibre wound based prepreg, coated with Cu for EC tests



Example of crack bridging by CNT in a polymer matrix, SEM by TU Braunschweig, Inst. F. Werkstoffe

Crucial: Select best production route

Important: Quality Assurance

e.g. Results of first COPE Batch

- Hand lamination causes faulty materials

→ no more hand lamination

- UD Fibre wound based prepregs achieve good results
- Pultrusion also yields good results

Precondition: Select best suited CNT

- Upper limit of CNT mass fraction is approx. 1%, sometimes 0.5% is even better
- Exploration of CNT post-processing (e.g. chemical treatments

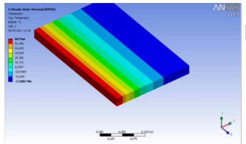
Choose best production route for property improvement

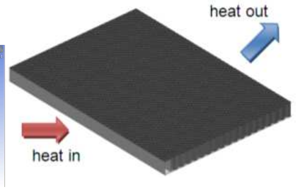
- Through thickness EC /TC can be improved, transversal EC/TC is fibre dominated,
- Inhibited crack propagation: Crack bridging is dominating process resulting in increased energy release rates, reduced hazard of delamination and increase of life time of CNT composite material

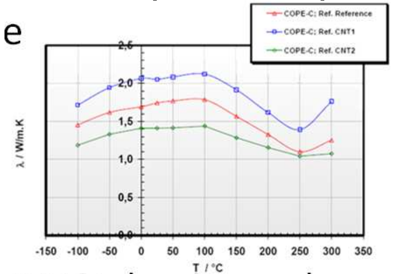
Final Samples/Demonstrators selected and tested for COPE/NAREMA/ CARBOSPACE

1. **COPE:** Sample containing ultra high modulus carbon fibre, < 1% CNT and epoxy resin best candidate material for a **radiator** ; It showed increased through thickness TC (max. 20%) /EC and infrared emissivity. FE-Analysis shows potential improvement of the heat transmission of max. 6% for a radiator sample

   Thermal Conductivity of CFRP in transverse to fibre direction can be improved using CNT







2. **NAREMA: Samples to demonstrate improved physical property:** Pultruded samples by INEGI, laminates by DLR, rods and screws by ICOTEC and hand laminates by UOP

3. CARBOSPACE: Demonstrators (realised with and w/o CNT)

Type A, Load Carrying Part Demonstrator; "Strut"
Type B, Functional Component "Electronic/EMI Box"
Type C, High Temperature Sandwich Demonstrator

HPS EMI Box

CNT-CFRP struts, image by ASTRIUM

CNT-CFRP blade, image by Invent

Nice side effects in NAREMA/COPE: Data base for CNT CFRP production (UOP), first trials with CNT based foams (UBAY) , use of multiple nano-materials like e.g. Graphene, CB, Nano-Fibres etc. in CFRP composites (UOP), extensive literature survey on CFRP composites with nano-fillers (UOP)

Part 3:

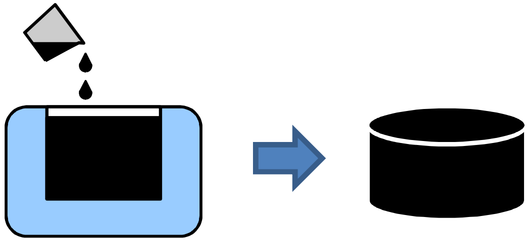
Creating Composites by using Infiltrated Bucky Paper Layers: Summary of ESA funded NACO Project

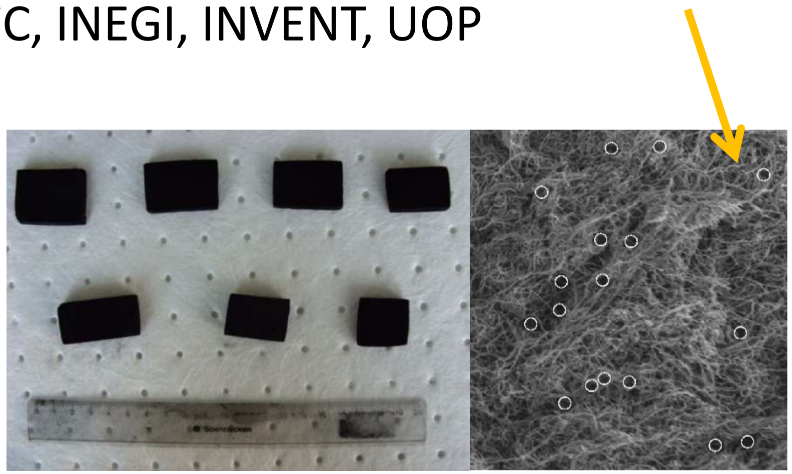
Project Outline

Non-Conventional Matrix / CNT Reinforced Composite NACO1 (ESA Contract No.: 20521/06/NL/Sfe), 2007 – 2010 , prime HPS, partners, AIT, ASTRIUM, DLR, ELECTROVAC, FC, INEGI, INVENT, PIEP, UOP
and subsequent project NACO2 (ESA Contract No.: 4000104354/11/NL/RA), (on-going since 2011), prime HPS, partners AIT, ASTRIUM, FC, INEGI, INVENT, UOP

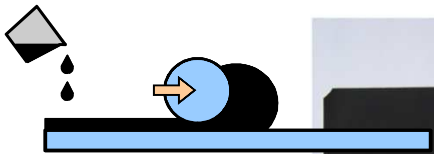
CNT Skeletons (FC)

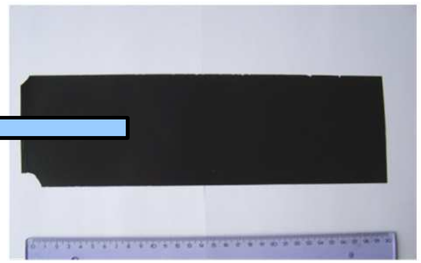
1. **Skeleton felts**

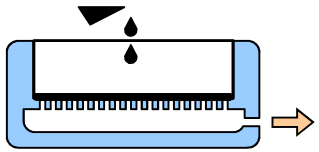




2. **Skeleton papers**



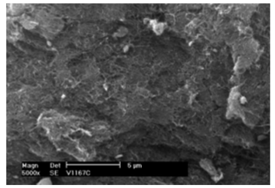




Infiltration of CNT skeletons (felts) with a metal matrix

Infiltration with Cu/Cu alloys by AIT

- Identification of thermal analysis methods for CNT skeletons
- Knowledge on relationship between CNT pretreatment/cristallite size and thermal properties
- Study of wetting behaviour between Cu alloys and CNT skeletons
- Assessment of different infiltration techniques, e.g. high pressure, low pressure and gas pressure infiltration
- Proof of infiltration of CNT skeleton BUT limitation in the infiltration thickness (<100µm) and severe reactions of alloying elements with CNTs



Infiltration with Al /Al alloys by ELECTROVAC

- It was not possible to infiltrate the raw felts by using gas pressure infiltration with and without vacuum
- It was not possible to infiltrate treated felts
- By thermal treatments between T=800-1000°, some reactions are observed between felts and Al-alloy
- Nano-tubes have disappeared
- Al_4C_3 and Al_2O_3 are formed
- Some AlN was detected (T treatment under N_2)

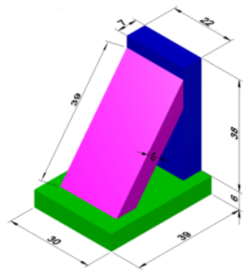
Note: Liquid metal infiltration has not been possible but by powder metallurgy it was possible. However, results were very poor.

Infiltration of CNT skeletons (felts) with a ceramic matrix by AIT

- **Aromatic Sol-Gel Process**
  - Only 3 simple steps (infiltration, curing, pyrolysis and hot pressing within one step
  - Total manufacturing time for CMC only ~80h
- **Resin**
  - Easy and safe to handle
  - NO reaction at RT;
NO vacuum required
  - Significantly increased pot life
  - Thermoplastic behaviour allows shaping of components
- **Samples**
  - Good electric conductivity (300-400 S/m) EDM possible!
  - Good friction behavior in air at RT (friction coefficient 0,15)
- **Demonstrator**
  - After Curing → Good machinability (cutting, grinding, …) Best bonding of specimens before pyrolysis
  - Stabilisation of manufacturing process for larger samples


Sample dissolved in sol-gel process


Samples after curing



Demonstrator

Infiltration and characterisation of CNT skeletons (bucky papers/felts) with a polymer matrix by INEGI/PIEP/UOP/AAC (1/2)

INEGI

Low pressure RTM, carboxylated CNT
Skeleton (bucky paper) impregnation by filtering,
Epoxy system: SICOMIN SR8100+SD882x

Good impregnation of CNT papers.
General improvement in mechanical and damping properties (storage modulus in the rubbery phase temperature range 40 - 70% higher)
Mechanical performance of composites below expectations: Maybe due to resin rich regions around CNT skeletons.

Recommendations:
Improve infiltration process in order to reduce the resin rich regions around the CNT skeletons and between layers.
Application of high external pressure during the resin cure.

PIEP

Skeleton (bucky paper, felt, different post-processings) impregnation under vacuum at room temperature
Epoxy resin: Epikote 862 / Epicure W

Dimensions of the CNT skeletons are deviated, particularly in thickness. Wet chemically oxidised skeletons present very high CNT content.

Skeletons present good interaction with resin, as evidenced by low value of contact angles measured in the steady region. Heat treated CNT skeleton present the higher initial contact angle and at long times the lower contact. Composites are properly impregnated and no voids or air are expected.

Poor dimensional stability of skeletons, being the heat treated CNT skeletons the best performers.

Felt composites point out to a poor impregnation by the epoxy resin and the likely presence of voids or air inside the composite.

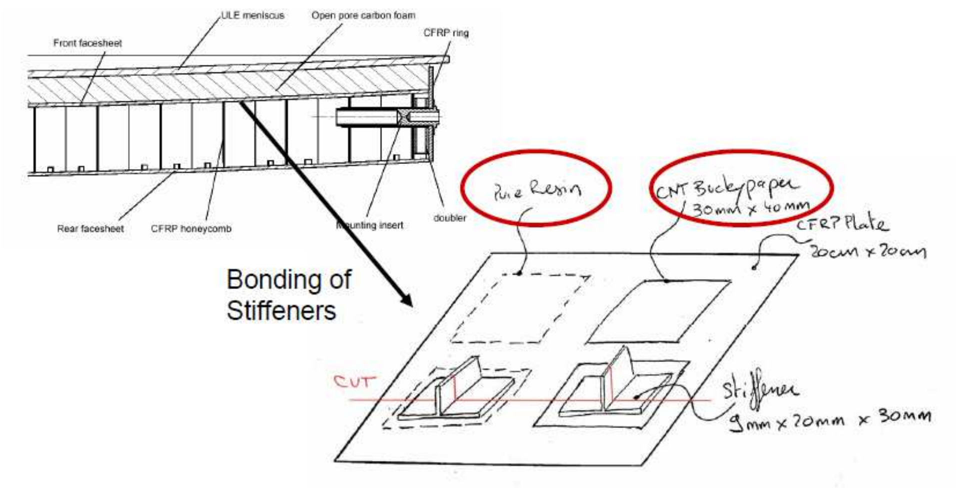
Infiltration and characterisation of CNT skeletons (bucky papers/felts) with a polymer matrix by INEGI/PIEP/UOP/AAC (2/2)

AIT
First VARTM, then route using capillary effect at 120° C, Skeleton (bucky paper, functionalised) Cyanate Ester: PT4000
Good wettability of CNT by CyE
No porosity in CNT layers but CYE top/bottom layers
Slight increase of TC from ~0,2 W/mK (CyE) to 0,4 W/m
Improvement of CTE from 45*10^{6}K^{-1} to 15*10^{6}K^{-1}

PMC properties in general

Material Characteristics	Polymer Matrix Composite
Electrical Conductivity	⇑⇑
Mechanical Properties	⇑ (especially at higher temperatures)
Coefficient of Thermal Expansion	⇑ (could be lowered in AIT PMC samples)
Thermal Conductivity	⇑ (considerable increase compared to the pure polymer but still below 1 W/mK)

Demonstrator: Bonding of stiffeners on CFRP plate



- Difficulties: Bonding techniques not prepared during NACO
- No screening of the bonding system

- Problemes during the demonstration phase:
  - Surface activation, thermal stresses, failure, debonding
  - Air inclusions, entrapments during application
  - Reaction with substrat or compatibility (Cyanate Ester)
- Testing: Thickness measurements, electrical resistance, Thermal diffusivity, ultrasonic scanning

- Slight influence of CNT on the contact bonding of stiffeners
- Global solution of bonding: CNT in CFRP and CNT in matrix

NACO1 lessons learned for subsequent project NACO2

For CMC and PMC: Further development of infiltration process: complete infiltration possible,

- soundness / repeatability of CNT skeleton production extremely important:

Good quality control is mandatory

- Optimisation potential: addressing the different interfaces

- Up to now only small dimensions investigated.

In NACO2

- **Stabilization of CNT skeleton manufacturing process and upscaling of dimensions.**
- **Stabilisation of the manufacturing processes of CMCs and PMCs in close cooperation with CNT skeleton provider FC.**
- **Quality control for the material / process is one of the major objectives of NACO2**
- **Optimisation of composite manufacturing processes**

  Go to the maximum sample/demonstrator size possible with existing facilities.
  PMC: different applications, e.g. multilayer CFRP, health monitoring, adhesive
  CMC: optimise the pyrolysis process and get bigger and reproducible samples
  Characterization: use of stabilized characterization methods.
- **Space Applications**

  PMC: demonstrator(s) should include more complex applications (health monitoring app- is being developed by UOP)
  CMC: demonstrator should yield e.g. an optical mirror targeting manufacturing feasibility assessment .

Which properties can be improved by adding CNT to composites?

Property	Rating: Influence of Nano-Filling
Through thickness thermal conductivity (e.g. nano-filled CFRP, recent results by UOP, Bucky paper interleaved CFRP composite)	↑
Through thickness electrical conductivity (e.g. nano-filled CFRP, CNT-filled CF/PEEK)	↑
Bending strength (CNT filled CF/PEEK)	↗
Interlaminar fracture toughness (e.g. nano-filled CFRP)	↑

Inside CNT

CNT-Polymer Matrix Boundary

CNT-CNT

Acknowledgements

- ESA/ESTEC (The Netherlands)

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- INEGI (Portugal)
- PIEP (Portugal)
- AAC (Austria)
- TUHH (Germany)
- PTJ (Germany)
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Thank you for your attention.

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