HPS
High Performance Space
Structure Systems GmbH
GERMANY

Novel Composites Reinforced with Bucky Papers or Bucky Disks for Space Applications

9th ESA Round Table on Micro and Nano Technologies for Space Applications

F. Hepp, E. K. Pfeiffer, O. Aschenbrenner, S. Forero, V. Kostopoulos, V. Liedtke, S. Linke, C. Macho, M. Martins, A. Masouras, L. Pambaguian, C. Pereira, A. Vavouliotis, H.-G. Wulz

Lausanne | 11^{th} June 2014

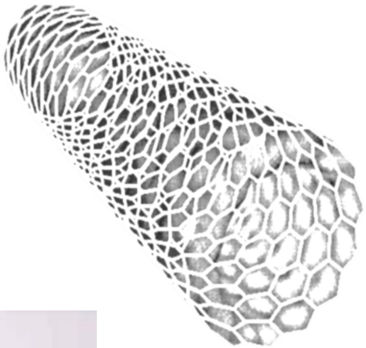
Table of Contents:

Part 1: Overview
Part 2: Production of Skeleton Materials
Part 3: NACO CNT Skeleton Ceramic Matrix Composite Materials
Part 4: NACO CNT Skeleton Polymer Matrix Composites
Part 5: Lessons Learned and Outlook

Part 1: Overview

Part 1: Motivation

Why use CNT papers and felts, although cost increase and higher complexity of composite production process is involved?



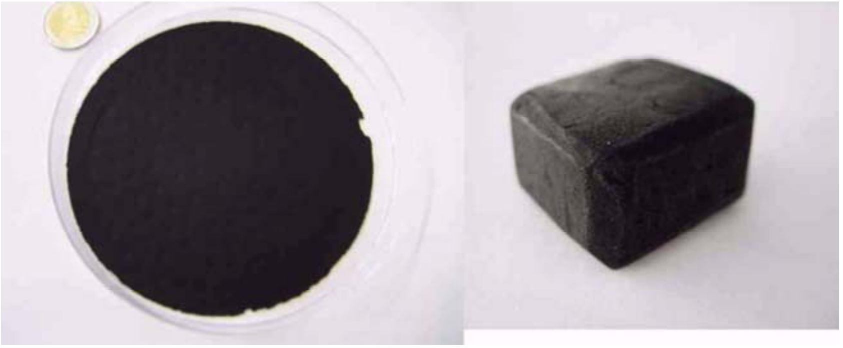
The aim is to :

Get high amounts of CNT into the Composite material to

improve material behaviour e.g.:

- electrical properties
- thermal properties
- mechanical strength

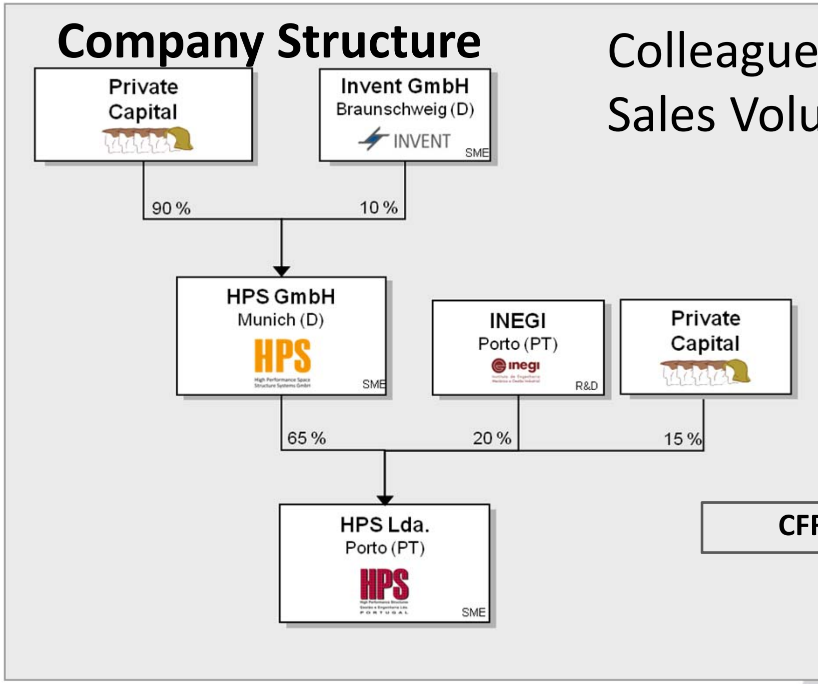
add other performances



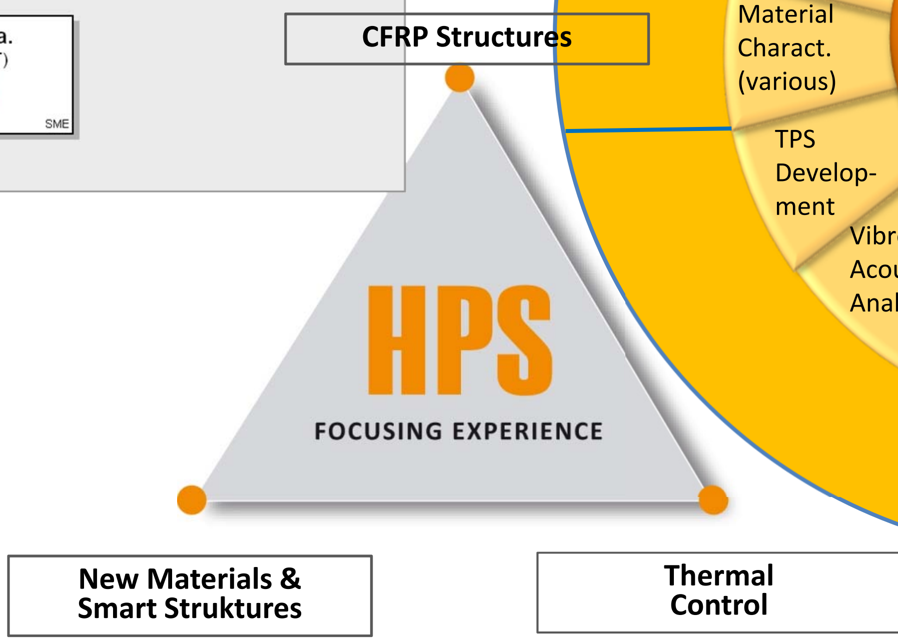
reduce mass for more payload
substitute parts that are currently made from metals and other materials

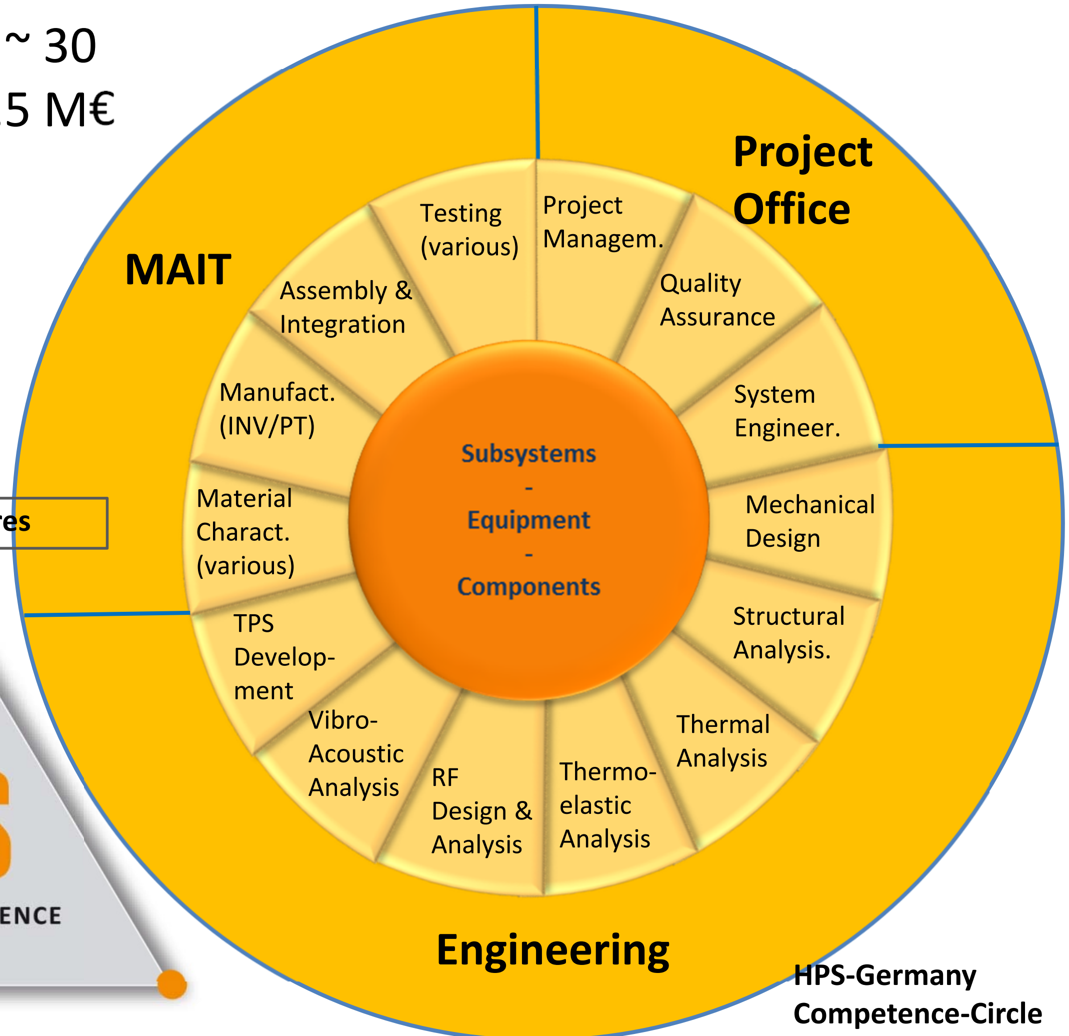
High Performance Space Structure Systems (HPS) GmbH

Company Structure



Colleagues in D ~ 30
Sales Volume: 3.5 M€



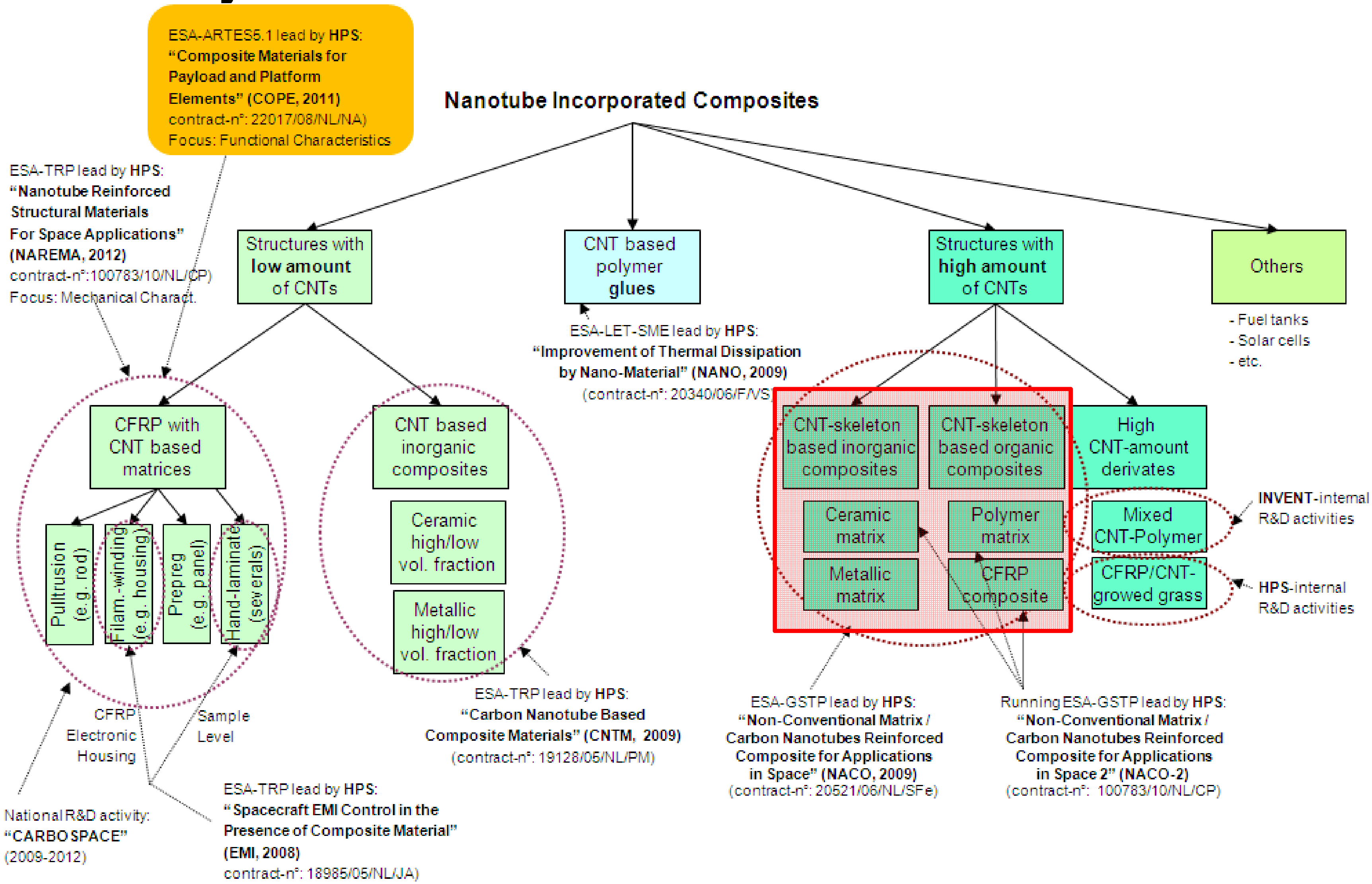


HPS-Germany Competence-Circle

Competences

- Components
- Composite Structures
- Satellite Subsystems

Nanotube-Projects at HPS



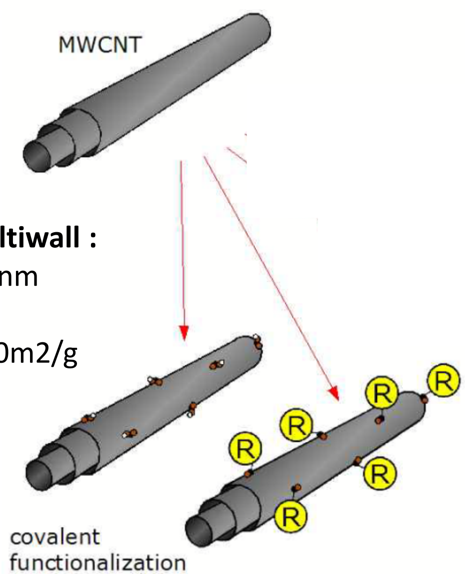
Project Outline

- **Non-Conventional Matrix / CNT Reinforced Composite NACO1** (ESA Contract No.: 20521/06/NL/Sfe), 2007 – 2010 , prime HPS, partners, AAC, AML/UOP, ASTRIUM, DLR, ELECTROVAC, FC, INEGI, INVENT, PIEP
  and subsequent project NACO2 (ESA Contract No.: 4000104354/11/NL/RA), 2010 - 2013, prime HPS, partners AAC, AML/UOP, ASTRIUM, FC, INEGI, INVENT,

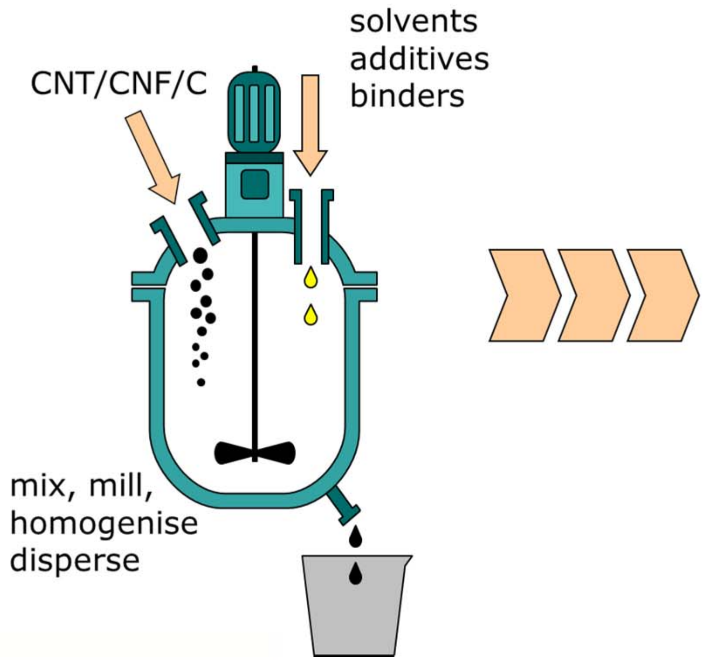
Part 2: Production of Skeleton Materials

2.1 Carbon Nanotubes as Primary Material for Skeletons

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



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

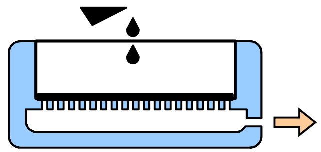


- purification
- homogenization
- functionalisation
- water and solvent based dispersions and pastes
- metallization
- CNT and CNF felts

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

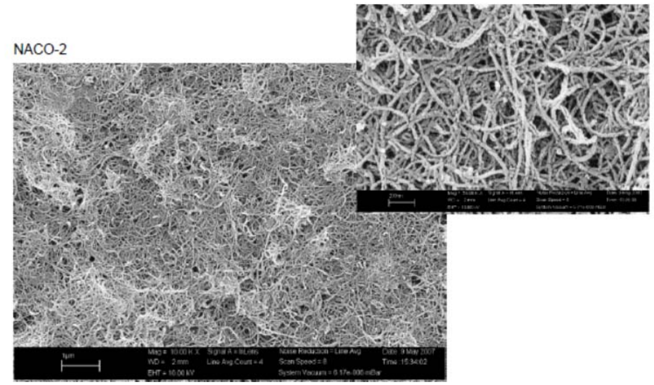
CNT Skeletons Produced by FutureCarbon

Skeleton papers by filtration (NACO)



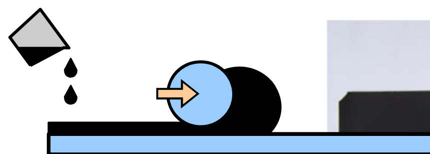
vacuum

about 8cm x 500 µm

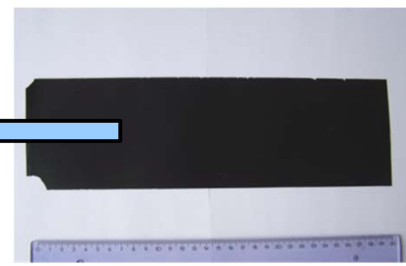


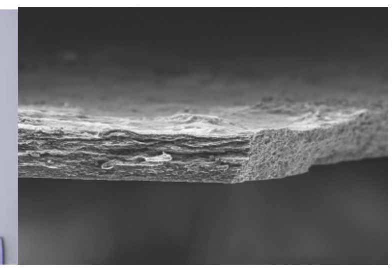
SEM: surface of carboxylated CNTBP

Skeleton papers by tape casting (NACO2)



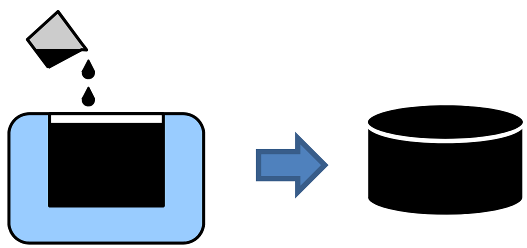
tape casting





max. 100cm x 10 cm x (50-150) µm

Skeleton felts or CNT foils by slip casting (NACO + NACO2)



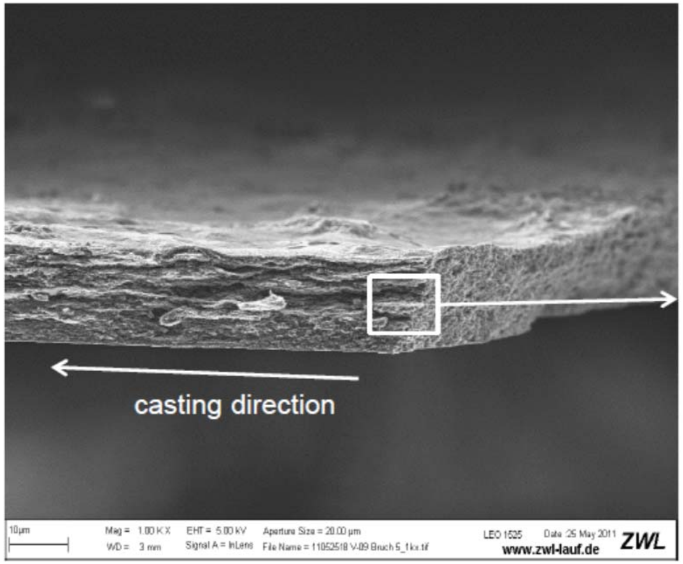
slip casting

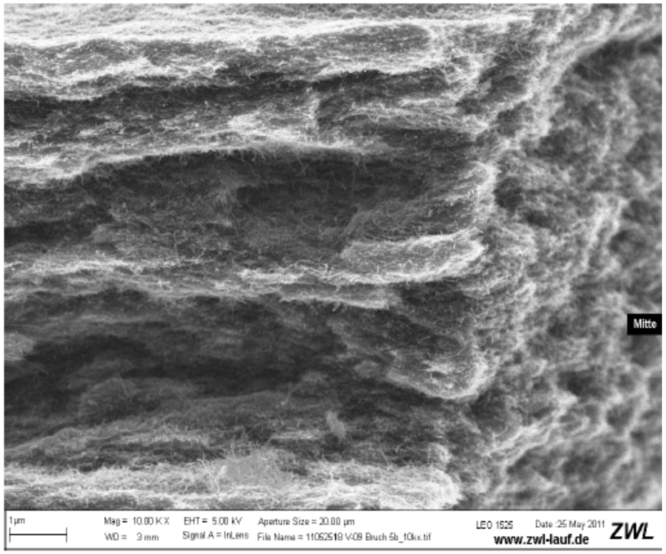
dry

max. 15 x 12 x 2.5 cm

CNT foils developed by FC and GSO in NACO2

SEM micrograph of a single layer : Breaking edge





CNT foils developed in NACO2:

Use of functionalised MWCNT and binder PAA (Content 30%)

Delivery on support foil

Density of felt skeletons: 0.20-0.25 g/cm³

Electrical sheet resistance of CNT foils: 8-15 Ω/sq

Electrical conductivity of about 5000 S/m

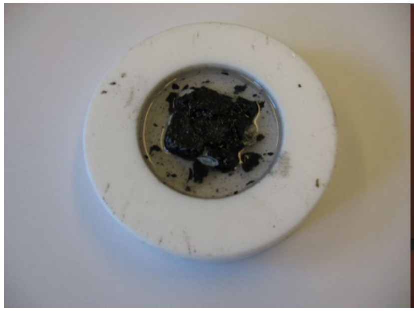
Part 3: NACO CNT Skeleton Ceramic Matrix Composites

Infiltration of CNT Skeletons (felts) with a Ceramic Matrix by AAC 1/2

- **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)

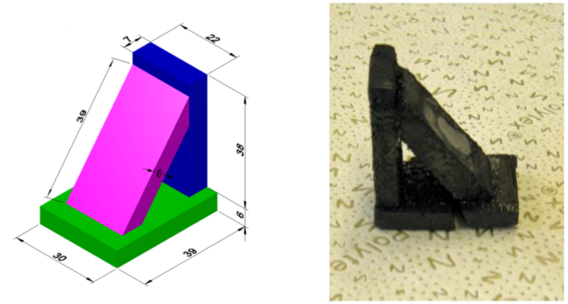


Sample dissolved in sol-gel process

Samples after curing

Infiltration of CNT Skeletons (felts) with a Ceramic Matrix by AAC 2/2

- **NACO Demonstrator**
  - After Curing → Good machinability (cutting, grinding, …) Best bonding of specimens before pyrolysis
  - Stabilisation of manufacturing process for larger samples
- **NACO2 Demonstrator**
  - Potential Application target: Optical mirror
  - Bigger CNT felts: Cracks during CMC production therefore impregnated CNT felts were milled and sieved with mesh size 250 µm
  - Curing + compaction + pyrolysis → less cracks, production of demonstrator possible
  - Different shapes of pockets by die sinking possible
  - Still amounts of oxygen in demonstrator after pyrolysis. After additional high temperature treatment, oxygen is significantly reduced neither damaging the demonstrator visibly nor destroying the CNTs by oxidation



Demonstrator NACO

Demonstrator NACO2
Spherical upper surface
different pockets by die sinking

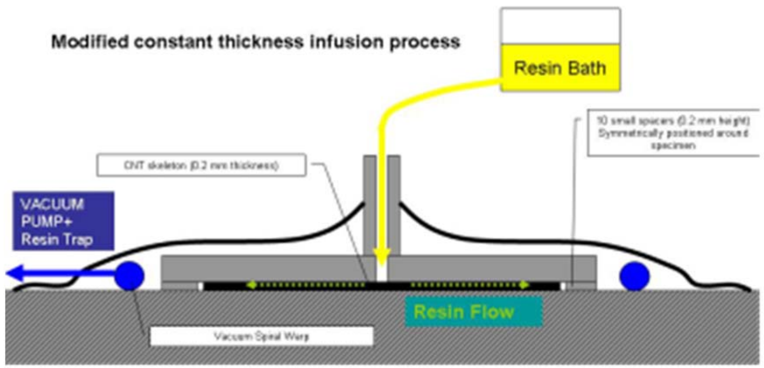
Part 4: NACO CNT Skeleton Polymer Matrix Composites

Infiltration and Characterisation of CNT Skeletons (bucky papers/felts) with a Polymer Matrix by INEGI/PIEP/AML UOP/AAC (1/3)

The processes used for NACO:

- fast RTM injection by partner DLR in a pre-study,
- low pressure RTM and infiltration from the sides of the CNT skeleton piles by partner INEGI
- modified VARTM by AML/UOP to provide a solid, constant thickness of the final product with proper mechanical spacing and to avoid direct pressure on the CNT,
- VARTM using pre-impregnated CNT skeletons by PIEP and
- Infiltration of each CNT skeleton and then stacking with a PTFE framework w/o using pressure on the skeletons, just using capillary effect at 120° C by AAC

Fast-RTM-Injection: infiltration of stacked paper possible, infiltration was mainly governed by the capillary forces (Image DLR)



Schematic diagram of VARTM technique used at UoP

Infiltration and characterisation of CNT skeletons (bucky papers/felts) with a polymer matrix by INEGI/PIEP/UOP/AAC (2/3)

Skeletons present good interaction with resin, as evidenced in previous contact angle measurements. Good wettability of CNT by infiltration systems (epoxy, cyanate ester) Good impregnation of CNT papers.

General improvement in mechanical and damping properties (40 – 70 % higher in the rubbery phase temperature range) could be improved with respect to the matrix material (INEGI)

Mechanical performance of composites below expectations: Maybe due to resin rich regions around CNT skeletons (PIEP, INEGI)

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

Slight increase of TC from ~0,2 W/mK (CyE) to 0,4 W/mK (AML/UOP)

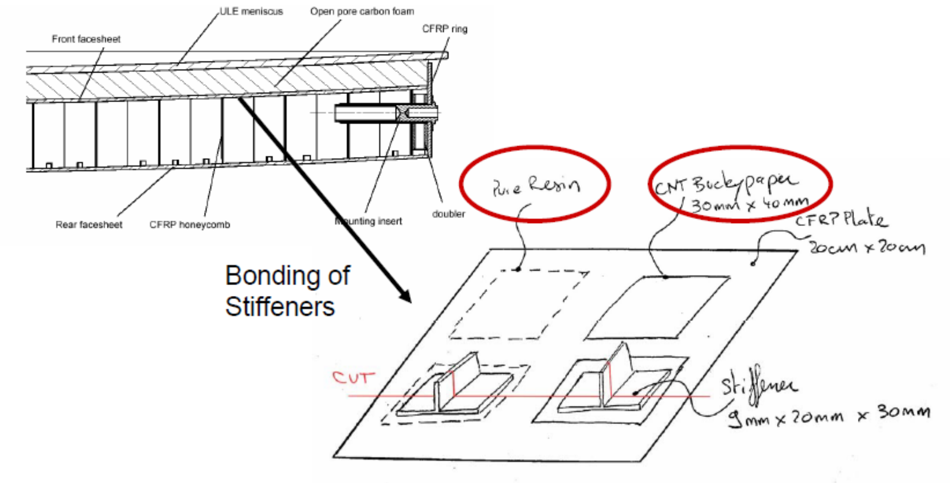
Improvement of CTE from 45*10^{6} K^{-1} to 15*10^{6} K^{-1} (AAC)

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)

Infiltration and Characterisation of CNT Skeletons (bucky papers/felts) with a Polymer Matrix by INEGI/PIEP/UOP/AAC (2/3)

Demonstrator NACO: 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

NACO Lessons Learned for Subsequent Project NACO2

- Stabilization of CNT skeleton manufacturing process and upscaling of dimensions. Repeatability of CNT skeleton production extremely important
- Stabilisation and optimisation 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 potential: addressing the different interfaces in the composites
- Characterization: use of stabilized characterization methods.
- Up to now only small dimensions investigated. go to the maximum sample/demonstrator size possible with existing facilities
- Space Applications

  PMC: demonstrator(s) should include more complex applications (e.g. multilayer CFRP, health monitoring application developed by UOP, adhesive for CFRP components)
  CMC: demonstrator should yield e.g. an optical mirror targeting manufacturing feasibility assessment.

NACO2 Study Objectives for PMC

Statement of Work:

› The main objective of this activity is to scale-up the material developments and thereby increase the TRL for CNT skeleton based ceramic and polymer composites.

› The developed materials shall be used for manufacturing and testing of demonstrators for typical space applications.

Work Logic:

› Development planning

› Composite development

› Demonstrator design, manufacturing and testing

› Space application and study synthesis.

Space Applications

Space Application	CNT-Skeleton
Satellite Panels	X
Optical Mirrors	X
Heaters	X
Electronic CFRP Housings	X
Health Monitoring	X
Bonded connections at CFRP Structures	X
Electrical grounding path	X
Optical Benches	X

Selected as:

- Satellite Panels ← **CFRP demonstrator**
- Optical Mirrors ← **Ceramic demonstrator**
- Health Monitoring ← **Add-on for CFRP-Dem.**
- Bonded connections at CFRP Structures ← **Add-on for CFRP-Dem.**

NACO2 PMC Test Campaign

1 # Stabilised CNT skeletons

2 # upsized CNT foils

3 # upsized and stabilised CNT foils

4 # demonstrator CNT foils

PMC- Production

Tests by PMC developers/partners

ESA/HPS/FC Visit

Round Robin

INV Pre-Tests

UOP TC, EC SEM

AAC EC

INE TC, DMA SEM

ESA TC, EC

Demonstrator

NACO2 PMC Overview of Results

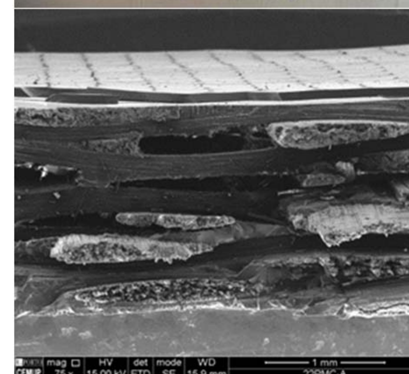
Assesssment of Results from Sample Campaign

+	Electrical conductivity
(+)	Thermal conductivity
–	Mechanical properties
+	Processability

NACO2 Demonstrator Campaign (1/2)

Scalable CFRP-CNT skeleton based composite laminates by INEGI

- Development of new production process for up-scaled composites
- Close coperation with FC to assess the properties of CNT felts (binder issue)
- manufacturing of composites with large and very thin CNT foils feasible



***1st image: CNT skeleton CFRP demonstrator sample by INEGI* 100x100mm^2, top surface is CNT foil**
2nd image: :cross section of demonstrator sample (pictures: INEGI)

Approaches of new sensing technologies by AML/UOP

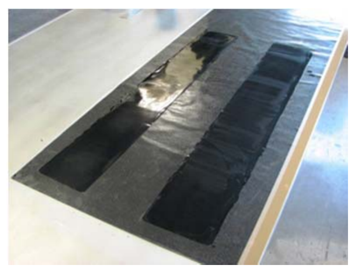
- Electrical resistance and thermo-mechanical deformation closely connected: Use as Structural health monitoring sensors
- CNT – Skeletons used, due to their high electrical conductivity, as sensing elements at various forms (stand – alone sensors, embedded to FRPs sensors and bonding film sensors)

3rd image: PMC-CNT standalone sensor,
4th image: CFRP facesheet (300 x 100 mm) with integrated CNT – paper layers and cleats produced by INVENT. Three cleats attached to the facesheet with a CNT foil serving as adhesive film one cleat without CNT foil. The structure was tested for static electrical measurements and SHM capabilities (pictures UOP)

NACO2 Demonstrator Campaign (2/2)

CFRP-CNT-hybrid components by INVENT

- Develop a large scale CFRP composite structure using CNT skeletons
- Test of methods for structural bonding of CFRP-CNT-hybrid components
- Set up of a material and process list for best working candidates
- Manufacturing of samples in prepreg and resin infusion technology, which were closer to real hardware parts according to geometry and layup
- Definition of a large scale demonstrator together with the project partners:
  Single 1000 x 300 x 30 mm sandwich plate (facesheet – honeycomb-facesheet), which upper facesheet is partially coated with CNT foils in the size of 1000 x 100 mm. On top of the upper facesheet, different cleat types were bonded). Some of them were also coated with CNT foil. Special areas of the facesheet with CNT cut-outs were also realized successfully.
-



1st image: CNT-foils (black, length 1000 mm width about 100 mm) on wet prepreg layup (dark grey) for facesheets prior to curing, 2nd image: Finished large scale demonstrator (1000 x 300 mm) 3rd image: Partial view of large demonstrator with two CNT foils on the top facesheet and cleats of different configurations. The cleat row on the right is electrically bonded with conductive adhesive (white). (pictures by INVENT)

NACO2 PMC Overview of Results

Impact of CNT Foils on Performance of Demonstrators

+	Electrical Conductivity
+	Assessment of SHM Functionality
o	Thermal Conductivity
+	Processability

- Large scale manufacturing of CNT-skeleton composite in CFRP (at least 100 x 30 cm for overall demonstrator size and CNT foils at 100 x 10 cm)
- Improvement of electrical conductivity at the surface and into the CFRP-fibres
- Development of a structural health monitoring sensor using up-scaled skeletons for CNT skeleton CFRP composites

Part 6: Lessons Learned and Outlook

Which Properties can be Improved by adding CNT to Composites?

Property	**Rating: Influence of CNT skeleton on composite**
Through thickness thermal conductivity (results by UOP, INEGI on sample level (on PMC)	↑
Electrical conductivity (on sample and on demonstrator level for PMC and CMC)	↑
Mechanical Properties (for PMC)	↗
SHM functionality	↑

Inside CNT

CNT-Polymer Matrix Boundary

CNT-CNT

Most Promising Space Applications

Space Application	CNT-Type
Satellite Panels including attachments, electr. bondings and heaters (electrical conductivity)	Skeleton, Spray, Prepreg
Optical Mirrors (Ceramic / Polymer)	Skeleton
Electronic CFRP Housings (already treated in other running activity)	Low vol.
Health Monitoring (tension monitoring)	Skeleton
CFRP RF-components like horns or waveguide-networks (CTE-mismatch, good coating, good alpha-epsilon)	High vol. fract., Endless Fibres
Secondary Radiators (good alpha/epsilon)	High vol. fract.; Prepreg
Optical Baffles (low reflectivity, sharp machining)	Endless fibres, Prepregs

Finally, a great thanks to ESA/ESTEC and national delegates for the funding of these activities..

..and many thanks to the NACO and NACO2 Project Partners !

- AAC (Austria)
- AML/UOP (Greece)
- Astrium (Germany)
- DLR (Germany)
- Electrovac (Austria)
- FutureCarbon (Germany)
- GSO (Germany)
- INEGI (Portugal)
- Invent (Germany)
- PIEP (Portugal)
- Siemens (Germany)

Thank you for your attention!

Dr. rer. nat. Felicitas Hepp
T: +49 089 452057677
hepp@hps-gmbh.com

HPS GmbH
Hofmannstr. 25-27
81379 München
www.hps-gmbh.com

HPS High Performance Space Structure Systems GmbH GERMANY