# New Research and Application Research Results with CNH – An Overview

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on the Commercial Use of Nanocarbons
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# CNH – Introduction (1)

Our Japanese partner eenanoTech has developed an industrial production process for Carbon Nanohorns (CNH) with following properties:

- Pure carbon material (no catalyst residues)
- Single walled carbon nanostructure
- High specific surface
- Dispersible in water (and in solvents)
- Available in industrial quantities

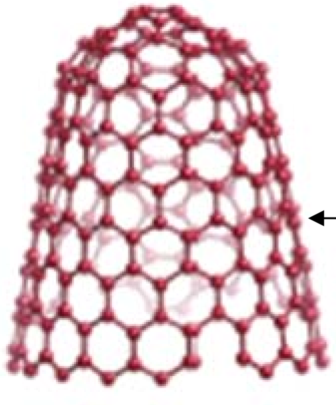
TIE GmbH supplies customers with CNH since 2010.

Since then different kind of research and development with regard to industrial applications have be started.

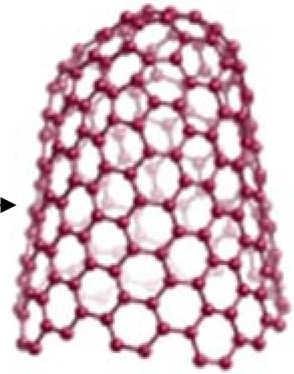
This presentation is an overview of findings and ongoing research for industrial applications.

# CNH - Introduction (2)

Carbon Nanohorns have already been described in the 1990s as nano-scale hornlike structures with a shape of a sewing thimble.



Schematic shape of carbon nanohorns



Due to geometric reasons (closed conical shape) Carbon Nanohorns are typically single walled.

The Carbon Nanohorns are typically not occuring in isolated horns, but in aggregated structures.

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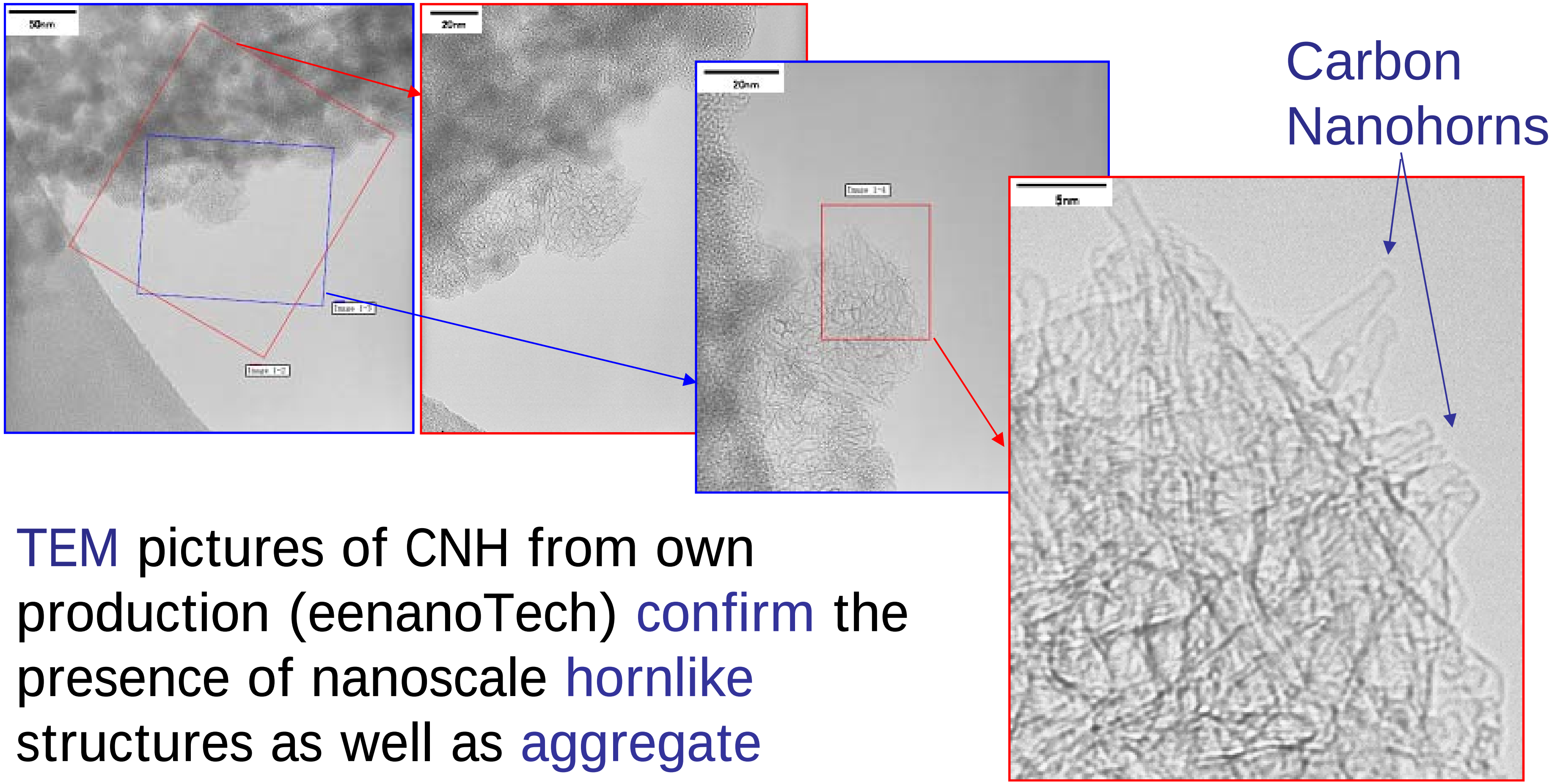
# TEM Pictures of CNH




TEM pictures of CNH from own production (eenanoTech) confirm the presence of nanoscale hornlike structures as well as aggregate structures (eenanoTech, 2009).

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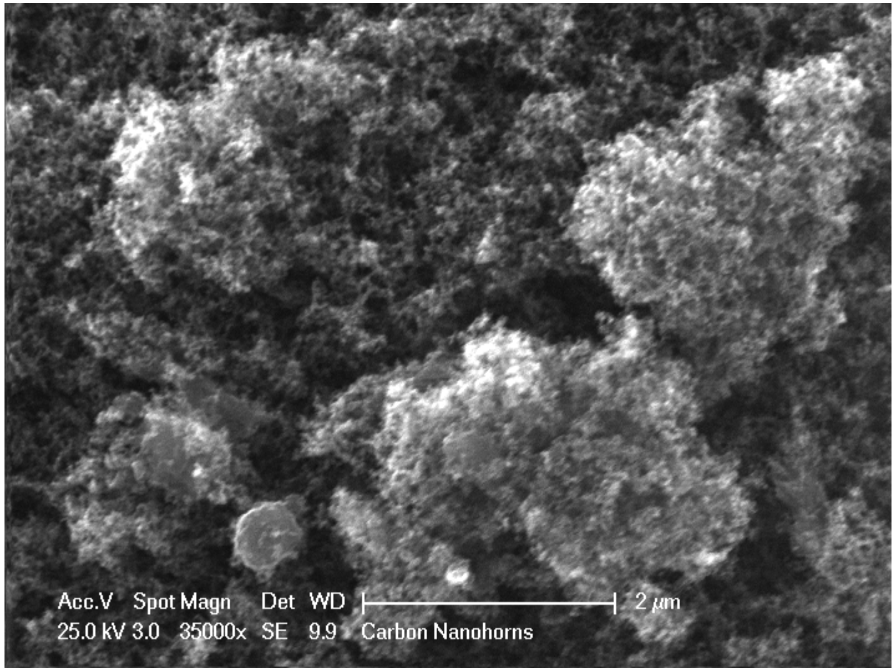
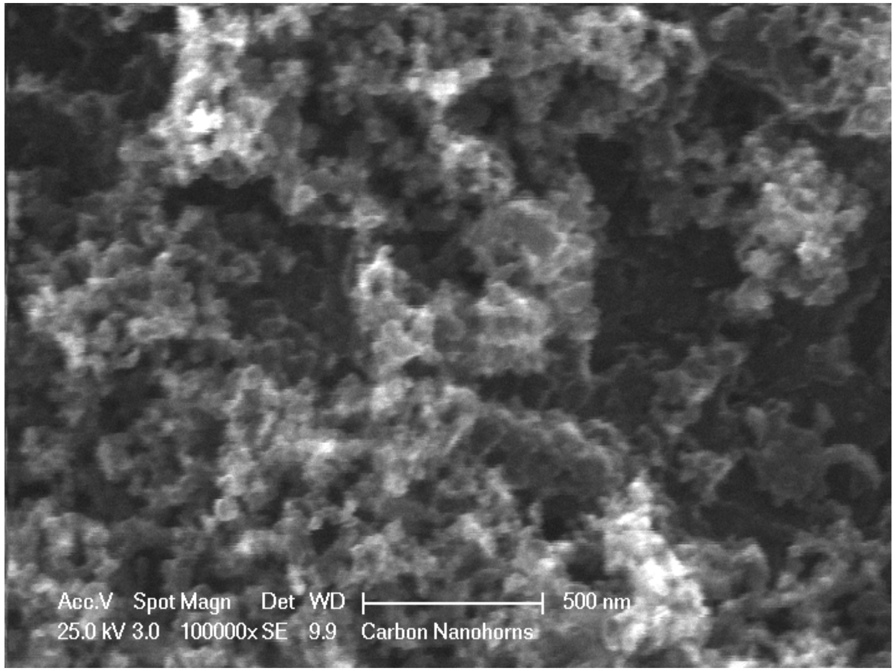
# SEM Pictures of CNH

Scanned Electron Microscope picture analysis performed shows aggregates of cauliflower shape, which size amounts up to several µm³, with a porous structure:
(TU Darmstadt, 2010)



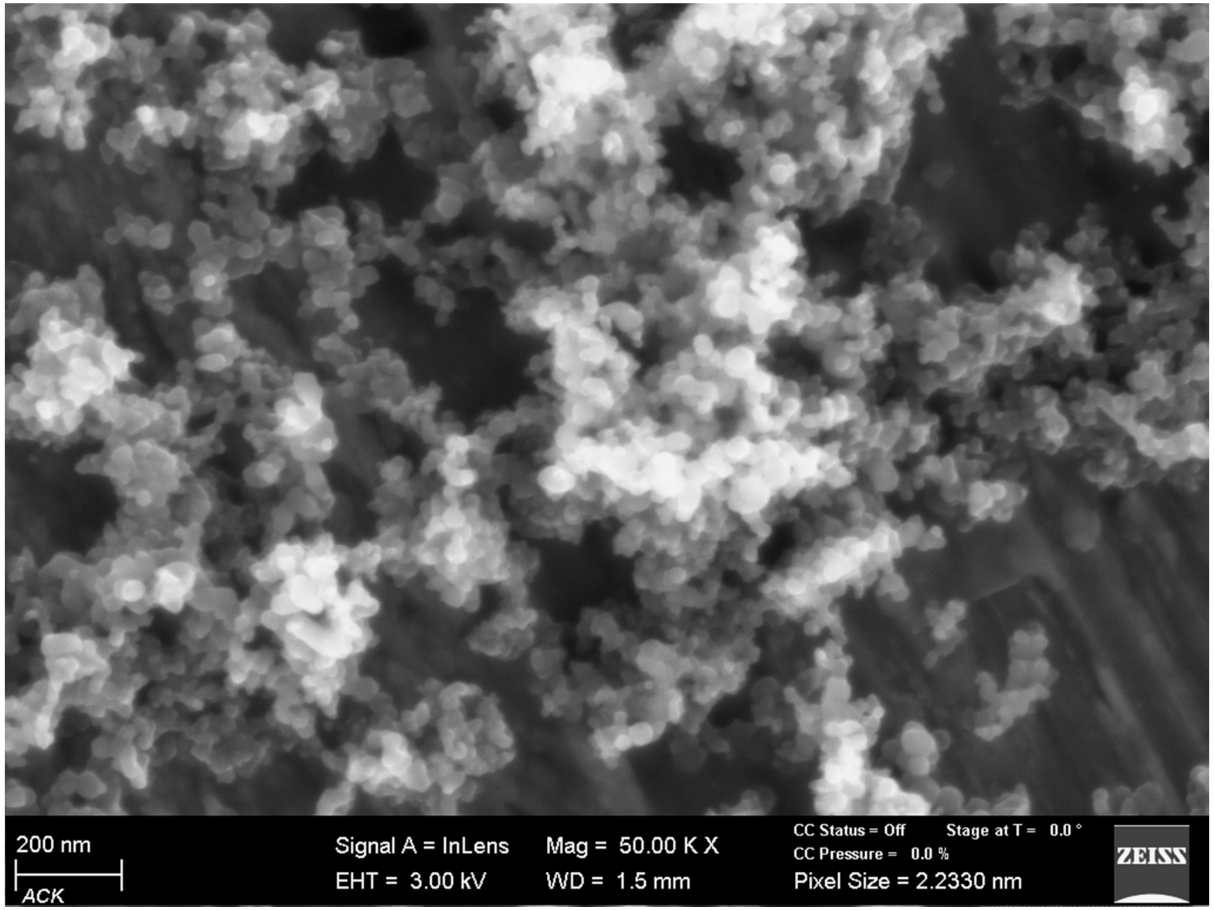



# FEM Pictures of CNH (1)

## High Resolution Field Emission Microscope (FEM) Pictures:

High resolution Field Emission Microscope Pictures (with Zeiss NTS systems) show nano-structures with a typical size of some 10 nm (typical range 20-150 nm) and porous and aggregates up to several µm.

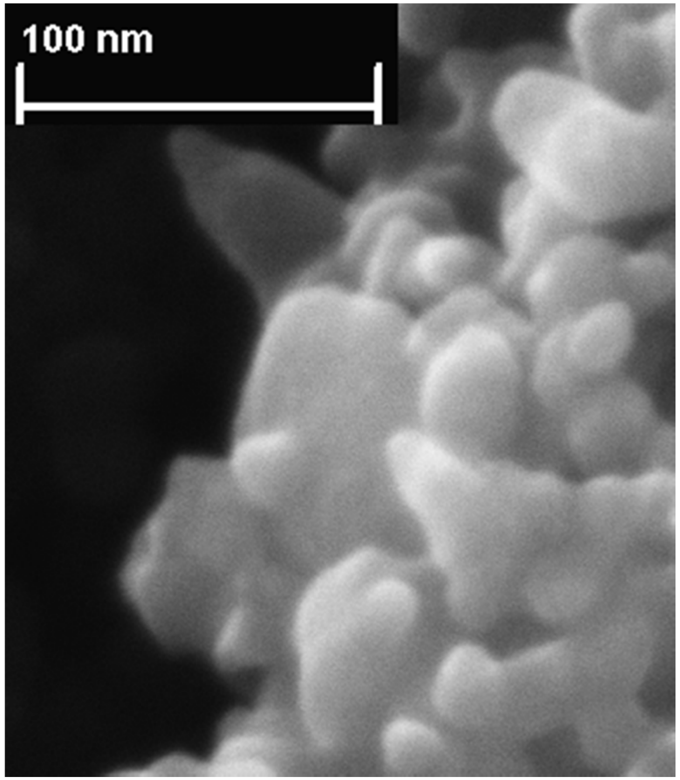
(Plejades, 2011)

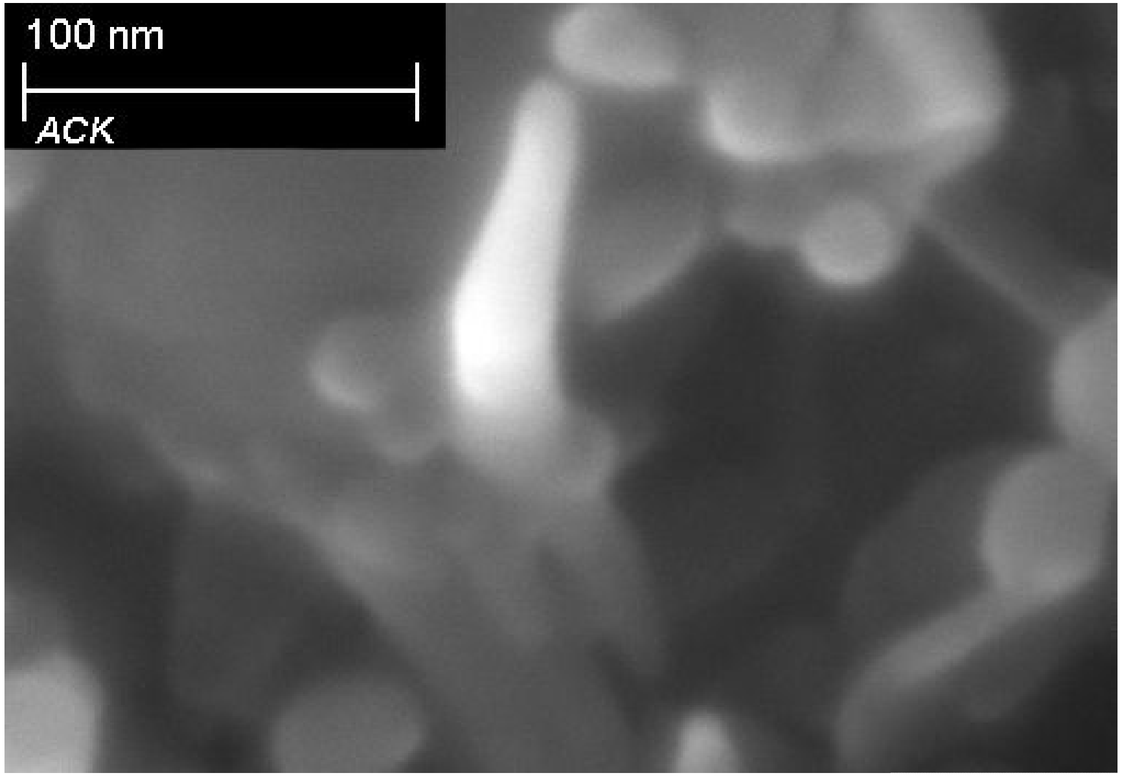


# FEM Pictures of CNH (2)

## Very High Resolution FEM Pictures (Zeiss NTS Systems):

The nano-scale hornlike sub-structures with typical size of 20-150 nm in length can be well seen (Plejades, 2011) .

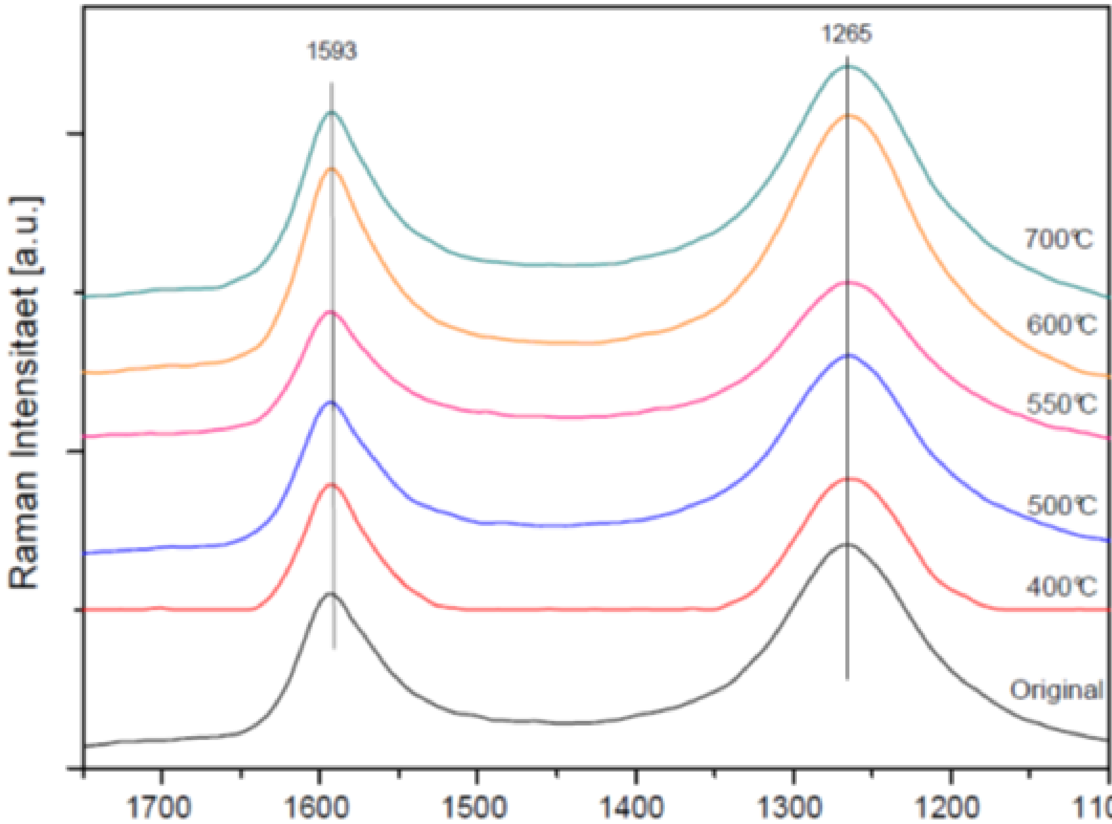


# Raman Spectrum of CNH

The Raman spectrum is typical of nanostructured carbon (graphene spectrum). The spectrum does not show any significant change of the $I_D/I_G$ ratio after thermal treatment with Argon, which confirms only very little (if any) amorphous carbon.

(TU Darmstadt, 2010).

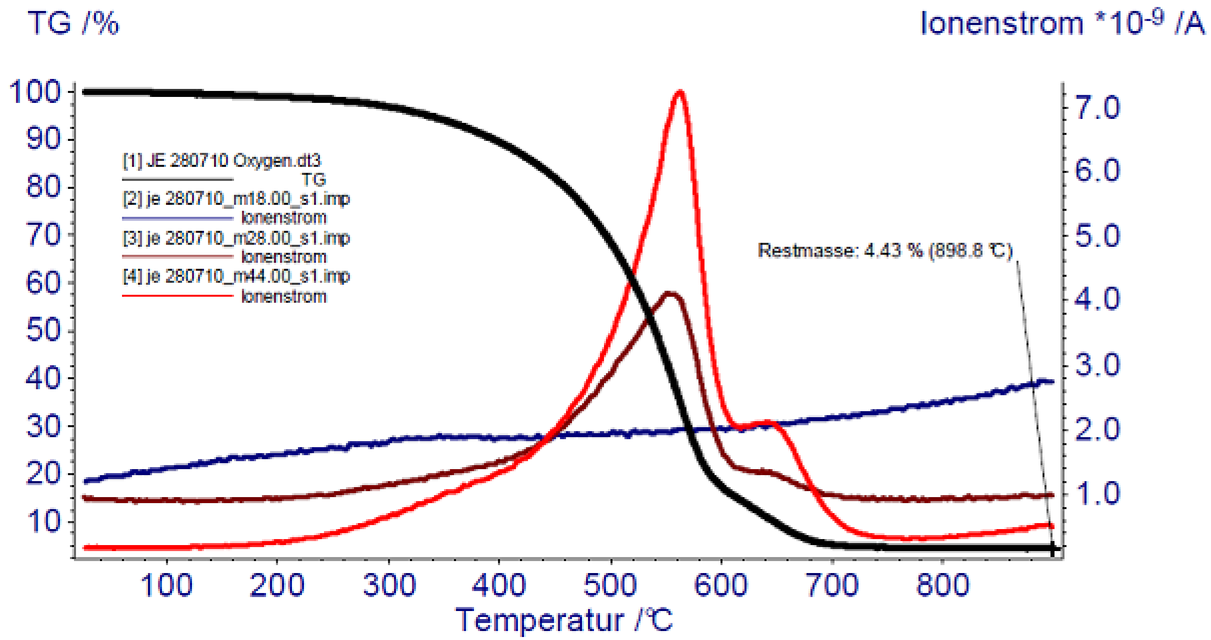


# Thermogravimetry of CNH

Thermogravimetric analysis confirms impurity of less than 5% (TU Darmstadt, 2010):

## Loss of mass:

- Starts at 260 ºC
- Is significant from 430 ºC upwards
- Reaches a maximum at 600 ºC.
- Above 720 ºC the residual mass amounts to 4.4 %.
- The break-down products consist in $H_2O$, CO and $CO_2$.
- Impurity coming probably from precursor (graphite)



# Characterization of CNH

Carbon Nanohorns (CNH) are:

Single walled nanostructures:

Length 20 – 150 nm, typical Ø 3 -25nm, building Agglomerates

Agglomerates: particle size ca. 20-150 nm or bigger, agglomerated, up to µm-sized agglomerates

| | | | |
|---|---|---|---|
| Bulk density: | | 35 | g/l |
| Specific surface: | > | 200 | m²/g |
| Pore volume: | | 1,1 | cm³/g |
| Typical pore Ø: | | 10-100 | nm |
| Hydrogen storage capacity: | > | 0,05 | wt-% ($H_2$/CNH) |

Purity: over 95% (graphite precursor, no contamination from production process, no catalysts)

# Availability of CNH

Carbon Nanohorns (CNH) are available in different forms:

- CNH Type A: dry powder, very pure > 95 %, extremely fine fraction, (air screened finest fraction)
- CNH Type B: dry powder, very pure > 95 %, very fine fraction, (unscreened)
- CNH Type F, „Foam“: CNH-Type B dispersed in pure water, ca. 8-10% CNH
- CNH Type W: CNH Type B moistened with pure water, ca. 80-90% CNH
- CNH may be also dispersed in solvents (like CNT)

# Safety properties of CNH

Carbon Nanohorns (CNH) have interesting safety properties:

- Nano-scale carbon substructures are maintained in bigger aggregates (up to some µm) with cauliflower/spheroid shape
  (spheroid shape makes them fall relatively easily (Stokes law), low aspect ratio making cell membrane penetration unlikely)
- Can be dispersed in pure water without tensides or functionalization (bound form)
- Can be dispersed in nonpolar solvents (bound form)
- Has no contamination (no cytotoxicity) due to production process (medical/chemical use)
- Material Safety Data Sheets available

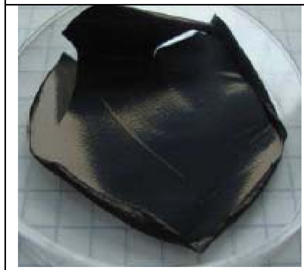
# Tests made or ongoing with CNH

## Functional tests performed and research ongoing with CNH, e.g.:

- Use as pure CNH powder (e.g. for tribology applications)
- Thin structures consisting of pure CNH
  (e.g. bucky paper, CNH impressed into surfaces)
- Massive structures consisting of pure CNH
  (e.g. pure CNH sinter)
- Functional fillers in plastics
  (e.g. in Polycarbonate, PEEK, Polyamide, resins, varnishes)
- Functional fillers in elastomers (e.g. rubber)
- Functional fillers in metallic or ceramic sinters
  (e.g. AlSi12, AL2O3)
- Functional fillers in plastic fibers (e.g. Nylon)

# Bucky Paper Tests by Fraunhofer IPA

## Results: Mechanical properties

| [1] Pure CNT bucky paper REFERENCE | [2] Pure CNH bucky paper | [3] 1:1 CNT-CNH bucky paper | [4] CNT bucky paper infiltrated with CNH dispersion (no centrifugation) | [5] CNT bucky paper infiltrated with CNH dispersion (after centrifugation) |
|---|---|---|---|---|
| • dark grey<br>• brittle structure<br>• smooth, shiny surface<br>• shrinking + folding through drying process | • black, very thin, cracking, lack of cohesion<br>• no free-standing bucky paper<br>• Lack of interconnection due to geometry of particles? | • higher brittleness than reference<br>• rough, matt surface<br>• darker than reference | black, thicker than [1]<br>top surface (in contact with dispersion) ≠ bottom surface (in contact with polymer filter)<br>top: very rough, cracking + peel off<br>bottom: very rough, no peel | black, thicker than [1]<br>top surface (in contact with dispersion) ≠ bottom surface (in contact with polymer filter)<br>top: less peel of than [4]<br>bottom: not as rough as [4] |
|  |  |  |  |  |
| Quite brittle | NOT POSSIBLE – | Very brittle | • Mechanically stronger than pure CNT bucky papers | |

(FhG-IPA, 2010)

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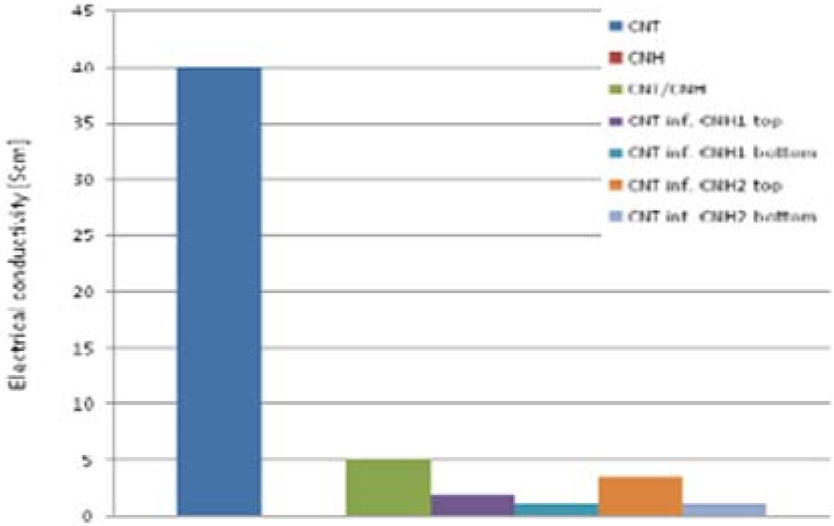
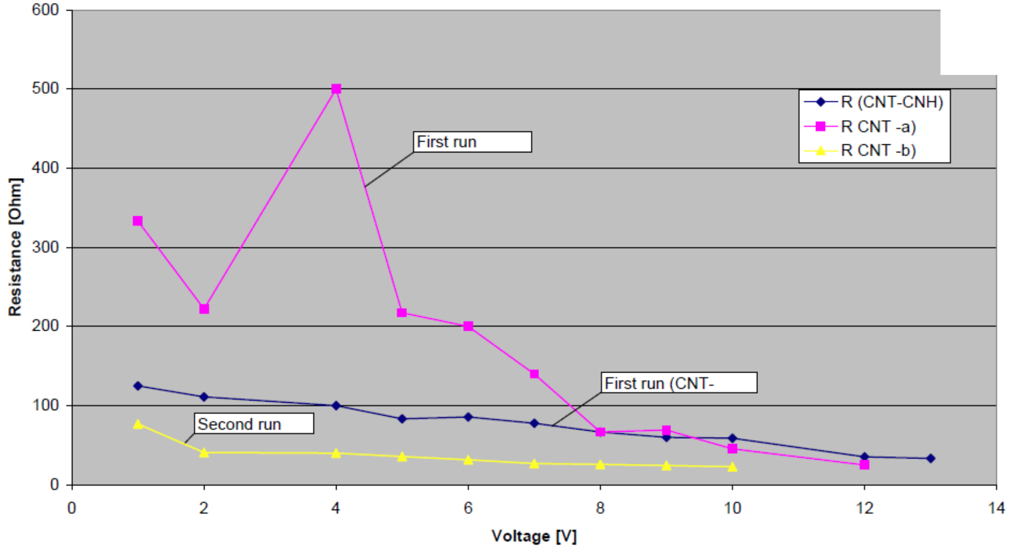
# Bucky Paper Tests by Fraunhofer IPA

Results: Electrical properties

Conductive thin layers are possible with combined CNT+CNH (FhG-IPA 2010)

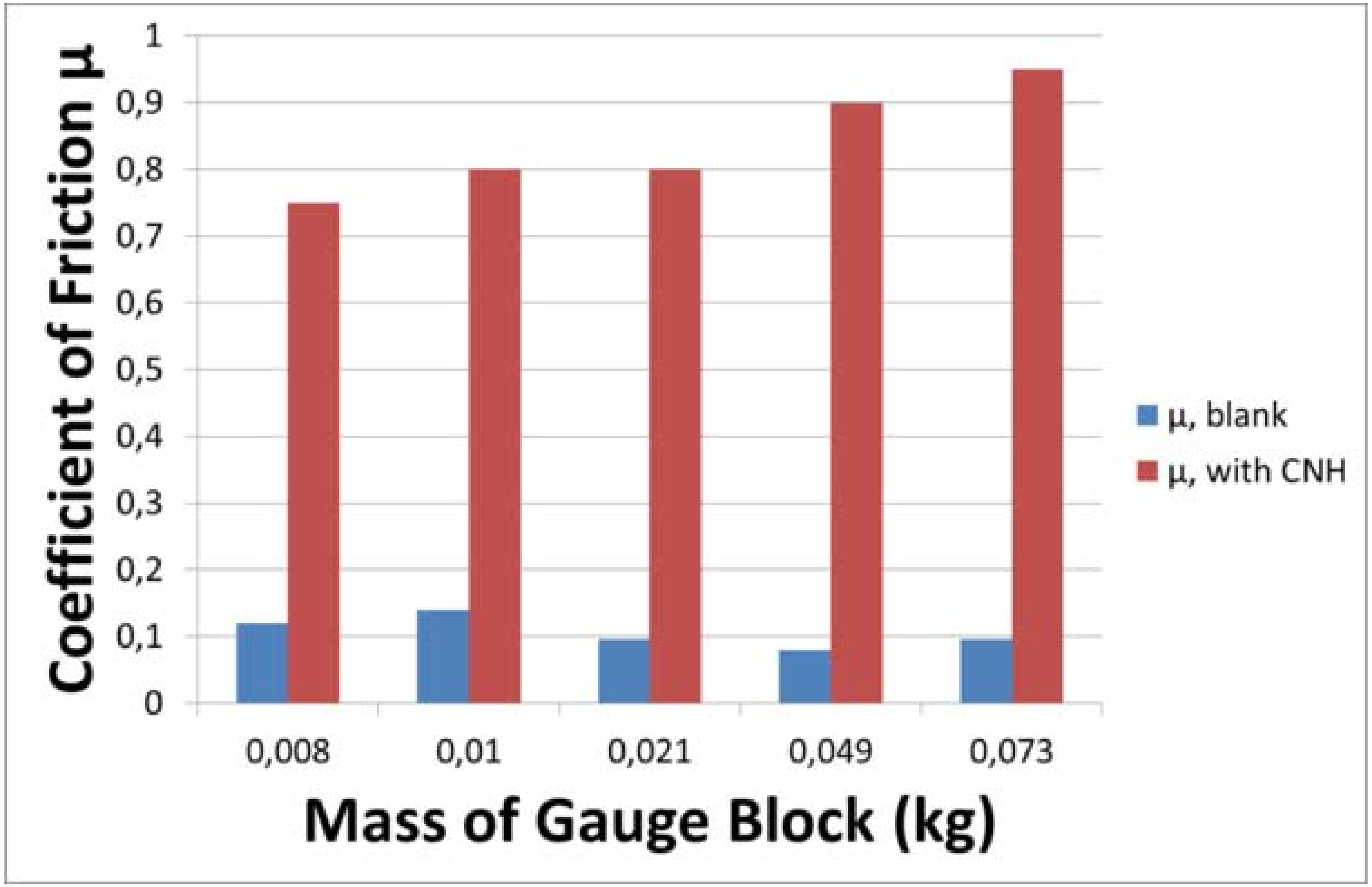



Conductivity can be increased through repeated treatment with high direct current (Plejades, LNP 2011)

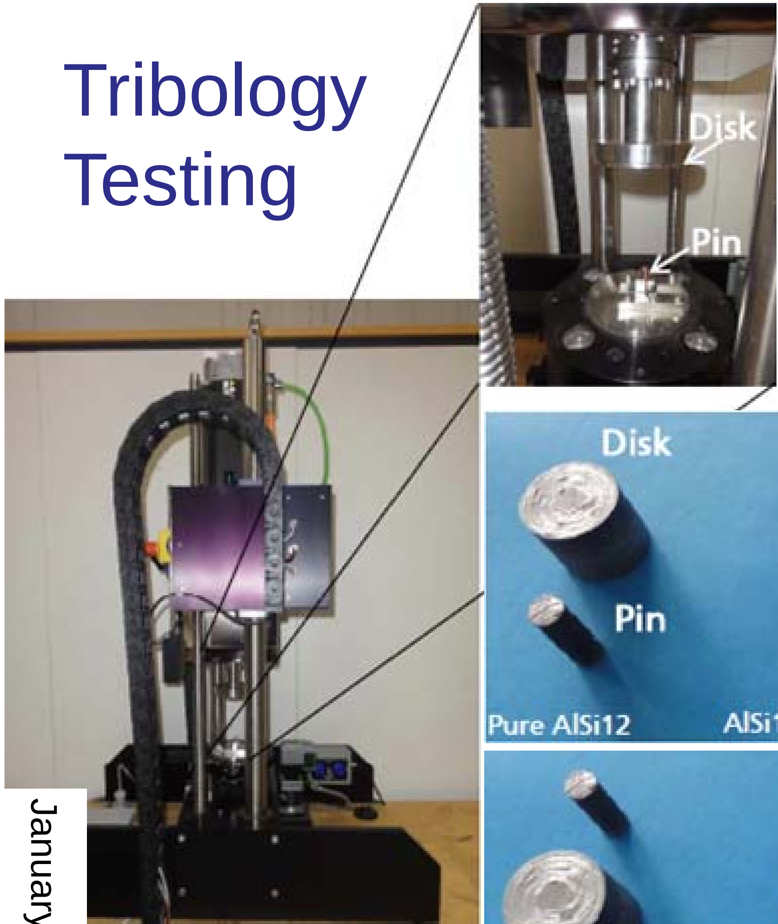
# Friction tests with CNH by

Results: CNH increase friction coefficients (LNP, 2009)
(friction between two polished metal surfaces)



# CNH in Metal Sinters by Fraunhofer IPA

## Tribology Testing




## CNH reduce density

| Sample | Density | relative density |
|---|---|---|
| # | g/cm³ | % (2.7) |
| Pure AlSi12 | 2,67 | 98,89 |
| 0.1wt% NH_Water | 2,66 | 98,52 |
| 0.5wt% NH_Water | 2,56 | 94,81 |
| 1wt% NH_Water | 2,48 | 91,85 |
| 0.1wt% NH_Air | 2,67 | 98,89 |
| 0.5wt% NH_Air | 2,5 | 92,59 |
| 1wt% NH_Air | 2,48 | 91,85 |


CNH Type A

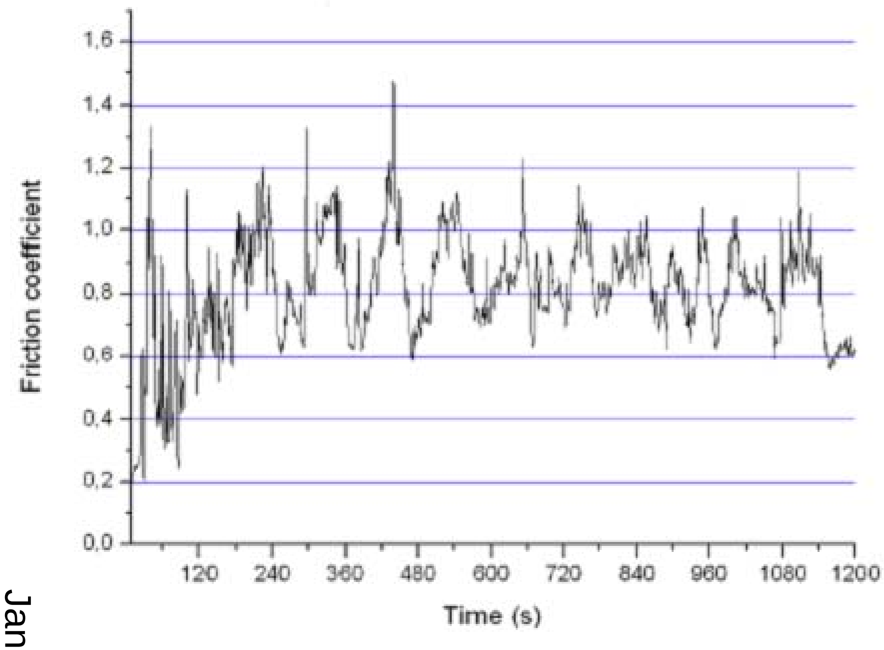
(FhG-IPA 2011)

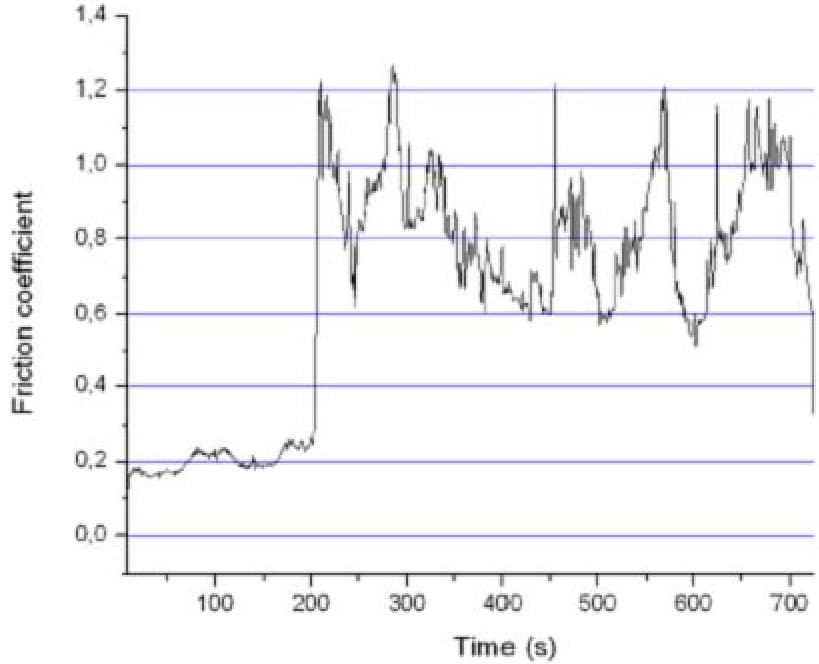

CNH Type B

# CNH in Metal-Sinter by Fraunhofer IPA

Results: CNH increase friction coefficient in metal sinters

(In the following graphs with AlSi12-sinters with 0,5% CNH)

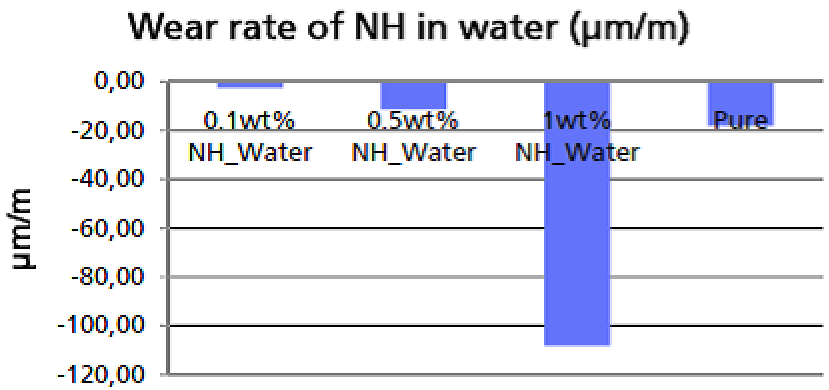



Note: FhG-IPA also tested Al2O3-ceramic sinters with CNH (FhG-IPA 2011)

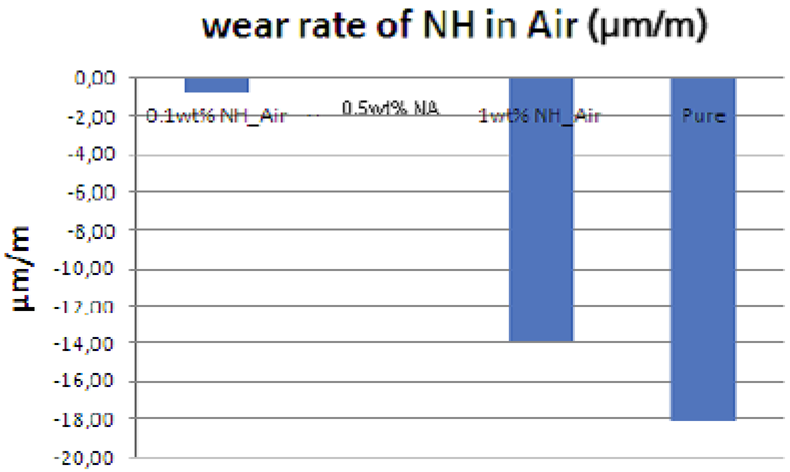
# CNH in Metal-Sinter by Fraunhofer IPA

## Results: CNH reduces wear rates in metal sinters




Nano Horns

| Sample | Actual wear | Total distance (m) | wear rate (µm/m) |
|---|---|---|---|
| 0.1wt% NH_Water | -128,94 | 49,76 | -2,59 |
| 0.5wt% NH_Water | -3409,27 | 298,66 | -11,42 |
| 1wt% NH_Water | -3336,18 | 30,85 | -108,15 |
| Pure | -316,89 | 17,50 | -18,11 |




Nano Horns

| Sample | Actual wear | Total distance (m) | wear rate (µm/m) |
|---|---|---|---|
| 0.1wt% NH_Air | -238,06 | 299,90 | -0,79 |
| 0.5wt% NH_Air | NA | NA | NA |
| 1wt% NH_Air | -4166,49 | 298,90 | -13,94 |
| Pure | -316,89 | 17,50 | -18,11 |

(FhG-IPA 2010)

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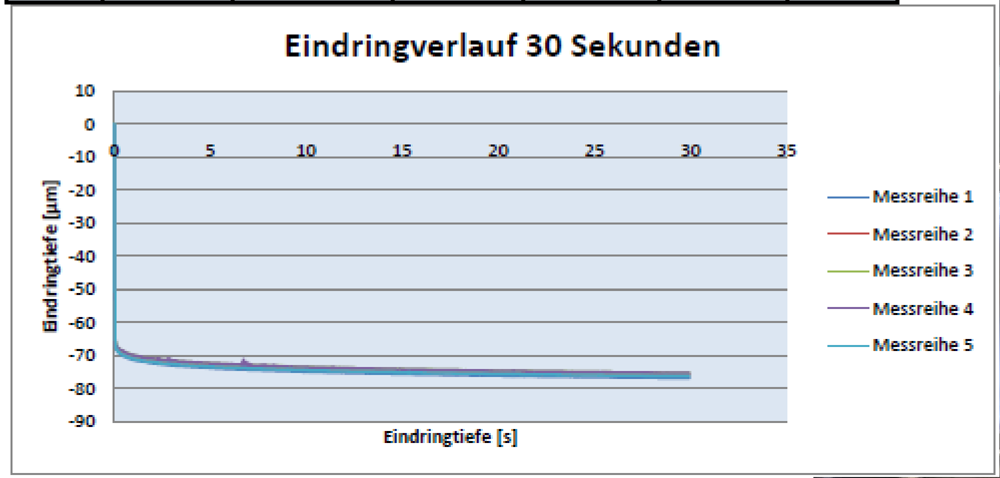
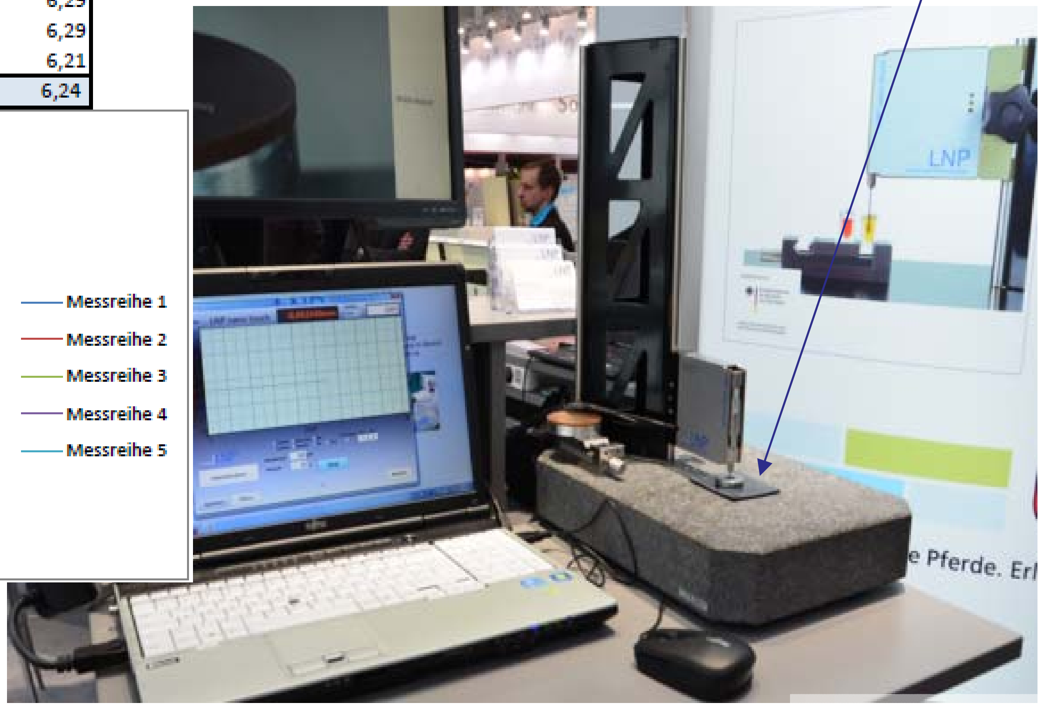
# CNH in Elastomers

Results: CNH increases hardness (IHRD) and stiffness (E-/ Young‘s modulus) in rubber. (eenanoTech, LNP, 2012)

| Messung | Eindringtiefe | Umrechnung D | IRHD Tabelle | IRHD berechnet | | E-Modul berechnet [N/mm2] |
|---|---|---|---|---|---|---|
| 1 | 76,881 | 46,129 | 73,3 | 73,25 | | 6,17 |
| 2 | 75,996 | 45,598 | 73,3 | 73,57 | | 6,24 |
| 3 | 75,380 | 45,228 | 73,9 | 73,79 | | 6,29 |
| 4 | 75,399 | 45,239 | 73,9 | 73,79 | | 6,29 |
| 5 | 76,314 | 45,788 | 73,3 | 73,46 | | 6,21 |
| Mittel | 75,994 | 45,596 | 73,54 | 73,57 | | 6,24 |

Rubber with CNH (2,3%)




Testing Rubber with LNP-Nanotouch Equipment

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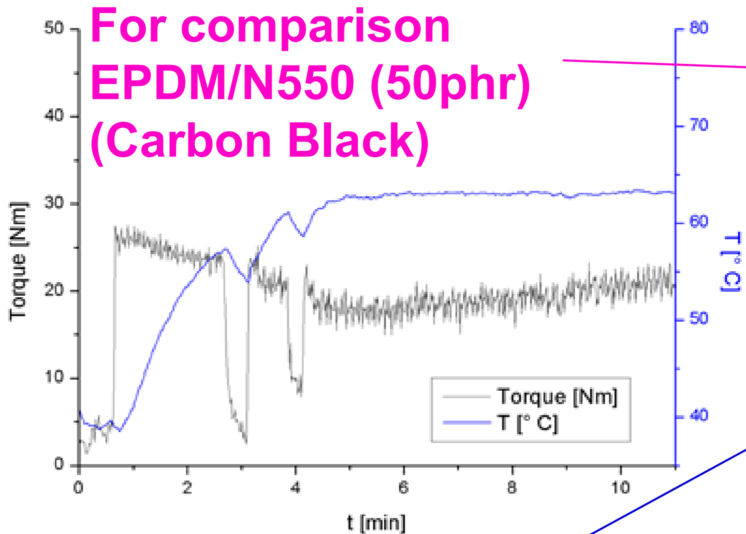
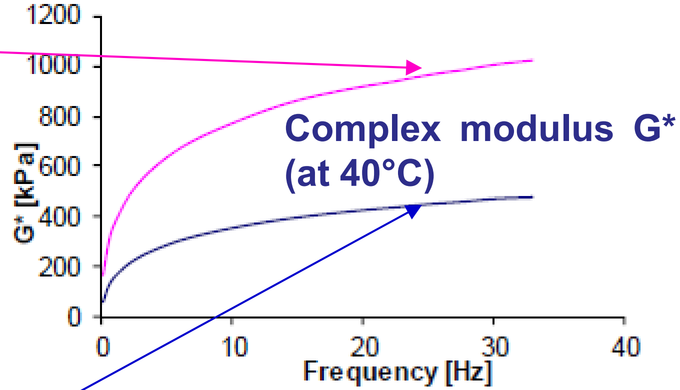
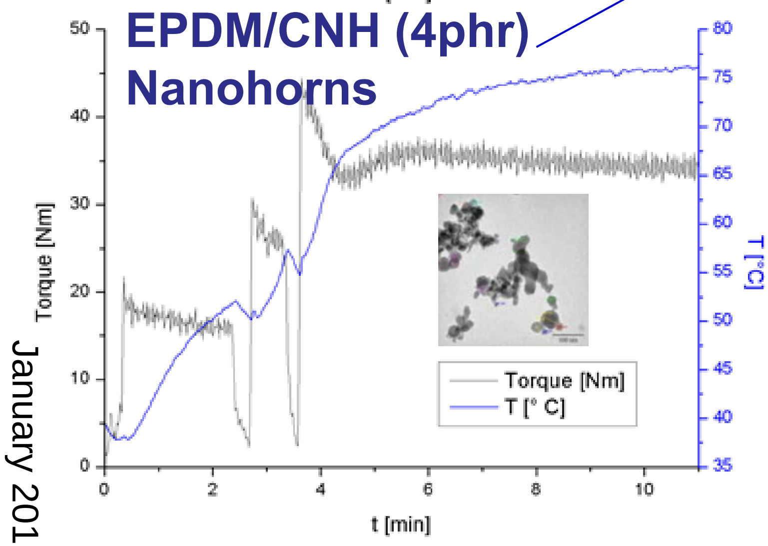
# CNH-Rubber Characterization by DIK

MIXING: (Filler after 3 min.)

TESTING: Dynamic-mechanic measurement




- Easy compounding
- Shear deformation is significantly reduced (complex modulus G*):

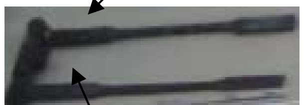
Mixing and tests performed by:
Deutsches Institut für Kautschuktechnologie eV (2013)

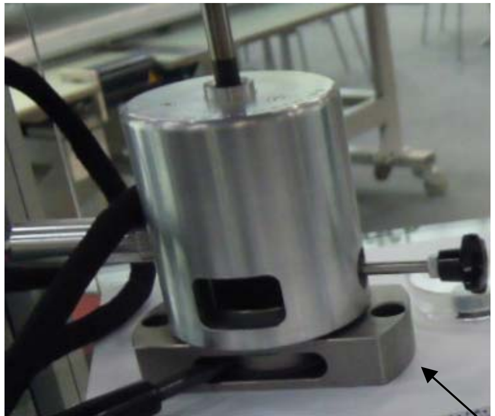
# CNH-Thermoplasts by

Ludwig Nano Präzision GmbH

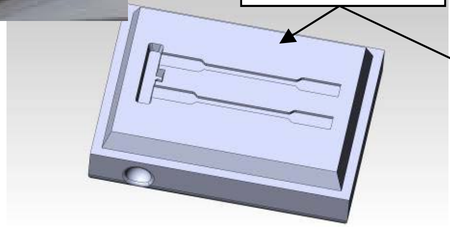
CNH-Thermoplast molding without losses have been developed to test different fillings (up to high grade filling >50% CNH) – tests ongoing.

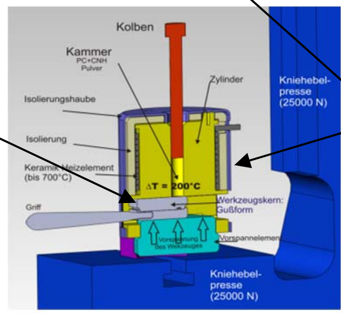

Work piece





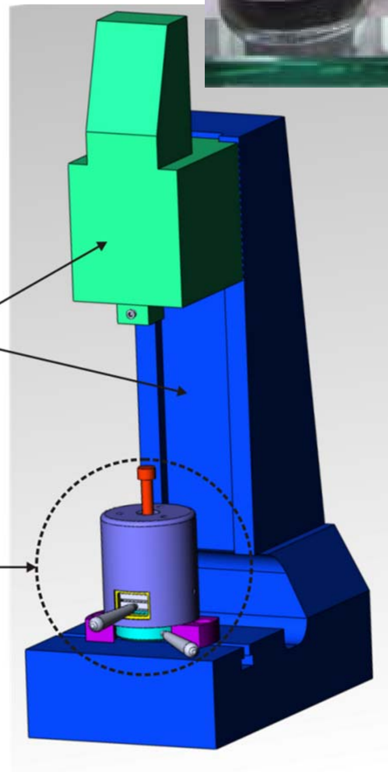
Cavity






Press 25KN

Tool



(LNP, Plejades, 2012)

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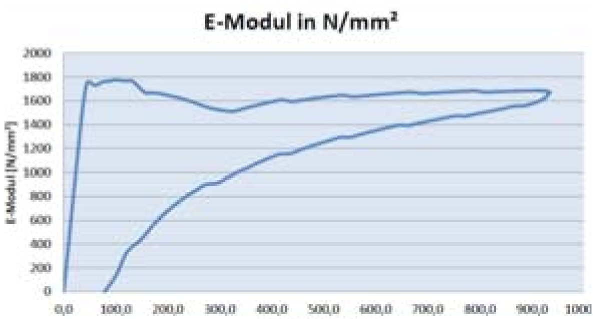
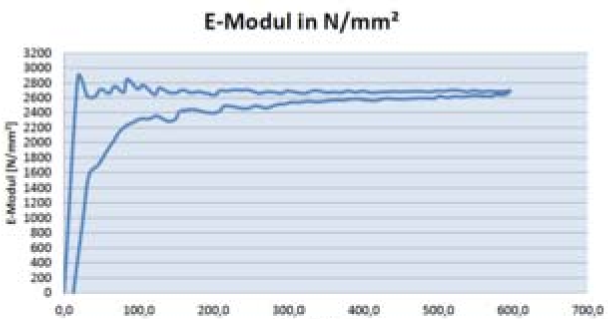
# CNH-Thermoplasts by Ludwig Nano Präzision GmbH

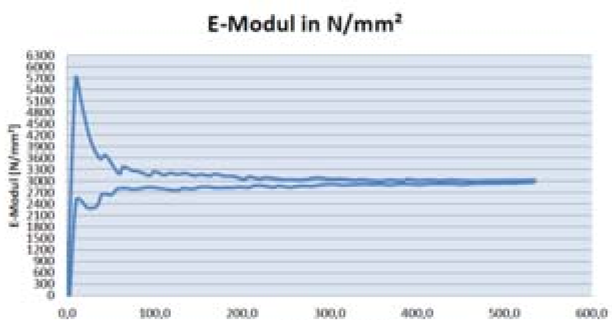
Test of E-/Young‘s modulus with 3-Point-Bending (Hertz-Test) show considerable influence of CNH in thermoplasts (further tests are ongoing).


**Pure Thermoplast with 0% CNH, Young‘s Modulus: ca. 1600 N/mm² (after 0,1 mm during 1st bend)**




**Thermoplast with 1% CNH, Young‘s Modulus: ca. 2600 N/mm² (after 0,1 mm during 1st bend)**

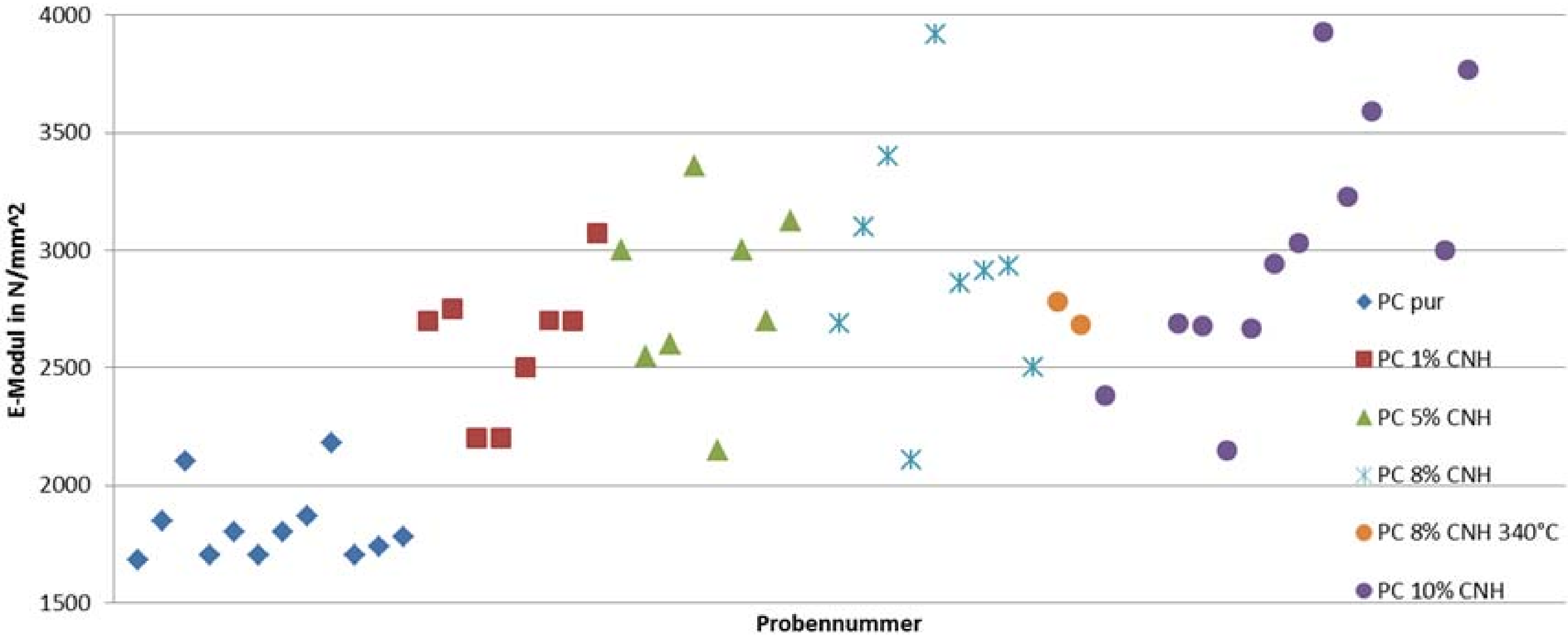



**Thermoplast with 5% CNH, Young‘s Modulus: ca. 3000 N/mm² (after 0,1 mm during 1st bend)**

(LNP, Plejades 2012)

# CNH-Thermoplasts by

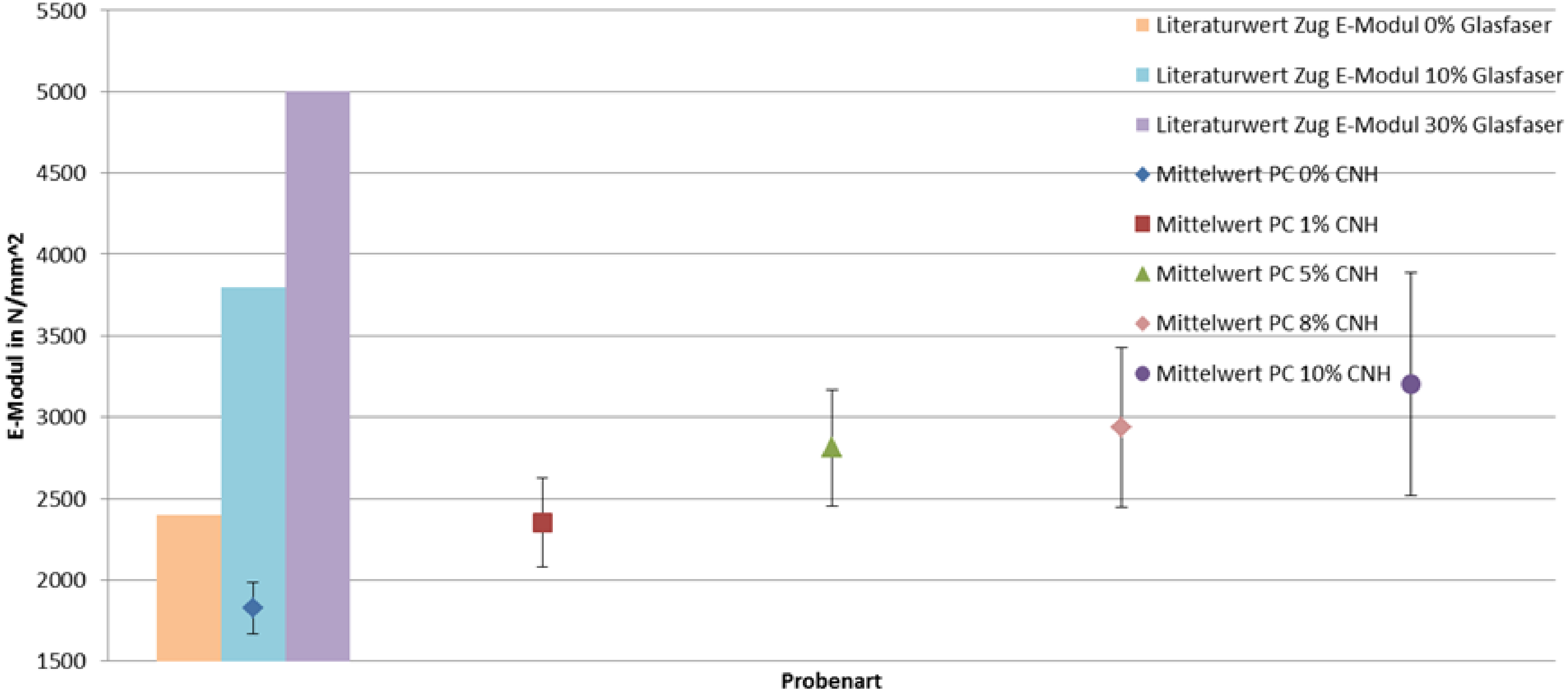
AGeNT-R&D project results for Youngs Modulus obtained with CNH-Fillers in Polycarbonate (PC):




(AGeNT – results; LNP, Plejades, 2012)

# CNH-Thermoplasts by

Effects on Youngs‘s Modulus with CNH-filler compared with glass fiber in Polycarbonate (PC):

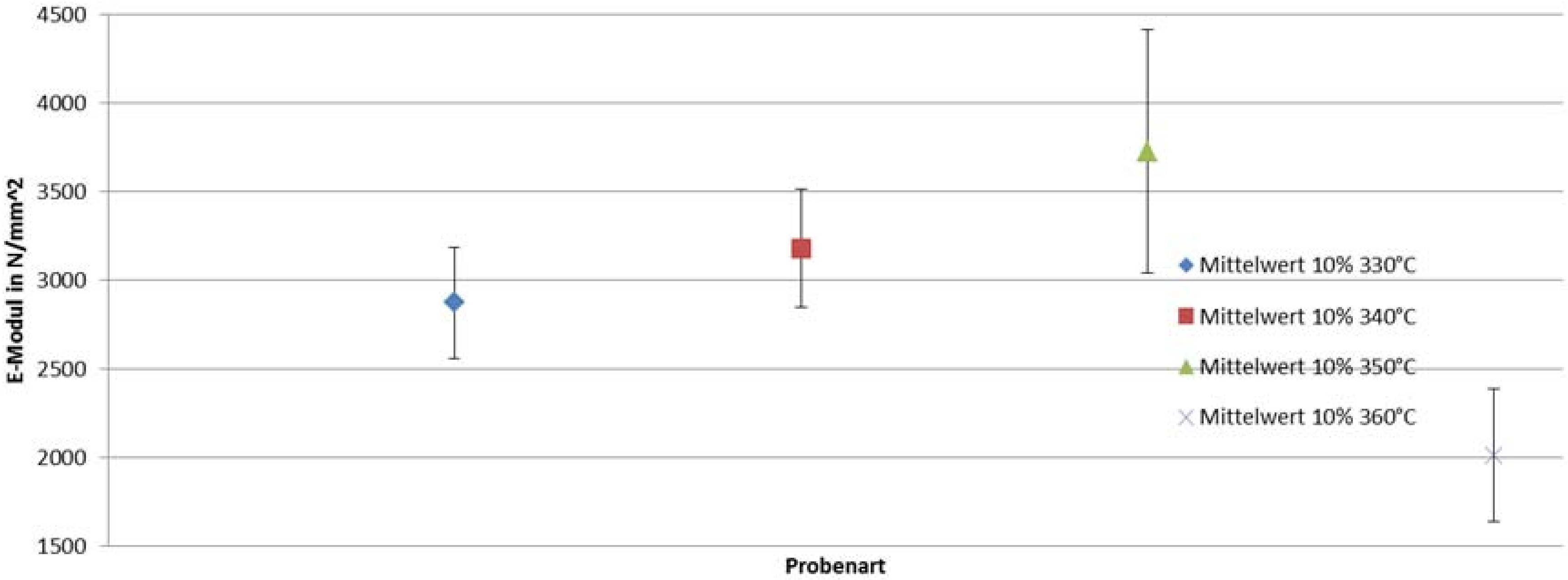



(AGeNT – results; LNP, Plejades, 2012)

# CNH-Thermoplasts by

Polycarbonate with CNH-Filler,

Young's Modulus changes in function of temperature:




(AGeNT – results; LNP, Plejades, 2012)

# Polypropylene (PP) with CNH-filler

Leibniz-Institut
für Polymerforschung
Dresden e. V.

Polyproylene (PP) with CNH-filler has been tested and compared to other fillers (e.g. SWCNT, MWNT, Nanodiamonds) by Leibniz Institut für Polymerforschung Dresden e.V. in 2012.

Results included:

- CNH show a good dispersability in polymer melts
- CNH-filler improve crystallinity and thermal stability slightly
- CNH-filler influence a little thermal conductivity without significant changes in electrical conductivity
- CNH-filler improve modulus and stress at break

CNH-filler improve hardness of PP

CNH-filler improves the fire behaviour by showing a lower heat release rate than PP

# Polypropylene (PP) with CNH-Filler

## Some results of IPF Tests (more available on demand):

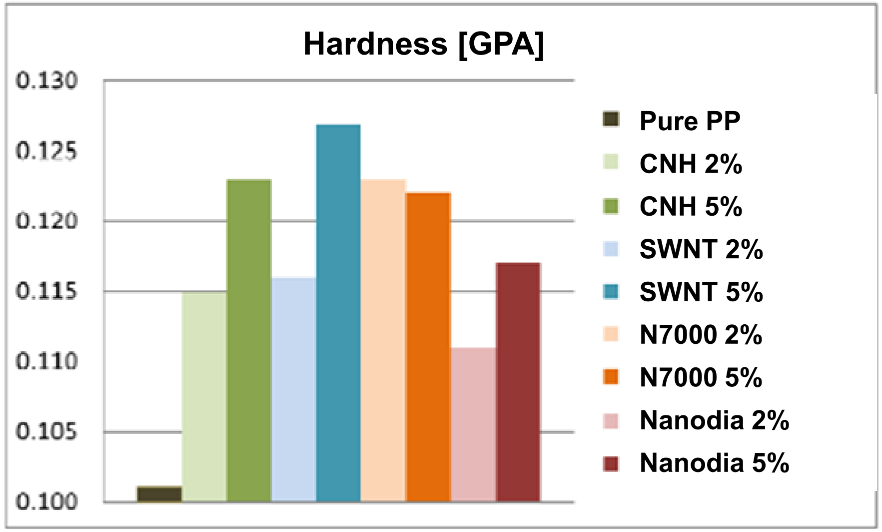
| Material | Stress at break $\sigma_B$ [MPa] | Elongation at break $\varepsilon_B$ [%] |
|---|---|---|
| HP400R extruded | 32.3 | 519.6 |
| CNH 1% | 41.1 | 9.3 |
| CNH 10% | 41.1 | 8.2 |
| SWCNT 1% | 35.2 | 14.7 |
| SWCNT 10% | 43.7 | 8.1 |

Mechanical Properties – **Break test**

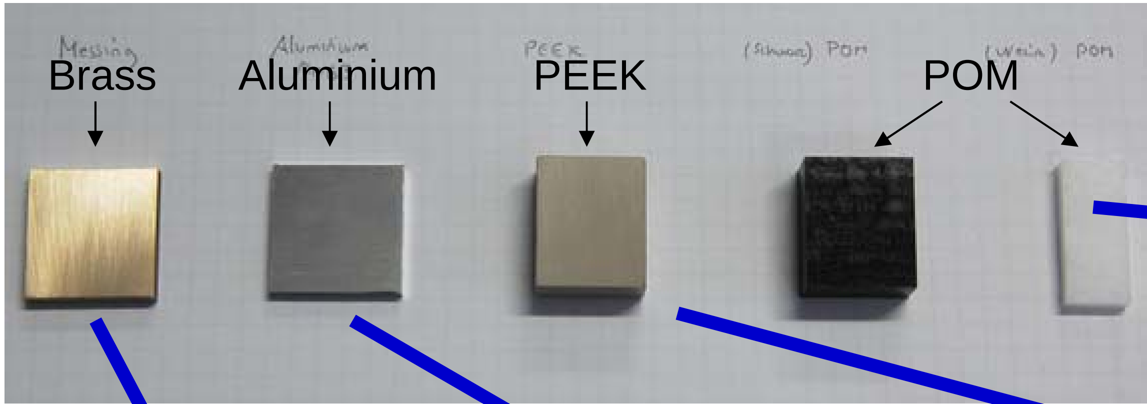
- CNH improve the stress at break
- At 1 wt% CNH effect much higher than in SWCNT
- Elongation at break already drastically reduced at low loadings

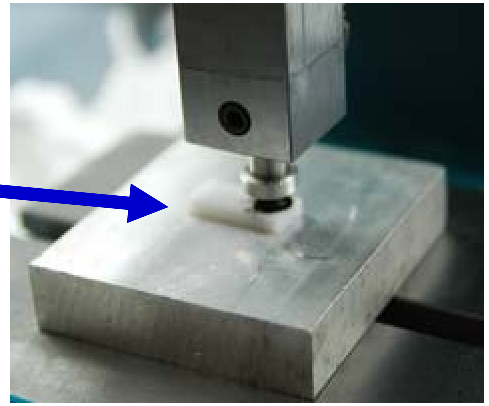
Mechanical properties – **Hardness**

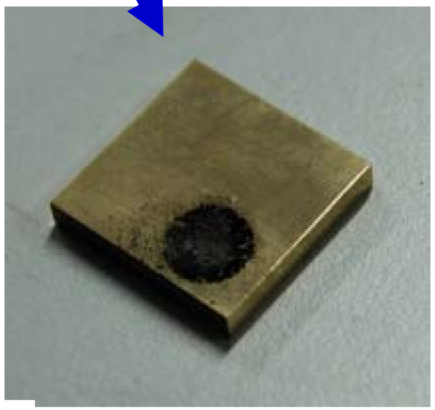
- Measured using Nanoindenter G200 with a Berkovich tip
- CNH improves significantly hardness, but slightly less than SWCNT

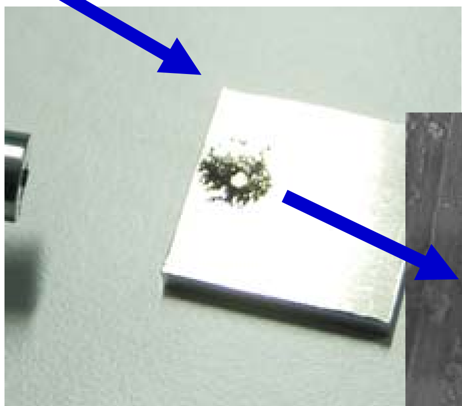


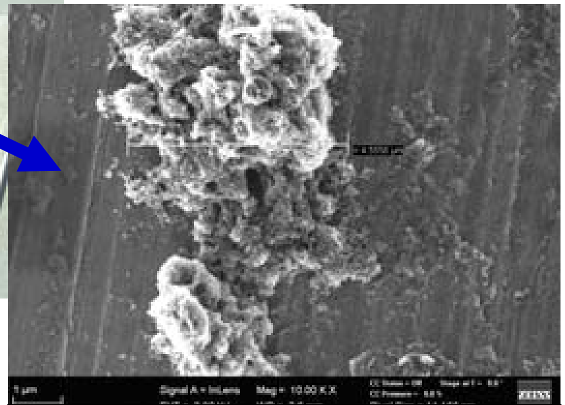
# CNH Impressed into Surfaces b









CNH impressed into Al surface

Functional test: CNH can be impressed into plastic or metallic surfaces

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# A Promising Nano Carbon Material !

| Material | Application / Testing / Effect |
| --- | --- |
| **Pure CNH** | Application as Powder, Sinter, Suspension, Bucky Papers.<br>Stable under a wide range of thermal conditions (up to 300 °C in oxygen atmosphere).<br>Electrical conductivity of CNH-sinter and Bucky papers is under observation.<br>Hydrogen storage capacity: under observation, so far no significant results. |
| **Doted CNH** | CNH can be produced with target metal doting, e.g. Pt. |
| **Solid Metals** | Application of CNH significantly increases the friction between metal surfaces. |
| **Metallic or plastic surfaces** | CNH can be impressed into metallic or plastic surfaces |
| **Metal Sinters** | CNH can be used in metal sinter materials with significant effects:<br>• Reduced Density/Weight.<br>• Improved Friction.<br>• Reduced Abrasion. |
| **Ceramic Sinters** | CNH-fillers can be used in ceramic sinter materials. |
| **Thermoplastic Resins** | CNH-fillers in thermoplastic resin (e.g. tested with PC, PA, ABS, PP, PEEK):<br>• Significantly Increased E-modulus<br>• Increase slightly thermal conductivity, less effects on electric conductivity |
| **Elastomers and Rubber** | CNH fillers in elastomers/rubber:<br>• Easy compounding<br>• Increased hardness and stiffness |

# See You at Next Exhibition !

Thank You !

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ご苦労さま!

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