# NANOPARTICLES AND CNTS IN HIGH PERFORMANCE CFRPS FOR AEROSPACE & SPACE APPLICATIONS: SOME TRULY BENEFITS & MECHANISMS

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## Abstract

High performance carbon fibre reinforced plastics (CFRPs) have been manufactured by addition of either ceramic fillers or carbon nanotubes (CNTs) for enhanced mechanical and thermal stability. Their matrix dominated materials properties, namely compression strength, impact resistance, properties under shear loadings as well as bending strength show exceedingly good results and enhancements compared to the reference. Especially material testing under high temperatures demonstrates a big potential for CNT reinforced matrices.

## 1 Introduction

Carbon fibre reinforced plastics for aerospace and space applications are highly stressed materials. Typically CFRP-structures are dimensioned via their fibres following external loading conditions. But it is well known, that laminate failure is often determinated by matrix behaviour caused by indifferent loading conditions. Remaining residual stresses in the laminate after manufacturing and limited matrix properties hinder the high performance materials to demonstrate their whole potential. In terms of critical loadings, there have to be especially named, transverse tensile-, compression- and shear- stresses and high thermal stresses that all initiate matrix cracking, first inter fibre fractures which lead to delaminations and laminates failure [1-3].

Hence the idea of strengthening the matrix is not surprising. It is one objective to reduce the chemical shrinkage of the resins, which induces residual stresses that deteriorate the material performance. But not only the chemical shrinkage leads to initial stresses also the different thermal expansions of fibres and resin. That coefficient of the matrix should also be reduced. Further more, the matrix itself should be strengthened. Higher modulus and resistance against crack propagation are the targets. The last goal to achieve is a higher thermal conductivity in order to cure smoother and transfer thermal loadings faster and more homogeneous.

Traditional micro scaled filler present some of these effects at high expense of viscosity of the resin and mostly by embrittlement of the material. Using fillers of nano scaled particles abolish these drawbacks. Moreover, the mechanical properties of the polymers are significantly improved by even low volume fraction of nanoparticles due to their high specific surface and chemical functionalization thereof [4-6]. Besides the particles sizes, shapes and dispersion uniformity, the degree of interaction between the filler and the polymer matrix play an important role [7]. Best performance is achieved with small particle size and narrow distribution as well as a strong interaction with the organic matrix, a covalent bonding which allows better load transfer between the polymer and the filler [4, 6, and 8].

In order to improve more critical material properties, especially so called “hidden properties” it seems to be a good idea to incorporate besides boehmite nanoparticles also CNTs into CFRP. Previous results point out very much enhanced mechanical properties as the resistance against crack propagation as well as improved thermal properties [9-10]. Concerning CNTs, nearly the same rules in terms of dispersion and interfaces seem to be valid [9-10]. These improvements of the matrix are to be transferred into CFRP. In terms of static loadings, improvements of compression strength and interlaminar shear properties have been found [11-14]. It is the idea now to not only investigate special properties of laminates, such as compression and shear properties as well as impact behaviour and bending strength but also failure behaviour and mechanisms which will be of particularly relevance. One study within that paper is also regarding high temperature applications of CNT filled CFRP for space applications.

## 2 Materials and Methods

Two various types of nanoscaled fillers are investigated for materials reinforcement. Block-shaped boehmite particles (Sasol Germany) with a primary particle size of 14 nm, having a taurine functionalized surface, presenting the ceramic filler, and carboxylized (CO-OH) multiwalled (MW) CNTs as well as “as produced” MWCNTs, both supplied by FutureCarbon GmbH, present the fillers with high aspect ratio. All have to be dispersed in various adapted dispersion processes. In two studies, an established and aviation-approved anhydride-curing epoxy resin (EP) (Araldite LY556-Huntsman) acts as the polymer matrix, cured in a standard cycle, in the space-study a high temperature cyanatester resin, PT-30, commercially available from LONZA, Switzerland fulfils that function. For the epoxy CFRP studies HTA carbon fibres were chosen, in case of the space study M55 carbon fibres were the selected ones.

### 2.1 Nanoparticles in epoxy resin: methods and characterizations

The boehmite particles were dispersed, by adopting a combination of dissolver and bead mill. High shear forces are provided to desagglomerate the boehmite clusters. Thus, a high loaded masterbatch was manufactured. The boehmite/epoxy dispersion was than mixed with a certain part of neat resin in order to produce various nanoparticles concentrations. Subsequently the dispersions were directly introduced into the resin-curing agent system and cured in casting moulds. The cured samples were observed by scanning electron microscopy (SEM) to obtain a further view on the particle size distribution and the nanoparticles themselves. The nanoparticles reinforced samples and neat epoxy resin samples as references were than characterised in terms of their mechanical properties. Tensile and fracture toughness tests in accordance with the German industry standard DIN were performed in order to determine essential parameters of the materials. In addition, the viscosities were determined. Thus, we managed to receive the influence of the concentration of nanoscaled boehmite on the range of properties of the reaction resin.

Selected nanocomposite formulations were than applied as novel matrix systems for CFRP composite materials. The composites were manufactured according to single line injection technique (SLI) [15]. Unidirectional (UD) carbon fibre (CF) fabrics were selected as the reinforcement material. The fibre volume fractions of the finished CFRP laminates were comparable with negligible variations from 59 to 61 vol. % in all cases. The novel fibre-reinforced nanocomposites were subjected to extensive mechanical testing. As described in precedent chapters, the deficits compared to laminates consisting of prepregs are mainly present in compression properties. Thus, celanese compression tests (DIN EN 2850) and interlaminar fracture toughness test (G1C) (DIN EN 6033) on UD laminates as well as compression after impact (CAI) tests (AITM 1.0010) on quasiisotropic laminates (16 layers fibre architecture: 0°/+45°/90°/-45°/+45°/90°/-45°/0°; symmetrical) were performed to detect at high sensitivity the influence of the nanoparticles on such properties of the composites. For quantification of the improvement, conventional CFRP composites, without filler, were manufactured to serve as reference materials.

## 2.2 CNTs in epoxy resin: methods and characterizations

Carboxylized CNTs were dispersed in a 7-step dispersing process on a three-roller mill. Within these steps the gap was positioned till the smallest gap of 5 µm little by little. A masterbatch of 4 wt.-% CNTs was manufactured. The CNT/epoxy dispersion also was thinned down in order to produce plates with various CNT concentrations. The dispersions were introduced into the resin-curing agent system and cured in casting moulds. Samples were observed by SEM to obtain a further view on the CNT distribution. The reinforced samples were than characterised like the nanoparticles reinforced plates also had been.

One selected formulation (0,5 wt.-% carboxylized MWCNT) was than applied for CFRPs. The CNTs-reinforced laminates where manufactured by laying-up UD in-house-prepregs after a filament winding process with continuous wetting of the fibres in an impregnation bath. The fibre volume fractions of the CFRPs were comparable with negligible variations from 64 to 66 vol. %. The novel CNT-CFRPs were also subjected to mechanical testing. Celanese compression tests and interlaminar fracture toughness tests (G1C) were performed. For quantification of the improvement, conventional CFRPs, without filler, were manufactured by the same procedure to serve here as reference materials.

## 2.3 CNTs in cyanatester resin: methods and characterizations

Two kinds of CNTs (carboxylized, and as produced) were added to PT-30 resin, in a 5-step dispersing process on a three-roller mill. Within these steps the gap was positioned till the smallest gap of 5 µm little by little. The amount CNTs was always 0.5 wt.-% of the resin. As PT-30 is a one-component resin system, no masterbatch was manufactured and no further components had to be added.

For characterisation, UD reinforced composites have been manufactured. The manufacturing process consisted of two steps:

(1) Preparation of prepregs by winding the carbon fibres around a heated drum (70°C), followed by wetting with resin, both neat and modified by CNTs.

(2) Laminating UD fibre layers to a composite by means of compression and thermal treatment in a steel tool. This process step had been carried out in an autoclave.

The laminates were than tested in terms of unidirectional bending strength (DIN EN 2562) at room temperature and 300 °C.

# 3 Properties of nanocomposites

## 3.1 Boehmite-epoxy nanocomposites

### *3.1.1 Dispersion quality and viscosity*

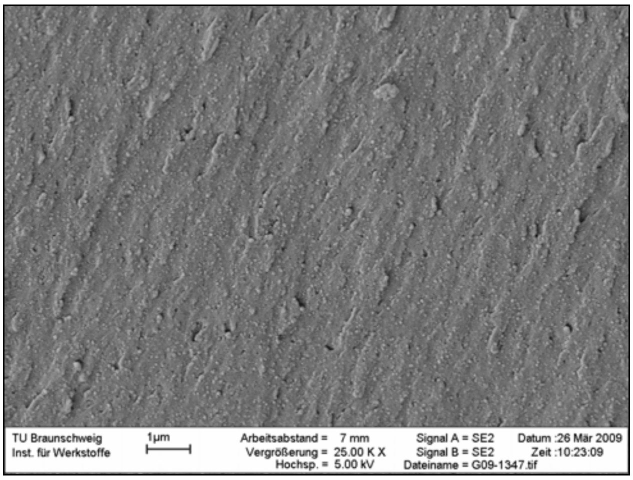


Fig. 1. SEM: 15 wt.-% boehmite in EP (cured sample)

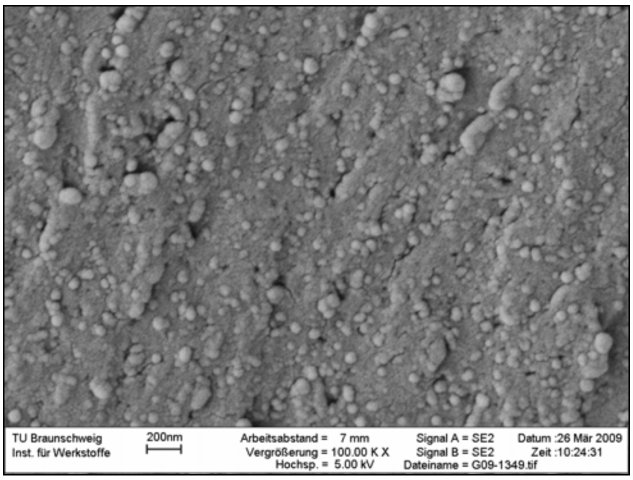


Fig. 2. SEM: 15 wt.-% boehmite in EP (cured sample) (higher resolution)

In these SEM-images (Fig. 1 and 2) it can be clearly seen that the nanoparticles are homoge-

neously and fine dispersed with only little agglomerates.
In terms of viscosity profiles, which are very much important in order to evaluate the injectability of these nano-resins, it can be observed that viscosities are augmenting and injection times are shortened, but completely undramatic (Fig. 3). With regard to a normal injection time of maximum 20 minutes, there is no detraction, which shows a retaining injectability for the modified resins.

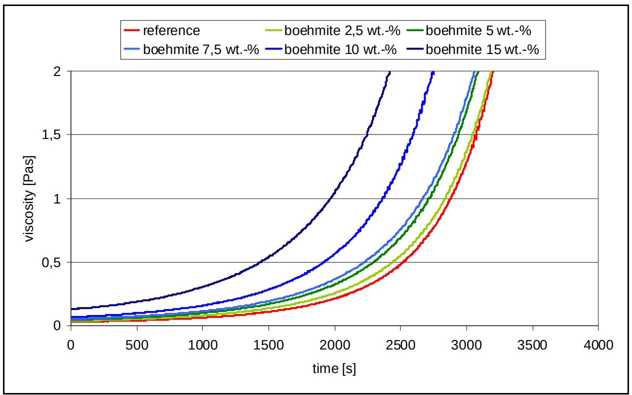


Fig.3. Isothermal (80°C) viscosity curves of boehmite reinforced matrices and neat resin (shear rate 40/s)

### *3.1.2 Mechanical properties*

The results of the mechanical tests versus pure resin are shown in Fig. 4 and 5. The increase in stiffness and strength of the boehmite nanocomposites with increasing filler content is clearly evident. The filler content of up to 15 wt.-% boehmite investigated in this study improved the tensile modulus by up to 23 % and the tensile strength (ultimate) up to 5 %. The fracture toughness (energy release rate) rises with rising filler content over 80 % enhancement. Both, the strength and the stiffness values for boehmite particle reinforced resins show a continuous linear increase over the range of filler contents investigated. The mechanical parameters here show no peaks, which means that the peak for this material has not been reached yet and the possibilities of the material may not have been exhausted yet. In contrast, considering the strain at break, there is evidence that the matrix becomes somewhat brittle for tensile failure. If the maximum at 15 wt.-% boehmite particles presents also the optimum for matrices in CFRP, needs to be confirmed in further experiments.

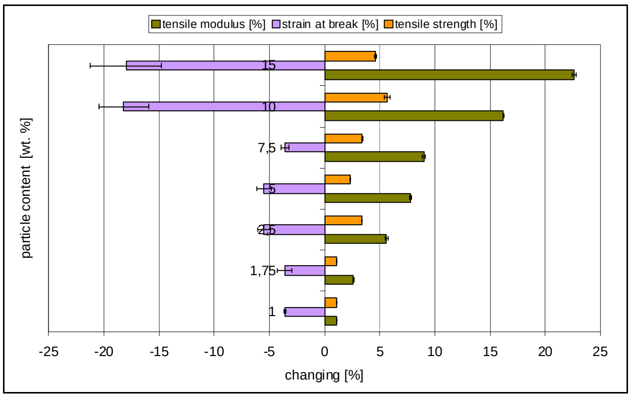


Fig.4. Properties changing of nanocomposites based on neat epoxy after tensile test containing various particle contents

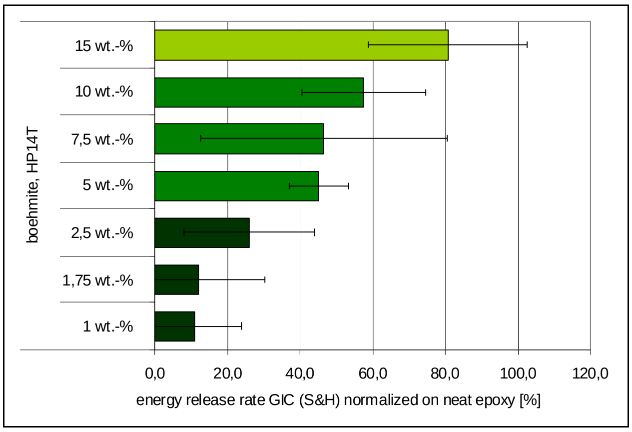


Fig.5. Energy release rate changing of nanocomposites based on neat epoxy

## 3.2 CNT-epoxy nanocomposites

### *3.2.1 Dispersion quality and viscosity*

In these SEM-images (Fig. 6 and 7) a homogeneous dispersion can be observed, with lasting little CNT clusters.

The viscosities (Fig. 8) of the resin systems containing CNTs are much different from the ones containing the boehmite nanoparticles. These high viscosities even at very low filler contents require other manufacturing technologies, such as filament winding.

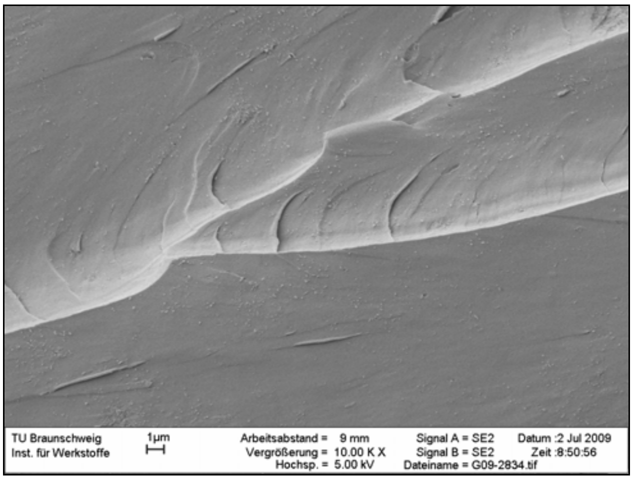


Fig. 6 SEM: 0,5 wt.-% carboxylized CNTs in EP (cured sample)

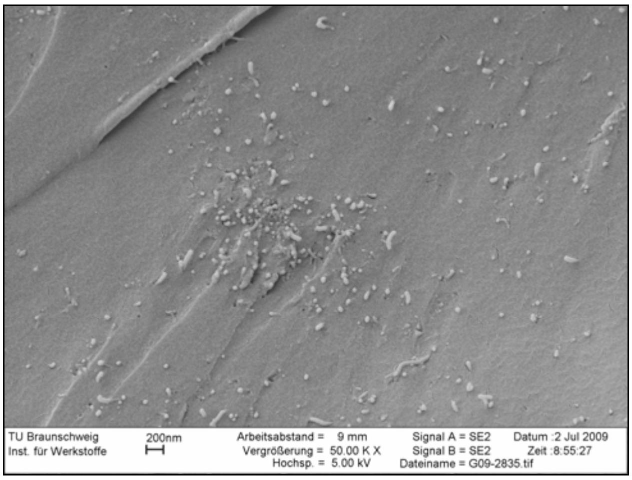


Fig. 7. SEM: 0,5 wt.-% carboxylized CNTs in EP (cured sample) (higher resolution)

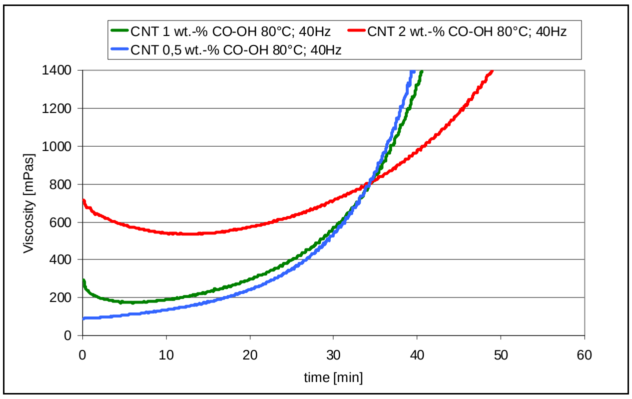


Fig.8. Isothermal (80°C) viscosity curves of CNT reinforced matrices (shear rate 40/s)

### *3.2.2 Mechanical properties*

Also for the CNT reinforced resins, mechanical properties versus pure resin are shown in figures 9 and 10. In terms of the tensile properties of the CNT-matrices there is only an increase in stiffness and strength for the samples containing 0,5 wt.-% of carboxylized CNTs. Higher filler contents lead to increase in stiffness but decrease in strength and immense high decrease in strain at break up to – 50 %. These matrices are very brittle with these high amounts of CNTs. The fracture toughness rises with rising CNT content over 140 % enhancement. The CNT-bridging mechanism could be the explanation when comparing the results with the ones for nanoparticles reinforced matrices.

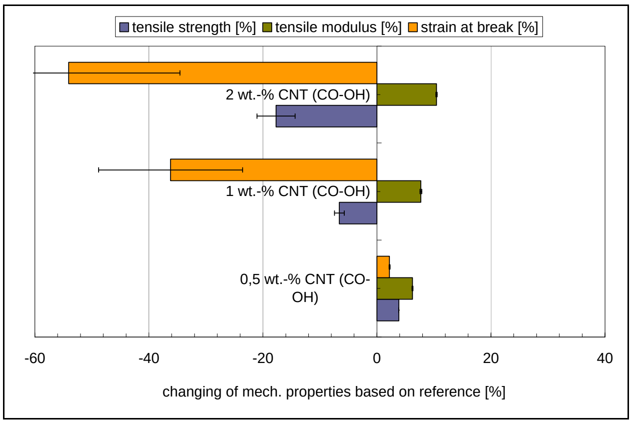


Fig. 9. Properties changing of nanocomposites based on neat epoxy after tensile test containing various amounts of CNTs

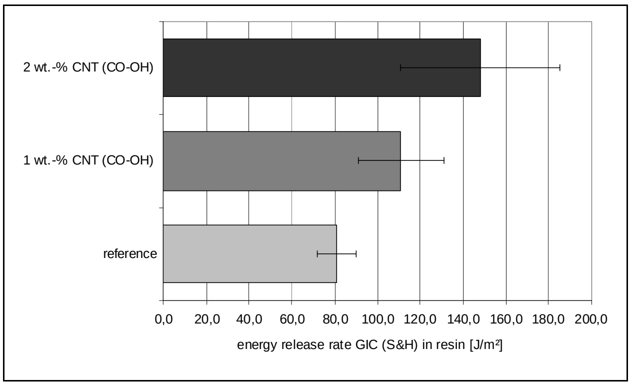


Fig. 10. Energy release rate in resin containing various amounts of CNTs

## 4 Properties of CFRPs

After having characterized the materials properties of nanofiller reinforced resins, it is now the time to transport these new properties into various carbon fibre based laminates.

## 4.1 Matrix containing boehmite particles

### *4.1.1 Compression properties*

Various matrices containing boehmite nanoparticles (filler content 1 wt.-% to 15 wt.-%) function as new matrices for CFRP.

Compression tests indicate multiaxial stress to the laminate, especially high transverse tensile strain and stress as well as shear stress. Hence, the stiffness and strength of the matrix and the fibre matrix adhesion is of great interest. These material properties are considerable enhanced by nanoparticles. In general there is an increase of the strength values of nearly every laminate (Fig. 11), which can be ascribed to higher stiffness, reduced resin shrinkage and coefficient of thermal expansion of the nanoparticles reinforced matrix, which leads to reduced residual stress. These matrices can carry higher shear loads to the fibres and prevent micro-buckling and kink band propagation by bearing the fibres up to higher loads.

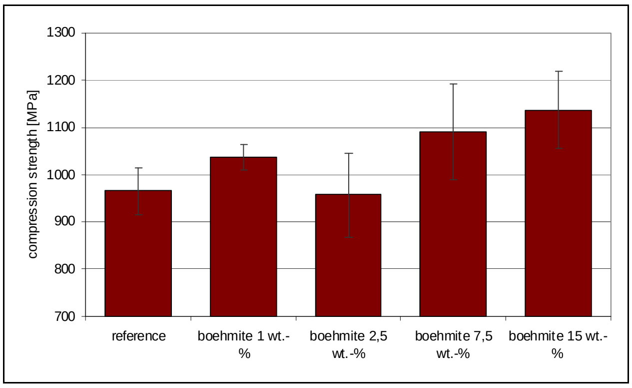


Fig. 11. Celanese compression strength of unidirectional CFRPs

### *4.1.2 CAI behaviour and $G_{1C}$ values*

Examples of results of compression after impact tests are summarized in figures 12 and 13. The residual strength after impact is significantly improved at low impact energies and still improved at higher impact loadings with additional boehmite nanoparticles (7,5 and 15 wt.-%). These results according to the corresponding damage areas, which are smaller with nanoparticles in the matrix. Effects may be the stiffer matrix, enhanced fibre-matrix adhesion and the higher fracture toughness of the matrix (Fig. 5), which may lead to slower crack propagation and delamination growth. The values for energy release rate (Fig. 14) confirm that assumption.

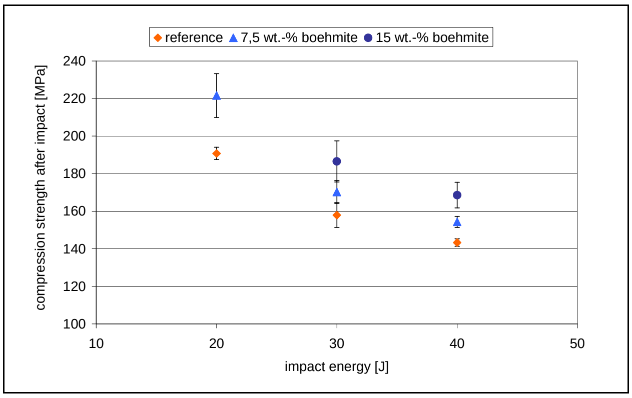


Fig. 12. Residual strength over impact energy of boehmite filled laminates

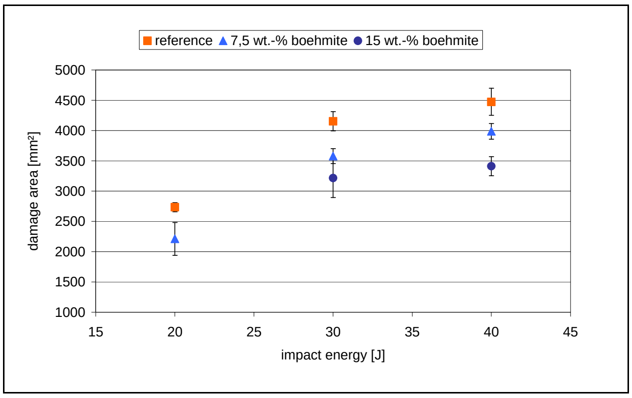


Fig. 13. Damage area over impact energy of boehmite filled laminates

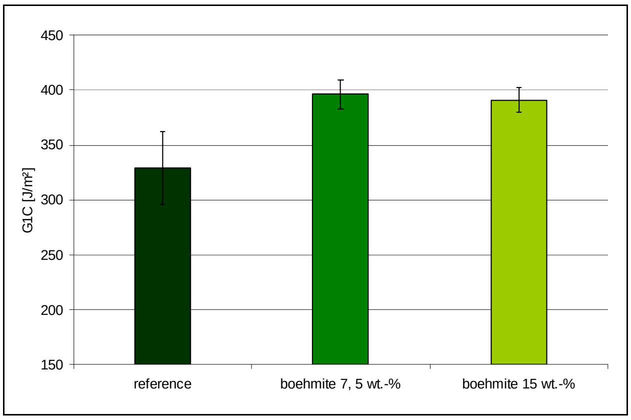


Fig. 14. Energy release rate in CFRP; reference and various boehmite particles contents in the matrix

## 4.2 Matrices containing CNTs

### *4.2.1 CNTs in epoxy resin*

A resin, filled with 0,5 wt.-% CNTs (CO-OH) serves as new matrix for CFRP in this study.

Compression tests show enhanced Young's modulus at room temperature, but not an enhanced strength (Fig. 15). Though, at higher temperature (Fig, 16, 100°C) strength and stiffness are considerably improved. This phenomenon can also be seen in the bending results (Fig. 18) in the space study. It could be a mechanism that CNTs increase their fracture toughening mechanism at higher temperatures. With the thermal expansion, the CNTs in the polymer network may stick the chains together by bridging effects. They may have more possibilities to form themselves along the load, transfer loads and hinder the cracks to propagate. This can be substantiated by the results for energy release rates shown in figure 17.

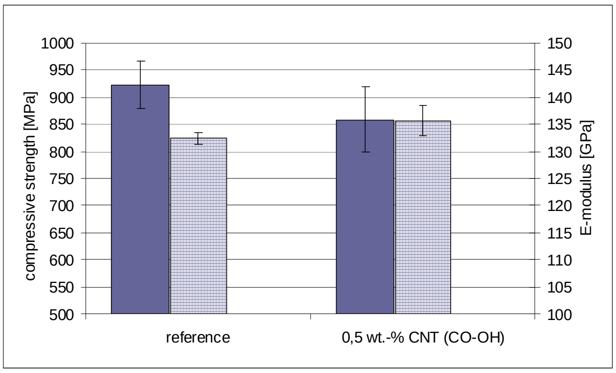


Fig. 15. Compression strength (blue) and modulus (blue chequered) of reference and CNT-CFRP at room temperature (RT)

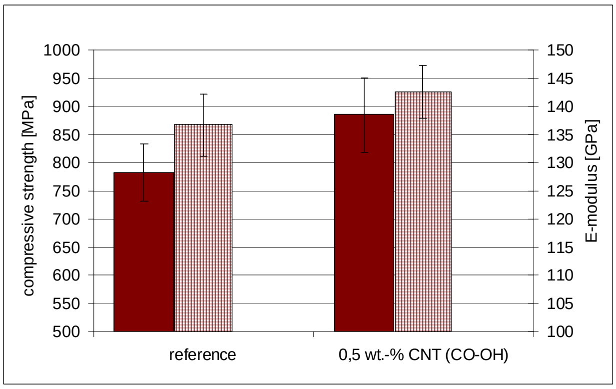


Fig. 16. Compression strength (red) and modulus (red chequered) of reference and CNT-CFRP at 100 °C

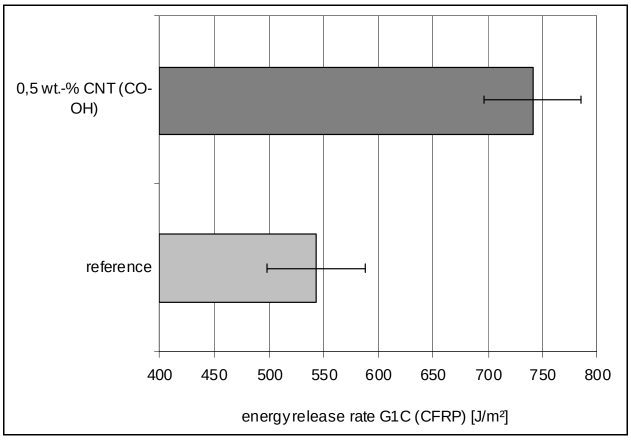


Fig. 17. Energy release rate in CFRP reference and CNTs in matrix

### *4.2.2 CNTs in cyanatester resin*

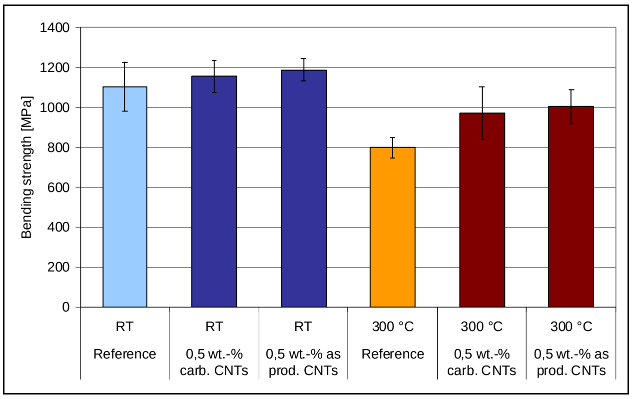


Fig. 18. Bending strength at RT (blue) and at 300°C (red) compared to reference (light blue and orange)

Figure 18 presents bending properties of cyanate ester resins filled with various CNTs and neat resin. It is obvious, that not only high temperature properties are significantly improved, but the increase there is much more significant. It seems that the non-functionalized CNTs harmonize better with the resin chemistry.

## 4.3 Reinforcement mechanisms

It has been described that nanoparticles reinforced matrices present higher stiffness, higher fracture toughness and lower residual stresses for CFRP. Depending on the failure mechanisms of each mechanical test, different reinforcing mechanisms are responsible. But it can be summarized that nanoparticles reinforced matrices act in particular by their enhanced stiffness and strength while CNT-reinforced matrices are effective because of their highly enhanced fracture toughness and their bridging behaviour especially at high temperatures. Figures 19 and 20 are polished micrograph images of CFRP samples which have been loaded up to a decisive elongation, which has been investigated experimental in advance. At that extension the testing had been stopped and the samples were observed under light microscope. By comparing the surfaces in figure 19 (neat EP) and 20 (EP and 15 wt.-% boehmite particles) it is obvious that there are lots of matrix cracks within the reference, while carrying the same loading, boehmite reinforced matrices show only some matrix cracks. The matrix is more stable to higher loadings and damage initiation starts at higher loadings.

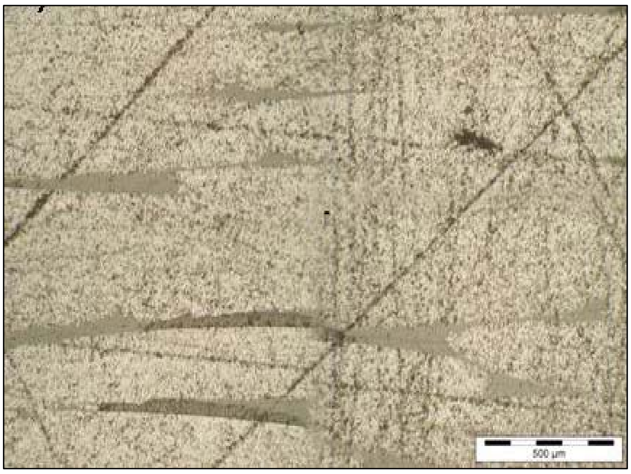


Fig. 19. Polished micrograph of CFRP reference

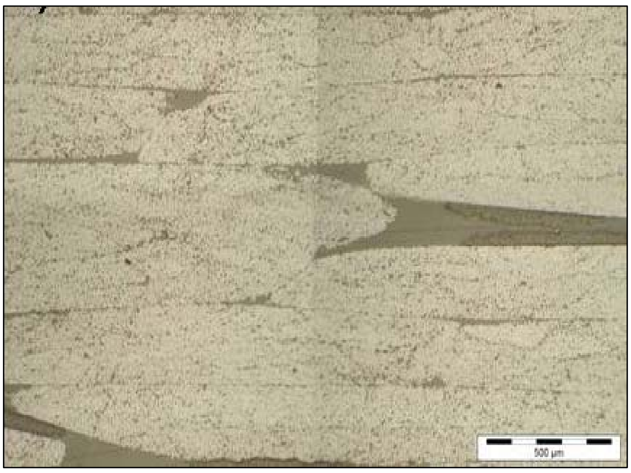


Fig. 20. Polished micrograph of CFRP containing 15 wt.-% boehmite in matrix

Figures 21 and 22 illustrate the difference in matrix fractures of neat resin in CFRP and CNT-reinforced resin. Much more fissured surfaces and fracture structures are visible, which clearly evidences the higher energy absorption during fracture.

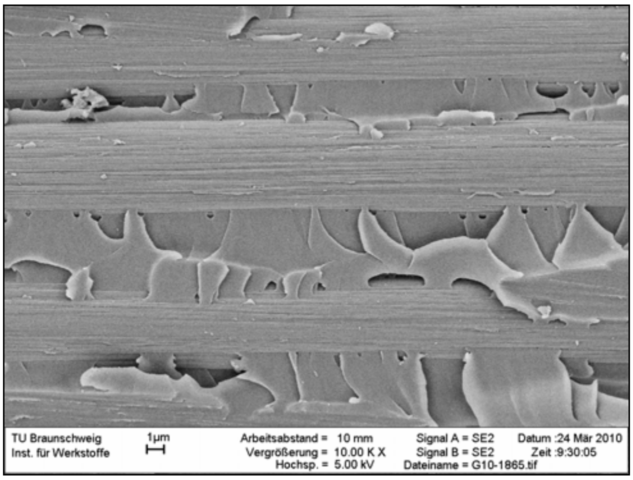


Fig. 21. $G_{1C}$-sample after fracture in SEM: Reference

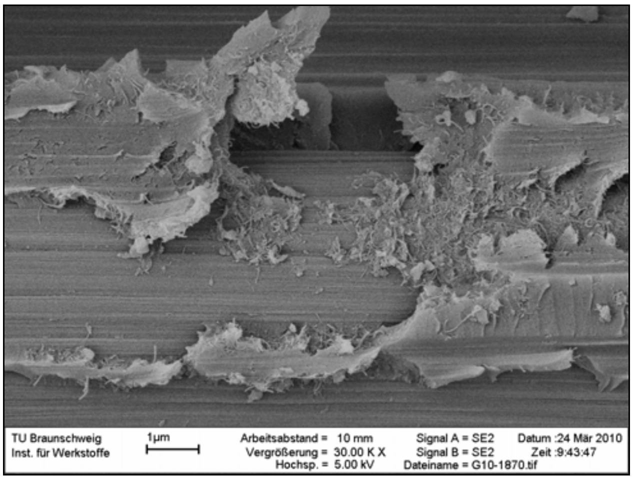


Fig. 22. $G_{1C}$-sample after fracture in SEM: 0,5 wt.-% CNT (CO-OH)

## 5 Conclusions

Besides the fact that further detailed investigations as fatigue tests and extended investigations of polished micrograph sections, which will show further differences e.g. damage initiation at higher loadings in materials containing nanofillers, are still open, the mechanical properties detailed in that study are significantly improved with ceramic nanoparticles as well as CNTs. While nanoparticles seem to act positively for shear dominated loadings and minimize crack propagation, CNTs show the tendency to develop their whole potential at special applications, such as high temperatures where they are especially effective by their bridging mechanism.

## 6 Acknowledgements

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## References

[1] Pansart S. A Comprehensive Explanation of Compression Strength Differences Between Various CFRP Materials through a Novel Micro-meso Model. DLR-Forschungsbericht 2008-03; ISSN 1434-8454

[2] Hartung D. Materialverhalten von Faserverbundwerkstoffen unter dreidimensionalen Belastungen. DLR-Forschungsbericht 2009-12; ISSN 1434-8454

[3] Puck A. Festigkeitsanalyse von Faser-Matrix-Laminaten, Modelle für die Praxis, Carl Hanser Verlag, 1996, ISBN 3-446-18194-6.

[4] Wetzel B et al. Epoxy Nanocomposites – fracture and toughening mechanisms; Eng Fract Mech 2006; 73:2375.

[5] Medina R et al. Improvement of tensile properties and toughness of an epoxy resin by nanozirconium-dioxide reinforcement; J Mater Sci 2008; 43:3245–3252.

[6] Zhang H. et al. Fracture of nanoparticle filled polymer composites; Institute of Composite Materials; 2007, Kaiserslautern.

[7] Schilde C, Nolte H, Arlt C, Kwade A. Effect of fluid–particle-interactions on dispersing nanoparticles in epoxy resins using stirred-media-mills and three-roll-mills. Compos Sci Technol 2010; 70: 657-663

[8] Harani H, Fellahi S, Bakar M. Toughening of epoxy resin using hydroxyl-terminated polyesters. J Appl Polym Sci 1999; 71:29–38.

[9] Gojny F H, et al. Carbon nanotube –reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. Compos Sci Technol 2004; 64 (15):2363–71.

[10] Calard V, et al. Thermal and electrical properties of carbon nanotube reinforced cyanate ester resin; High Performance Fillers for Polymer Composites 2009.

[11] Arlt C, et al. Compressive Strength: The Key to Future CFRP Production, 1st CEAS-DGLR, Berlin, Germany, 2007.

[12] Arlt C et al. Reduction of Residual Stress and Enhancement of Compressive Strength in CFRP for aerospace applications. 11th International AVK Conference Proceedings, Essen, 2008, Germany.

[13] Arlt, C. et al. Untersuchungen zum Einfluss des Designs von Nanopartikeln auf ausgewählte matrixdominierte Verbundeigenschaften von CFK-Werkstoffen. DGLR- Kongress; 2009; Aachen.

[14] Fan Z, Santare M H, Advani S G. Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes. Composites: Part A 2008; 39: 540-554.Smith J, Jones B and Brown J**.** *The title of the book*. 1st edition, Publisher, 2001.

[15] Kleineberg M, Nickel J, Pabsch A, Sigle C, Schöppinger C. Vorrichtung und Verfahren zur Herstellung von faserverstärkten Kunststoffen bzw. Kunststoffbauteilen nach einem modifizierten RTM-Verfahren. DE 198 53 709 C1, 2000

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