

## Mechanical and Fracture Mechanical Properties of Matrix-Reinforced Carbon Fiber Composites with Carbon Nanotubes

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**Abstract.** Carbon fiber reinforced Plastics are materials with high strength and stiffness at low weight compared to metals. These properties make the materials ideal candidate for structures in aerospace applications, where they are often used under bending conditions. Due to the strongly anisotropic composition the CFRP typically fail in compression by fiber buckling. In order to improve this weakness, nano-tube and nano-fiber reinforced matrix was used to build CFRP. Four-point bending tests showed that stiffness and strength could be improved by the fillers, whereas negative influence was found on fracture energy.

### Introduction

Carbon fiber reinforced polymers CFRP are high performance materials. Their high strengths combined with their relative low densities make them the ideal choice for materials of vehicles on ground and in the air. Low weight and high stiffness allow slender structures and less total weight, which finally permits smaller engines and less power consumption. These excellent properties are achieved by the combination of a polymer matrix and a high performance fiber or fabric[1]. These construction principles implicate strong anisotropy in the mechanical properties. High tensile strength in fiber direction is combined with low strength properties perpendicular to the fibers or fabric, mainly governed by the matrix. Also the typical compression-tension anisotropy, where the material fails at lower loads in compression, due to fiber buckling, compared to tension, can be observed. Therefore, a strategy is necessary to overcome these drawbacks.

As a first idea one could think to use a stronger or better cross-linked. A second idea could be to improve the matrix by adding an additional phase, which stiffens the matrix, while at the same time the toughness is kept constant or improved as well [2] - this strategy is followed in this work. The filler material investigated are carbon nanotubes CNT, and Carbon nanofibers CNF. Critical procedure is mixing the nano-fillers with the matrix to achieve a fine dispersion of the filler. Several methods are described in the literature [3] for this purpose, one of them is shearing the material with a three roll mill (calender).

Typical loading mode of CFRP is bending because these materials are often used as beams or shell like structures. Under these loading conditions the materials fail by delamination or buckling on the pressure side of the structure. These failure modes can be best tested by bending experiments as well as mode I delamination tests.

The objective of this work was to reinforce epoxy based CFRP with CNT and CNF, respectively, and to compare the resulting mechanical properties with conventional CFRP.

## Materials

**Resin.** The resin used was a commercially available epoxy from Sika GmbH, Stuttgart, Germany based on BADGE (Biresin CR170, component A) with an amine hardener (Biresin CH170-3, component B). The mass ratio for the mixture of both components was 100:16 (A:B)[4].

**CNT.** Multiwall carbon nanotubes from Nanocyl (NC7000, Nanocyl SA, Sambreville, Belgium) were used as fillers. The fibers are characterized by an average length of 1.5  $\mu\text{m}$  and an average diameter of 9.5 nm resulting in an aspect ratio of 158:1 [5].

**CNF.** Carbon nano fibers were bought from Sigma-Aldrich. They were produced by a floating catalyst vapor-grown method by Pyrograf Products Inc. (Cedarville, USA). Their diameter is between 125—150 nm with a length between 20—200  $\mu\text{m}$  [6]. The resulting aspect ratio is 1600:1.

**Dispersion of Nano-fillers.** Nano-fillers were fine dispersed in component A of the resin with a three-roll mill (TRM, Exakt 80E, Exakt Advanced Technologies GmbH, Norderstedt, Germany). Pre-mixed resins with a filler content of 0.7 wt% were used. The shearing procedure was repeated four times with decreasing gap size in order to smoothly disperse the fillers. Detailed procedure is described in Singer et al. [4].

Dispersion is a critical point in nano-filled matrix production since the nano-fillers, due to their high aspect ratio and large surface, tend to agglomerate [7]. The agglomerates can reach several times the diameter of the fillers and may act as crack initiator.

**Composites production.** Immediately prior to the lamination process, resin and hardener were mixed in a closed glass vessel under vacuum at a pressure of 10 kPa. A weave with an areal weight of 245 g/m<sup>2</sup> and a fineness of 200 tex of high tenacity carbon fibers was used (SGL CARBON SE, Wiesbaden, Germany). Composites were produced by a wet hand lay-up procedure followed by hot pressing at 140 °C for 1 hour at 3 MPa. Plates with a final thickness of approx. 4 mm and 20 layers of weave were produced.

On the side where the double cantilever beams were cut off a thin Teflon foil was inserted at half thickness of the plate, acting later as crack initiator.

From the plates four-point bending specimens (80x15x4 mm<sup>3</sup>) as well as double cantilever specimens (125x11x4 mm<sup>3</sup>) were cut with a water jet.

## Methods

Four-point bending and double cantilever beam testing was used to characterize the material:

**Four-point bending test 4PB** were performed with a span size of 66 mm and a loading span of 22 mm in order to characterize the elastic properties as well as measure the bending strength of the material. Testing geometry was based on ASTM D7264 / D7264M-07 [8].

**Double cantilever beam DCB** experiments were used to characterize the interlaminar fracture toughness in mode I loading. Experiments were based on ASTM D5528-13 [9]. The experiments were performed with a 10 kN universal spindle machine (ZwickRoell GmbH & Co. KG, Ulm, Germany). Specimens were prepared with a 25 mm teflon insert. Small aluminum blocks were glued on the bars on one side used for mounting and loading the specimens. The specific fracture energy was evaluated from the integral of the load displacement curve divided by the ligament area.

**Digital image correlation.** Digital image correlation is a very versatile tool to measure surface deformations of materials. On the black surfaces of the CFRP to be measured a white and random pattern is sprayed with an aerosol can. During the deformation measurements, pictures are taken regularly from the specimens under load. By a post-processing procedure from the comparison of the deformed with the un-deformed speckle pattern local deformations and finally strains are calculated. This is done by selecting some facets, i.e. squared sub-regions of the pattern, which contain unique information about the position. The movements of the facets are finally evaluated and their size determine the local resolution of the deformation measurement. For the measurement

for this work a Q-400 DIC from Dantec Dynamics (Skovlunde, Denmark) was used with software Istra 4D x64 version 4.4.4.494. The system uses two cameras and calibration targets and can measure out of plane movements and provide absolute values of deformation with this configuration.

The DIC technique was used to measure the displacements of the specimens under investigation.

## Results and Discussion

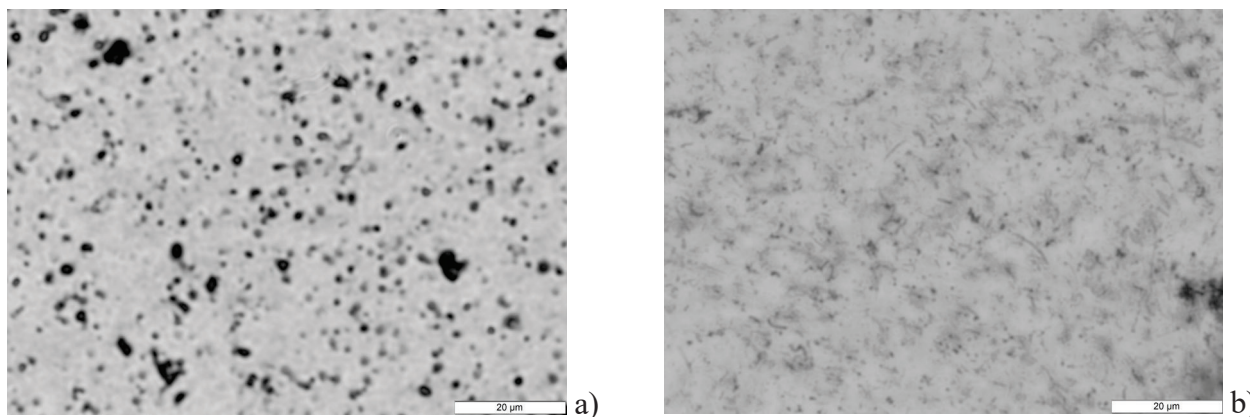


Figure 1: Light microscope images after the last pass through the TRM a) carbon nano-tubes, b) carbon nano-fibers

With the TRM fine dispersions of CNT and CNF could be produced. This is visible in the photographs of figure 1 showing the homogeneous dispersed tubes (figure 1a) and fibers (figure 1b). The larger dots in the figure 1a are agglomerates of CNT which could not be more refined. In figure 1b some single large fibers are visible, in general the carbon nano-fibers are smoothly dispersed.

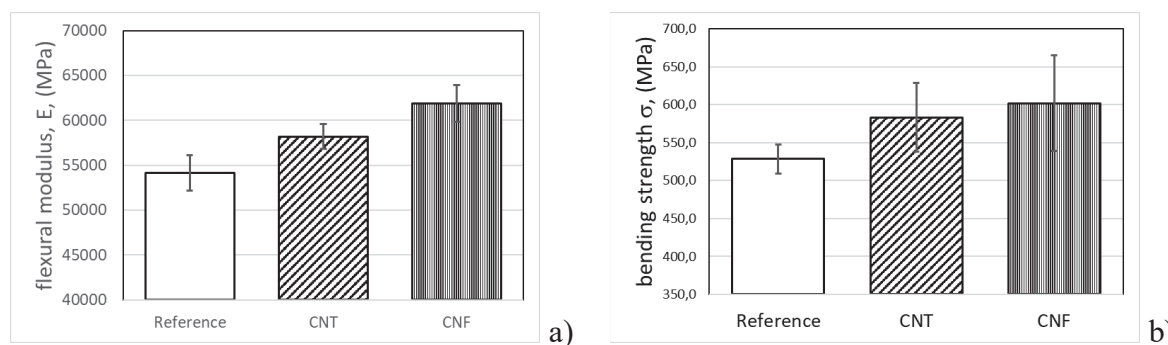


Figure 2: a) flexural modulus, b) bending strength of reference- (empty bars), CNT-reinforced- (oblique hatched bars) and CNF-reinforced-CFRP (vertically hatched bars)

Compared to the not-reinforced reference material the CNT reinforced material showed higher bending modulus of  $58,2 \pm 1.4$  GPa for the CNT modified resin compared to  $54.1 \pm 2.0$  GPa of the neat resin, which is a plus of 10%. The longer CNF reinforcements showed even higher flexural modulus of  $61.9 \pm 2.0$  GPa, a plus of 14% (see figures 2a and b).

An increase in bending strength could also be found for the reinforced materials compared to results of the neat resin  $529 \pm 19$  MPa. The flexural strength of the CNT reinforced material increased to  $583 \pm 45$  MPa and that of the CNF reinforced material to  $602 \pm 62$  MPa.

Both reinforcement methods increased the flexural modulus as well as the strength compared to the neat resin matrix. Evaluation of the DIC images showed that the buckling of the mat is less pronounced and happens at higher loads compared to the reference material.

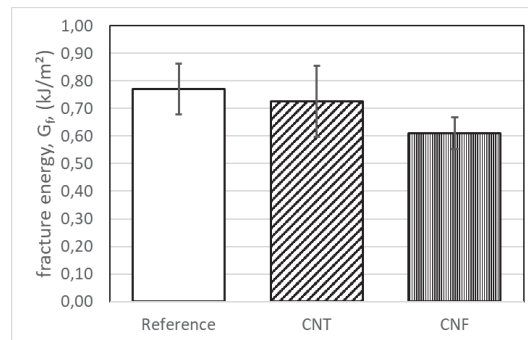


Figure 3: Mode I fracture energy from DCB testing of reference- (empty bar), CNT-reinforced- (oblique hatched bar) and CNF-reinforced-CFRP (vertically hatched bar)

The results of fracture mechanical tests in mode I performed on double cantilever beams did not show similar improvements as were found for the flexural properties (see figure 3). The fracture energy of the reference material was  $0.77 \pm 0.09$  kJ/m<sup>2</sup> that of the CNT reinforced material  $0.73 \pm 0.13$  kJ/m<sup>2</sup> and that of the CNF reinforced material was even lower and reached only  $0.61 \pm 0.06$  kJ/m<sup>2</sup>. From the resulting data it seems, that the fillers were not able to improve the fracture mechanical properties but worsen their properties. This is in contradiction with the literature, where the fracture toughness of filled resins in general increases. There are several factors which could explain this results: as reinforcement fibers, unmodified raw material was used. The fibers could not attach to the resin and might therefore not be able to transfer substantial load. While they are not able to act as load carrying reinforcements their volume act as failure and initial cracks. This behavior is not important for the 4PB test were in the middle part, between the span, the sample is loaded by a pure moment and the failure mode is axial buckling followed by perpendicular delamination.

## Conclusions

The addition of nano-fillers like CNT or CNF was shown to improve the bending modulus and the bending strength, while they did not increase the fracture energy in modulus I of the material. The increased stiffness of the compound resulting from a stiffer matrix is able to substantially retard fiber buckling and therefore increase the strength of the CFRP.

The toughness in mode I could not be increased with the presented reinforcements. This seems to be in contradiction with the assumption, that a fine dispersion with artefacts well below the critical size for neat resins, should increase the toughness by fiber bridging and pullout effects during fracturing. This mechanism might be suppressed by weak attachments of the fibers to the matrix. Fibers might act as additional voids and crack initiators.

## Summary

In this paper three CFRP materials were investigated, all of them based on the same combination of an epoxy thermoset and a woven reinforcement of carbon fibers. Three variation of the matrix were used, neat resin, filled with as bought carbon nanotubes or carbon nanofibers. The fillers were dispersed with a three roll mill in order to achieve a fine distribution of them. Four-point bending experiments as well as double cantilever beam fracture tests were performed in order to characterize the composite. While positive effects on bending stiffness and strength were observed, the fracture energy decreased by adding the fillers.

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