

# EVALUATION OF THE POTENTIAL OF CARBON NANOTUBES AS REINFORCEMENT OF AN EPOXY MATRIX AND ITS APPLICATION TO FIBRE REINFORCED POLYMERS

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## ABSTRACT

Carbon Nanotubes (CNTs) exhibit a high potential for the reinforcement of polymers. Composites of epoxy resin containing low content of double-wall carbon nanotubes (DWCNT) were produced and characterized. Increased mechanical properties (Young's modulus and fracture toughness) were observed. A high potential exploitation of nanotube/epoxy-composites can be their utilisation as matrix material for conventional fibre reinforced polymers (FRP). Nanotubes are expected to improve matrix-dominated properties of FRPs (e.g. interlaminar shear strength). Samples consisting of a glass fibre non-crimp fabric and a nanotube-modified epoxy resin were manufactured by RTM (resin transfer moulding). The glass fibre reinforced polymer (GFRP) with nanotube-modified epoxy matrix showed an improved interlaminar shear strength in comparison to the GFRP with neat epoxy matrix. The tensile properties were not affected by the nanotubes due to the dominating effect of the fibre reinforcement.

## 1. INTRODUCTION

Nano-reinforcements for polymeric materials are presently considered as potential candidates for the improvement of material properties. The dimensions in the nanometer region and the resulting unique properties are expected to produce composites with improved performance. A special interest in the collectivity of nano-fillers is brought towards carbon nanotubes (CNTs) [1-2]. Their mechanical properties, an enormous aspect ratio, a high Young's modulus and strength, in combination with an electrical and thermal conductivity make them an interesting material for the use as nano-filler in polymers and open up new perspectives for multifunctional materials, e.g. conductive polymers with improved mechanical performance. The percolation threshold of nanotube/epoxy nanocomposites could be reached at very low filler contents [3-5] in comparison to conventional carbon black, due to the aspect ratio of several thousands. Therefore electrically conductive composites with increased mechanical properties are accessible.

The mechanical reinforcement of polymers with nanotubes is a special but very interesting issue. Their high aspect ratio in combination with a low density [6] and a high strength and stiffness [7-9] should lead to a significant improvement of the mechanical properties already at very low filler contents. The efficiency of the reinforcement is addicted to the degree of exfoliation, respectively dispersion and the interfacial adhesion towards the polymer matrix. The enormous surface area of nano-fillers of up to more than 1000 m<sup>2</sup>/g and the observed entanglement of some CNTs results in a strong agglomeration and therefore in difficulties regarding their dispersibility in polymer matrices.

Progress in achieving a good dispersion of nano-particles in epoxies has recently been made by using a mini-calander to respectively disperse carbon nanotubes and carbon black in an epoxy resin [10]. This method is a common and well established technique to disperse various micro-particles in different matrices, e.g. color pigments for cosmetics or lacquers. A major advantage of this method is, besides the improved dispersion, the possibility of manufacturing large amounts of nanocomposite without losing its efficiency.

The interfacial adhesion between the carbon nanotubes and the polymer is the second topic to be investigated. Progress has been made by Wagner and co-workers [11-13] whom performed

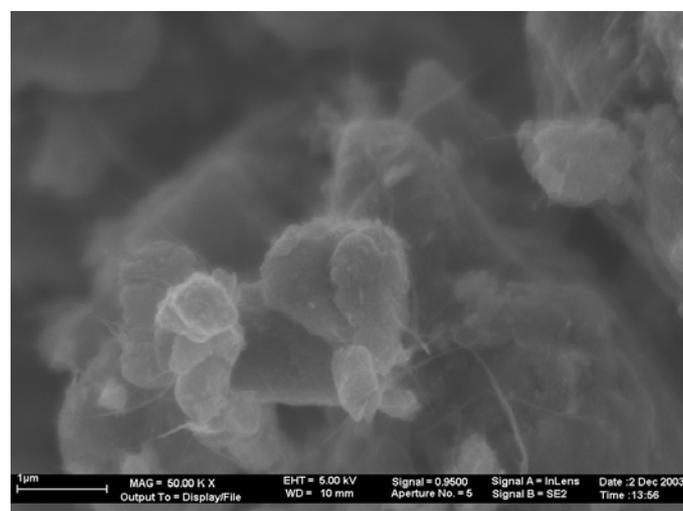
specially developed pull-out tests for individual nanotubes from polymer matrices. The interfacial shear strength between CNTs and polymers is dependent on the polarity of the CNT surface and the matrix and the potential interfacial area. Nevertheless it can be considered as being rather weak. A chemical functionalisation of the CNT surface has been identified as an efficient tool to overcome this problem. A tailored functionalisation, e.g. amino-functionalisation for amine curing epoxies, enables a reaction between the nanotubes and the epoxy resin under formation of covalent bonds, which finally leads to higher stress transfer from the matrix to reinforcement. The formation of covalent bonds between the CNTs and matrix increases the dispersibility, resulting in improved mechanical properties [10,14-15]. The observed functionalisation effect on a strengthen of the interface had been substantiated by theoretical studies based on molecular dynamics simulations [16].

A combination of a nanotube-modified matrix with conventional reinforcements (e.g. carbon-, glass- or aramid-fibres), could result in a new generation of multi-functional materials [2]. Recently Hsiao et al. [17] and Meguid et al. [18] investigated the tensile and shear strength of nanotube reinforced composite interfaces by single shear-lap testing. They observed a significant increase of the interfacial shear strength in comparison to the neat epoxy matrix at contents between 1 and 5 wt.% of multi-wall nanotubes. In this paper we present the first example of a GFRP consisting of a glass fibre non-crimp fabric and a nanotube modified matrix with only 0.1 wt.% amino-functionalised double-wall carbon nanotubes, produced by RTM- technique. We describe the production procedure and the results of the tensile- and ILSS-testing.

## 2. EXPERIMENTAL

### *2.1 Materials*

The epoxy matrix used in this study consists of a modified DGEBA-based epoxy resin (L135i) and an amine hardener (H137i), supplied by Bakelite MGS Kunstharzprodukte GmbH, Stuttgart/Germany. This system is characterised by its extreme low viscosity ( $\eta_{RT}=250$  mPa s) and is a standard resin for infusion processes (e.g. RTM). The amino-functionalised double-wall carbon nanotubes were obtained by Nanocyl, Namur/Belgium and appear in an entangled and condensed form (Fig. 1). These nanotubes consist of two graphitic shells and have an average outer diameter of 2.8 nm together with a length of several micro meters.



**Fig. 1** SEM–image of amino-functionalised DWCNT

## 2.2 Dispersion and processing parameters

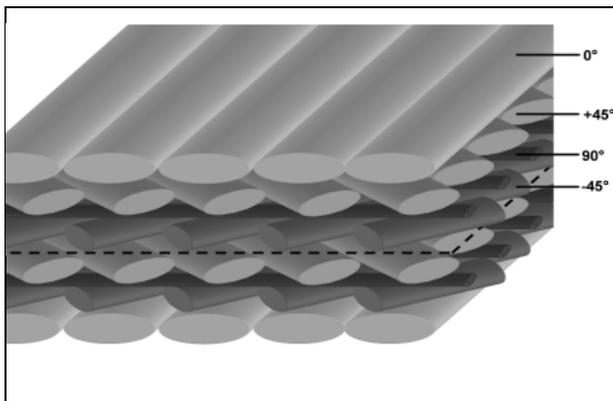
In order to disperse the DWCNT-NH<sub>2</sub> in the epoxy resin, we manually mixed the nanotubes with the resin and added the suspension batch-wise to a mini-calander (Fig. 2). The gap size between the ceramic rolls (Al<sub>2</sub>O<sub>3</sub>) was 5 µm and speed was set to 20 (1<sup>st</sup> roll), 60 (2<sup>nd</sup> roll) and 180 rpm (3<sup>rd</sup> roll). The dwell time of each batch of CNT-EP suspension on the rolls was approximately two minutes while nanotubes were dispersed in the resin by the high shear forces. A first primary dispersion of the agglomerates is performed in the knead-vortexes, whereas the final distribution of the CNTs occurs in the area between the rolls. The suspension was collected, mixed with the hardener for 10 minutes by stirring, cured for 24 hours at room temperature (RT) and finally post-cured at 60 °C for 24 hours.



**Fig. 2** Mini-calander used to disperse CNTs [19]

## 2.3 Resin transfer moulding (RTM)

GFRPs were produced by RTM, using a glass-fibre non-crimp fabric (Seartex Wagener GmbH/Germany). The schematic composition of the layers and the volume contents can be taken from in Fig. 3. The resin was mixed with the amine hardener and degassed for 20 minutes in a previous step before injection. The final sample remained in the mould for curing. The curing conditions of the GFRPs were identical to the neat resin as described previously, except the post-curing was elevated to 80°C.



Layer	Vol.-content
0°	48.7 %
+45°	23.0 %
90°	4.8 %
-45°	23.0 %
Binding yarn	0.5 %
Glass fibre content of the GFRP	~37%

**Fig. 3** Composition of the glass-fibre non-crimp fabric used in this study

## 2.4 Mechanical characterisation

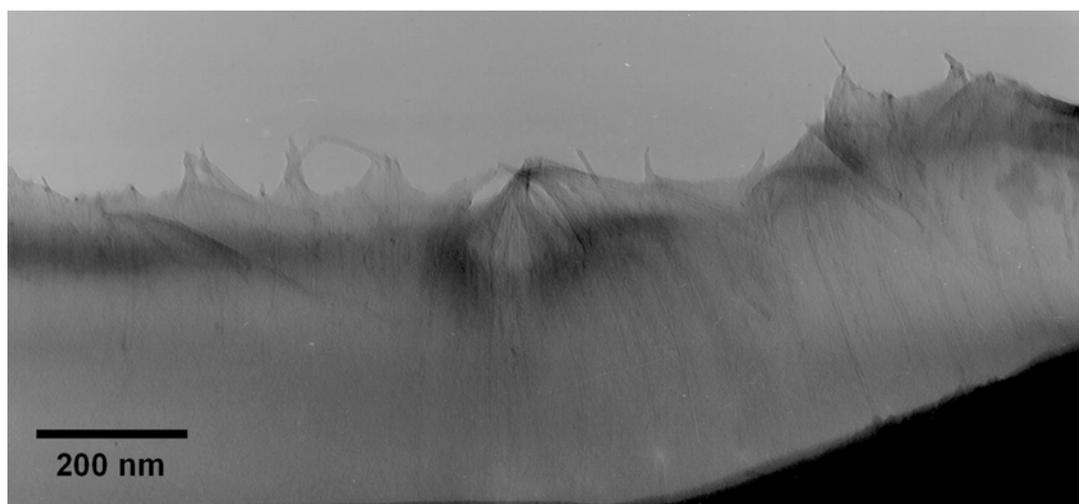
The tensile tests on the nanocomposite and the GFRPs were conducted according to DIN EN ISO 527.1/2. The characterisation of the tensile properties of the plain polymer was performed

with dog-bone specimen, respectively CT-specimens for the fracture toughness tests (ASTM D 5045-96), using a Zwick universal tensile tester with a cross-head speed of 1 mm/min. The FRPs were tested in 0° and 90° direction using a Schenk 63 kN-hydro pulser.

The interlaminar shear-strength has been measured by three-point bending tests using the short-beam method according to ASTM D 2344-84. The influence of the post-curing on the shear strength has been investigated by testing post-cured and non-post-cured samples.

### 3. RESULTS & DISCUSSION

Calendering is an effective method to disperse carbon nanotubes in an epoxy resin, as we reported recently [10]. The efficient exploitation of the potential reinforcing effect of carbon nanotubes is referred to a large interfacial area between the matrix and the CNTs and therefore to a good exfoliation and dispersion. The application of a mini-calander turned out to be suitable to exfoliate and disperse nanotubes and other nano-scaled particles in liquid polymers. Fig. 4 shows a TEM-image of a nanocomposite containing 0.1 wt.% amino-functionalised DWCNTs. The nanotubes were well exfoliated and impregnated by the epoxy resin. The CNT/epoxy-nanocomposites showed an enhanced Young's modulus and fracture toughness in comparison to the neat epoxy [10]. In Table 1 some of the obtained data concerning the mechanical properties are compared.



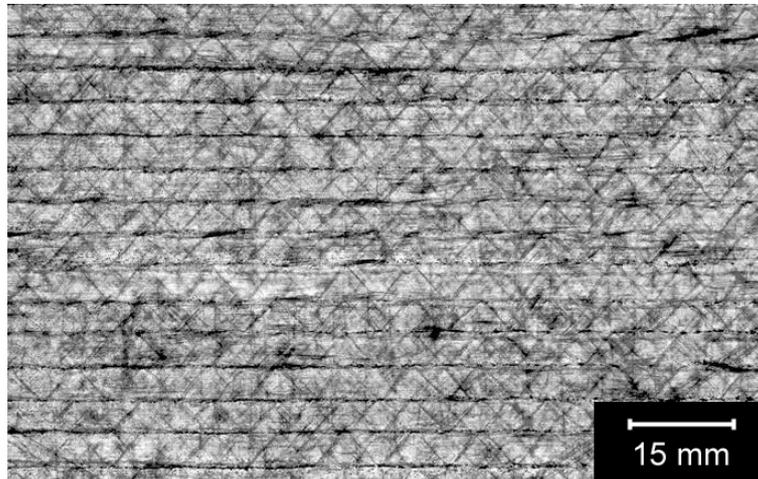
**Fig. 4** TEM-image of a DWCNT-NH<sub>2</sub>/epoxy-nanocomposite

“**Table 1.** Mechanical properties of tested (nano-) composites.”

Property	L135i/H137i-epoxy	Epoxy/0.1% DWCNT-NH <sub>2</sub>
Young's Modulus [GPa]	3.29 (± 0.10)	3.50 (± 0.11)
Tensile strength [GPa]	63.8 (± 1.03)	63.6 (± 0.96)
Strain to failure [%]	7.25 (± 0.24)	7.65 (± 0.15)
Fracture toughness K <sub>IC</sub> [MPa·m <sup>1/2</sup> ]	0.65 (± 0.062)	0.77 (± 0.058)

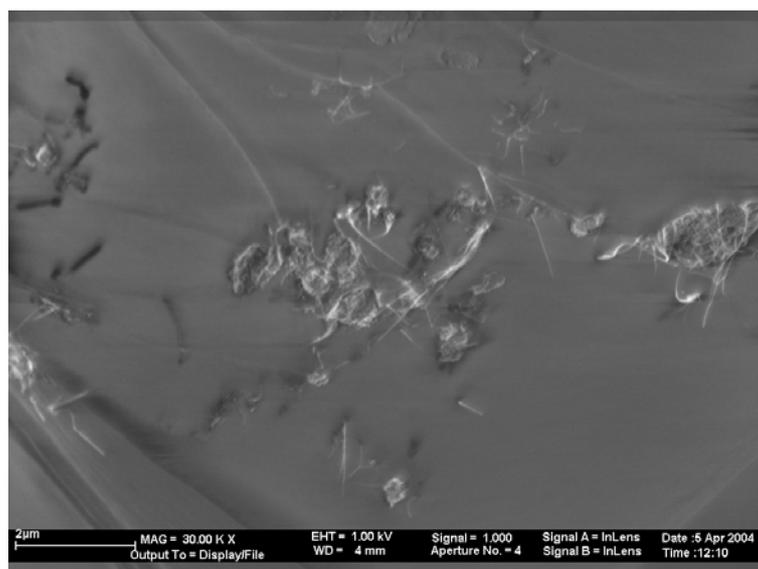
The nanotube-modified epoxy resin was used to manufacture GFRPs by RTM-technique. It was still possible to manufacture the nanotube-modified epoxy resin with a nanotube content of 0.1 wt.% despite the slightly increased viscosity. Nevertheless much higher filler contents ( $\phi_{\text{CNT}} > 0.5$  wt.%) will lead to processing problems due to a dramatically increasing viscosity which have not been solved up to now.

Fig. 5 shows an optical micrograph of the manufactured composite. Generally we could not see any filtering effect by the glass fibres. The nanotube concentration seems to be constant over the entire composite. The inhomogeneous appearance of the composite is caused by an accumulation of matrix between the glass rovings and partly by a formation of aggregate structures due to the re-agglomeration of the CNTs. The horizontal line are related to matrix-rich areas between the glass rovings in 0°-direction. The fibres bundles in this direction are separated from each other, with matrix-rich areas occurring.



**Fig. 5** Optical micrograph of a produced GFRP with CNT-modified epoxy matrix. Only the matrix-rich areas and the binding yarn becomes visible due to similarities of the refraction index of the glass fibres and the epoxy resin.

Some smaller agglomerates could be observed by SEM-investigation shown in Fig. 6. The micrograph has been taken from the fracture surface of a tested tensile specimen. The matrix contains aggregates with a loose structure, which emerged by a re-agglomeration during degassing of the resin before injection. The degassing leads to a froth up of the nanotube/epoxy-suspension, accompanied by an acceleration of the re-agglomeration of the CNTs, as a consequence of the increasing surface area.



**Fig. 6** SEM-micrograph taken from a fracture surface of a tested GFRP-specimen. Some small aggregates could be observed in the matrix-rich areas. The observed loose structure is caused by the re-agglomeration of the CNTs.

In order to suppress the re-agglomeration it is necessary to either stabilize the nanotube suspension or to use nano-particles with a smaller surface area. For an efficient reinforcement of epoxies with carbon nanotubes, one has to find a compromise between dispersibility and surface area. A high specific surface area (SSA), e.g. for SWCNTs, aggravates the exfoliation and dispersion and accelerates a re-agglomeration, but enables a good stress transfer via the enormous interface. A smaller SSA, as in the case of MWCNTs, improves the dispersibility, but is less efficient regarding a mechanical reinforcement. A final statement to which type of CNTs should be qualified for this purpose cannot be given yet and is part of the ongoing research activities.

The determination of the tensile properties of the composites was performed by tensile testing in 0°- and 90°-direction. The measured values for the tensile strength are shown in Fig. 7. From these data, no influence of the carbon nanotubes on the strength could be observed. The composites show fibre-dominated behaviour of the tensile properties both directions.

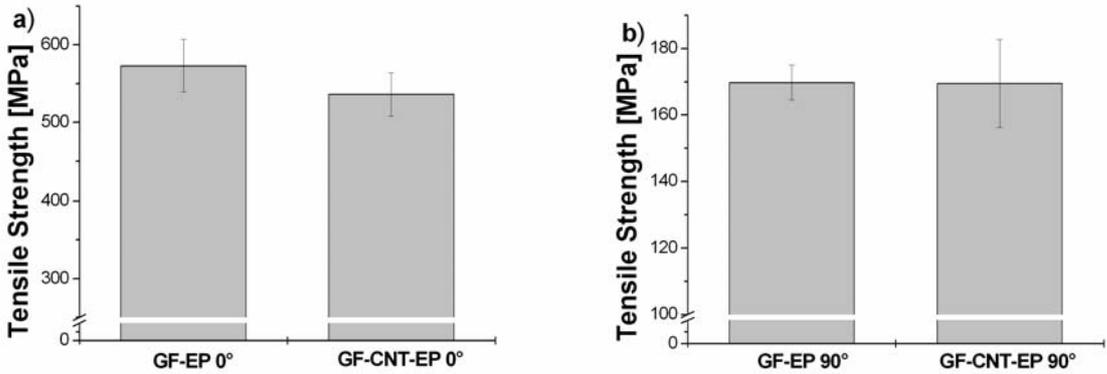


Fig. 7 Experimentally obtained tensile properties of the GFRPs (a) in 0°-direction and (b) in 90°-direction

In contrast to this, the interlaminar properties show matrix-dominated behaviour. The determination of the interlaminar shear strength by short beam three-point bending tests resulted in a significant increase of the ILSS for the DWCNT-NH<sub>2</sub>/epoxy-nanocomposites in comparison to the GFRP with a neat epoxy matrix (Fig. 8).

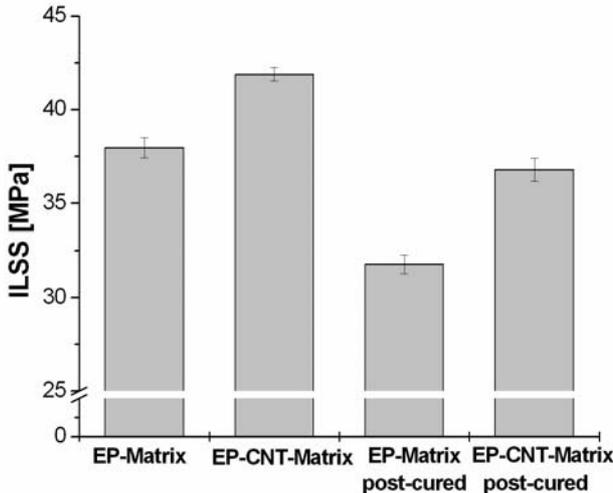


Fig. 8 Interlaminar shear strength (ILSS) of the GFRPs

The experimentally obtained ILSS of the GFRP with an epoxy-matrix (37.9 MPa  $\pm$ 1.9 MPa) was increased by more than 10% for the composite with nanotube-modified matrix (41.9  $\pm$ 1.3 MPa). The post-curing generally decreased the ILSS of the FRPs, but the gain in ILSS caused by the carbon nanotubes increased (+16%). A further cross-linking of the epoxy resin is induced, resulting in lower ductility of the epoxy matrix. The amount of thermal residual stresses could explain the decrease of the level of ILSS, which was observed and reported for the ultimate tensile strength (UTS) of similar FRPs [20]. However, the post-curing leads to the formation of covalent bonds between the nanotubes and the epoxy matrix. The interface is strengthened enabling a better stress transfer from the matrix to the nanotubes.

#### 4. CONCLUSIONS

Carbon nanotubes exhibit a high potential to improve the (fracture-) mechanical properties of epoxy systems already at very low filler contents. A significant enhancement of fracture toughness (+18%) had been observed for a nanotube content of only 0.1 wt.% DWCNT-NH<sub>2</sub>. We were able to demonstrate the applicability of nanotube/epoxy-systems as matrix for FRPs and the capability of RTM-technique to manufacture these nano-reinforced composites. A manufacturing of resins with nanotube contents of more than 0.5 wt.% is still an unsolved problem, due to the enormous surface area of CNTs and the resulting increase in viscosity.

The nanotube-reinforced GFRPs exhibit a noticeably improved interlaminar shear strength despite an observed re-agglomeration of the CNTs. A post-curing of the composites decreased of the level of the ILSS, which could be explain by the increased density of cross-links leading to a lower ductility and increasing amount of residual thermal stresses. However, the influence of the reinforcing nano-phase became more significant. A further formation of covalent bonds between the amino-groups on the nanotube surface and the epoxy matrix strengthens the interface, enabling an improved stress-transfer, resulting in the observed behaviour.

The tensile properties were not affected by the presence of the nanotubes, neither in 0°- nor in 90°-direction, because of the glass fibre-dominating effect.

The combination of conventional fibres (e.g. glass-, carbon-, aramid-fibres, etc.) with an additional nano-phase reinforcement (e.g. carbon nanotubes) exhibits a high potential for structure applications. Already small amounts of carbon nanotubes in epoxies leads to increased matrix-dominated material properties (e.g. ILSS). As a result, a new generation of materials with multi-functional properties, such as a combination of electrical and thermal conductivity together with improved mechanical performance are accessible.

#### ACKNOWLEDGEMENTS

The companies Bakelite MGS Kunstharzprodukte GmbH / Stuttgart and Exakt GmbH & Co. KG / Hamburg, Germany are acknowledged for the supply of the epoxy resin and the mini-calander respectively. Special thanks to Andreas Gagel (TUHH, Polymer Composites section) for the RTM-manufacturing. The German Research Foundation (DFG) SFB 371-TP C9 and the European Commission (Scientific-Network: "Carbon Nanotubes for Future Industrial Composites: theoretical potential versus immediate application (CNT-Net)"; Contract N°: G5RT-CT-2001-050206) are gratefully acknowledged for financial support.

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