

# Critical consideration of the potential of carbon nanotubes as structural modifiers for epoxy matrix composites

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## ABSTRACT

Carbon Nanotubes (CNTs) in general are considered to be highly potential fillers to improve the material properties of polymers. However, questions concerning the appropriate type of CNTs, e.g. single wall CNTs (SWCNT), double-wall CNTs (DWCNT) or multi-wall CNTs (MWCNT) are still to be answered. This study focuses on the evaluation of these different types of nanofillers, their influence on the mechanical and physical properties of epoxy-based nanocomposites and the relevance of surface functionalisation. The influence of filler content, the varying dispersibility, the aspect ratio, the specific surface area and an amino-functionalisation on the composite properties are discussed and correlated to the identified micro-mechanical mechanisms.

The paper considers the requirements for an efficient mechanical reinforcement and an enhancement of the electrical and thermal conductivity based on experimental data. The nanocomposites exhibit an enhanced strength and stiffness and even more important, a significant increase in fracture toughness (43% at 0.5 wt.% amino-functionalised DWCNT). Furthermore, CNTs induce an electrical conductivity at low filler contents, with a dependence on the CNT-type. The results concerning the thermal conductivity prove their limited capacity, to improve the thermal conductivity of polymers, despite their potentially high thermal conductivity.

**Keywords:** Carbon Nanotubes; Nanocomposites; Mechanical properties; Electrical conductivity; Thermal conductivity; Fracture toughness

## 1 INTRODUCTION

In recent years, the development of nanocomposites has become an attractive new subject in materials science. Nanoparticles in general are regarded as high potential fillers to improve the mechanical properties of polymers. Furthermore, dependent on the applied type of filler, nanoparticles can influence the electrical and thermal conductivity of the final nanocomposite.

Interesting candidates with potentially unique properties are carbon nanotubes (CNTs)<sup>1-4</sup>. CNTs exhibit an exceptionally high stiffness and strength<sup>5-8</sup>, a diameter dependent specific surface area (SSA) of up to 1315 m<sup>2</sup>/g<sup>9</sup>, as well as an aspect ratio in the range of several

thousands. According to their graphitic structure, CNTs possess a high thermal conductivity and an electrical conductivity, which can be either semi-conducting or metal-like.

The combination of the previously mentioned material properties make CNTs highly desirable candidates to improve the properties of polymers. Besides, the development of CNT/polymer nanocomposites opens new perspectives for multifunctional materials, e.g. conductive polymers with improved mechanical performance and with a certain potential of damage sensing and "life"-monitoring<sup>10</sup>.

This paper aims to identify and discuss parameters influencing the mechanical properties, as well as the electrical and thermal conductivity of CNT/epoxy nanocomposites. Therefore, the influence of the particle content, the interfacial area, the influence of a surface functionalisation and the aspect ratio on the material properties were investigated.

## 2 EXPERIMENTAL SECTION

### 2.1 Epoxy matrix system

The epoxy matrix used in this study consists of a modified DGEBA-based epoxy resin (L135i) to be cured with an amine hardener (H137i), supplied by Bakelite MGS Kunstharzprodukte GmbH, Stuttgart/Germany. This epoxy system, characterized by its low viscosity ( $\eta_{RT}=250$  mPa s), is a standard resin for infusion processes (e.g. RTM – resin transfer moulding).

### 2.2 Carbon Nanotubes

*All CNTs used in this comparative study were produced via the CVD-route.*

Single-wall carbon nanotubes were purchased from Thomas Swan Ltd. &Co., UK. The SWCNTs exhibit an average diameter of  $d < 2$  nm and a length of some micrometers.

The DWCNT (-NH<sub>2</sub>) were obtained from Nanocyl, Namur/Belgium. They appear in an entangled cotton-like form. These nanotubes consist of two graphitic shells and have an average outer diameter of 2.8 nm and a length of several micrometers. The amino-functionalisation was accomplished by ball-milling purified DWCNTs in ammonia. The degree of functionalisation, specified by the manufacturer, is about one percent in relation to the carbon content. It has to be mentioned that the ball-milling process leads to a considerable reduction of the effective length and unfortunately also to a condensed packing of the CNTs.

The MWCNTs were also obtained from Nanocyl. For this study we used thin MWCNTs (purified) and amino-functionalised MWCNTs with an average outer diameter of about 15 nm and a length of up to 50  $\mu$ m. The functionalisation process was similar to the one described for DWCNTs.

### 2.3 Carbon black

Nanocomposites containing highly conductive carbon black (CB) were used as reference material. The CB, Printex XE2 from Degussa/Germany, is highly graphitized and commonly used as conductive filler for anti-static applications or as color pigment for printing ink. It is usually used to increase the electrical and thermal conductivity of polymers, but also to enhance the stiffness. The CB tends to form aggregates, consisting of bonded spherical primary particles with a diameter of 30 nm, forming again agglomerate structures.

### 2.4 Dispersion and processing parameters

The composites investigated in this study were all manufactured in the same way. In order to disperse the nanofillers in the epoxy resin, we first manually mixed the CNTs (CB) with the epoxy resin (without hardener). This suspension was added batch-wise to a mini-calander (Exakt 120 S, Exakt Vertriebs GmbH/Hamburg, Germany) for final high shear mixing. The gap size between the ceramic rolls of the mini-calander (Al<sub>2</sub>O<sub>3</sub>) was 5  $\mu$ m and the 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 suspension was approximately two minutes. The suspension was collected, mixed with the hardener for 10 minutes by intense stirring, cured for 24 hours at room temperature (RT) and finally post-cured at 60 °C for 24 hours.

## 2.5 Mechanical characterization

Tensile tests on nanocomposites were performed according to DIN EN 527.1/2 with dog-bone specimens using a Zwick universal tensile tester at a crosshead speed of 1 mm/min. A statistical evaluation of the results was performed on the base of at least eight individually tested specimens of each sample. The experimental investigation of the fracture toughness was performed according to ASTM D 5045-99. Compact tension (CT) specimens were tested at a crosshead speed of 1.3 mm/min. The deformation of the samples was measured by detecting the crack opening displacement (COD) using a highly sensitive extensometer (MTS) with a gauge length of 5 mm. A minimum of 6 specimens of each sample was tested for statistical evaluation.

## 2.6 Electron microscopy

Scanning Electron Microscopy (SEM)-images were taken with a Leo FE-SEM 1530 at different acceleration voltages (0.9 – 1.5 kV). The samples were investigated without gold-sputtering to avoid covering of the nano-scaled reinforcements. The qualitative determination of the dispersion was accomplished by Transmission Electron Microscopy (TEM), using a Philips EM 400 at 120 kV, on thin films (~50 nm) of nanocomposites. The films were obtained by ultra microtome cutting at room temperature.

## 2.7 Electrical conductivity

The investigation of the electrical conductivity was performed by dielectric spectroscopy using a HP 4284a Impedance Analyzer. The samples, each five specimens with 10x10x1 mm dimensions, were tested with voltage amplitude of 1.0 V in a frequency range between 20 Hz and 1 MHz. The conductivity  $\sigma$  was calculated from the complex impedance ( $Z^*$ ) according to following equation, with the sample thickness ( $t$ ) and cross section ( $A$ ).

$$\sigma(\nu) = 1/|Z^*(\nu)| \cdot t/A \quad \text{Eq. 2.7-1}$$

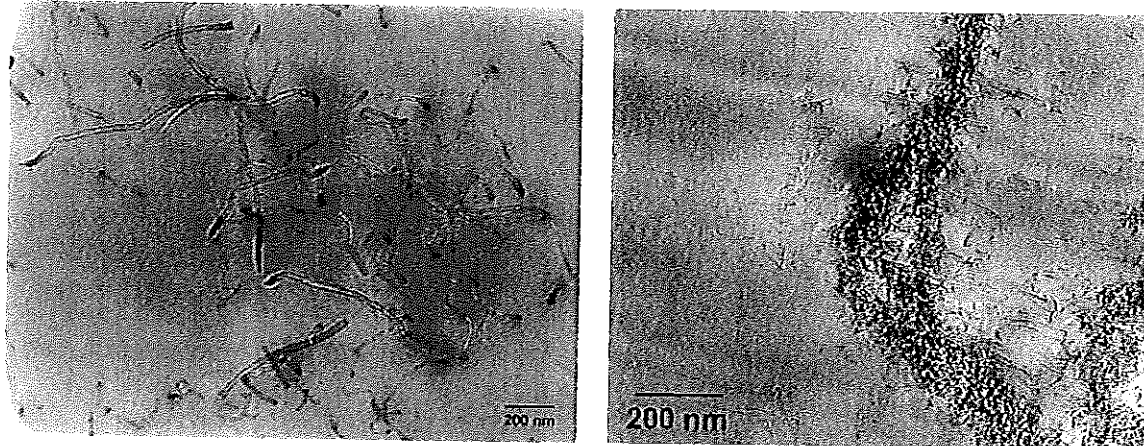
## 2.8 Thermal conductivity

The thermal conductivity was measured using a Hot Disk thermal analyzer (Hot Disk AB, Uppsala/Sweden)<sup>11</sup>. It is a non-destructive "Transient Plane Source"-technique (TPS), where a plane sensor is placed between two similar slaps of material. The sensor lay-up is a nickel double spiral embedded in capton. The samples were treated with a heat-pulse of 0.03 W for 20 s, while the temperature rise is detected. By fitting the data according to Gustavsson et al.<sup>12</sup>, the thermal conductivity of the individual samples was obtained. A minimum of eight individual measurements was performed on bulk specimens (20x20x6 mm).

## 3 MECHANICAL PROPERTIES

In order to efficiently exploit the potential of CNTs to improve the mechanical performance of polymers, one has to be aware of aggravated challenges when comparing with conventional micro-scaled filler particles. The extraordinary large SSA of nanoparticles, being several decades larger compared to conventional reinforcement fibers (e.g. short carbon fibers: SSA  $\ll 1 \text{ m}^2/\text{g}$ ), leads to special challenges, which can be summarized in (i) an appropriate dispersion of the reinforcements in the matrix, (ii) a sufficient interfacial bonding and receiving representative information about nano-structural influences (CNT-structure-property relationship and nano- (micro-) mechanical mechanisms).

The surface area of nanotubes can act as desirable interface for stress transfer, but undesirably induces strong attractive forces between the CNTs themselves, leading to excessive agglomeration behavior. Various methods to disperse nanotubes in polymer resins, such as stirring and sonication, have been reported in the literature<sup>13,14</sup>. Most of these methods are either limited in capacity or not powerful enough to separate the agglomerates into individual nanotubes or lead to a damaging of the CNTs<sup>15-17</sup>. The calendering method introduced previously<sup>18</sup> has turned out to be effective with regard to the achieved dispersion and exhibits the opportunity of up-scaling the capacity to reach technical demands (s. Figure 1). The specific surface area turned out to be the determining factor for the state of dispersion. The smaller the SSA, the better the CNT-distribution in the matrix. A surface functionalisation turned out to be a useful tool, which supports a separation of the agglomerates.



**Figure 1**– TEM-micrographs of the achieved dispersion for (left) MWCNTs and (right) DWCNTs in the epoxy matrix.<sup>22</sup>

The second issue in the development of CNT/polymer composites is the interfacial adhesion between the CNTs and the matrix polymer. A sufficient stress transfer from the matrix to the tubes is required to efficiently exploit the potential of CNTs as structural reinforcement. The introduction of tailored chemical groups (e.g. amino-, carboxyl- or glycidyl-groups for epoxies) enables covalent bonding between CNTs and epoxy, improving the interfacial stress transfer and positively affecting the dispersibility of the nanofiller. The described effect of a functionalisation on the mechanical properties has been predicted by simulations<sup>19</sup> and also experimentally proved by previous work<sup>18,20,21</sup>.

### 3.1 Strength & Stiffness

The results of the mechanical properties of all tested nanocomposites<sup>22</sup> are summarized in Table 1. In general one can say, that the addition of small amounts SWCNTs and DWCNTs increases the UTS moderately, whereas MWCNTs lead to a slight reduction. CB, as reference material, does not significantly influence the UTS of the epoxy matrix at the very low filler contents. The amino-functionalisation of the CNTs improves the dispersibility by increasing the surface polarity and induces an incorporation of the nanotubes into the matrix network, thus resulting in a generally larger improvement of the UTS. A content of 0.5 wt.% DWCNT-NH<sub>2</sub> led to an increase in UTS from 63.7 MPa (epoxy) to 69.2 MPa (+10 %).

The usage of amino-functionalised nanotubes turned out to be more efficient concerning an improvement of both the Young's modulus and the tensile strength. This proves the relevance of surface functionalisation to improve the dispersion of the CNTs and to induce a reaction to the epoxy, which incorporates the nanotubes into the epoxy network. The formation of covalent bonds with the epoxy results in a significantly enhanced interfacial adhesion. We observed a maximum increase of the Young's modulus for a composite containing 0.5 wt.% DWCNT-NH<sub>2</sub> (2978 MPa) by +15% in relation to the neat epoxy resin

(2599 MPa). However, the less efficient improvement at higher filler contents can be referred to an increasing amount of observed agglomerates and demonstrates the necessity of a proper impregnation with the matrix.

Besides the observed functionalisation effect, the overall size of the provided interface could be identified as another major parameter concerning to mechanical reinforcement. The composites containing MWCNT (-NH<sub>2</sub>) showed a less efficient enhancement of the Young's modulus and the UTS. The decreasing efficiency at higher filler contents can again be related to the reagglomeration, which was less intensive as for the amino-functionalised MWCNTs.

The effect of a surface functionalisation becomes visible by directly comparing the stress-strain ( $\sigma/\epsilon$ ) curves of the tested samples. Figure 2 shows representative  $\sigma/\epsilon$ -curves of the epoxy resin and two composites containing each 0.3 wt.% of DWCNTs and DWCNT-NH<sub>2</sub>, respectively. The presence of 0.3 wt.% DWCNTs leads to an increase in UTS and strain to failure, when compared to the neat epoxy resin. However, using the same DWCNTs, but with an amino-functionalised surface, an even larger improvement can be observed.

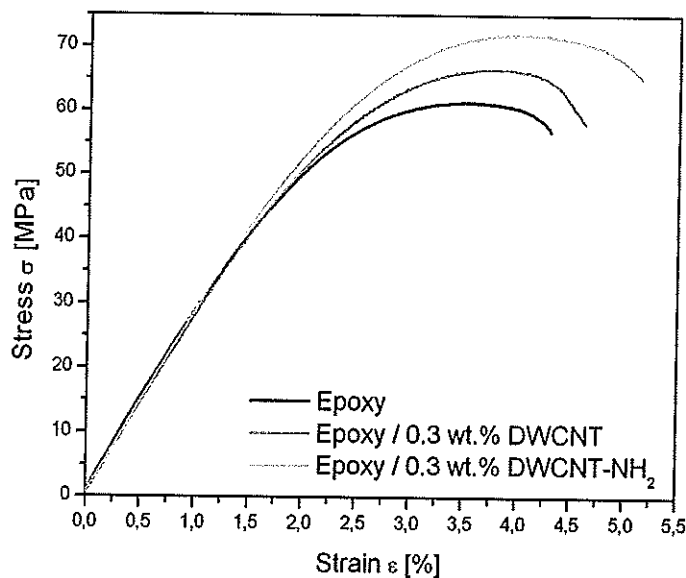


Figure 2 – Stress/Strain-curves of some nanocomposites showing the synergistic reinforcing effect<sup>22</sup>.

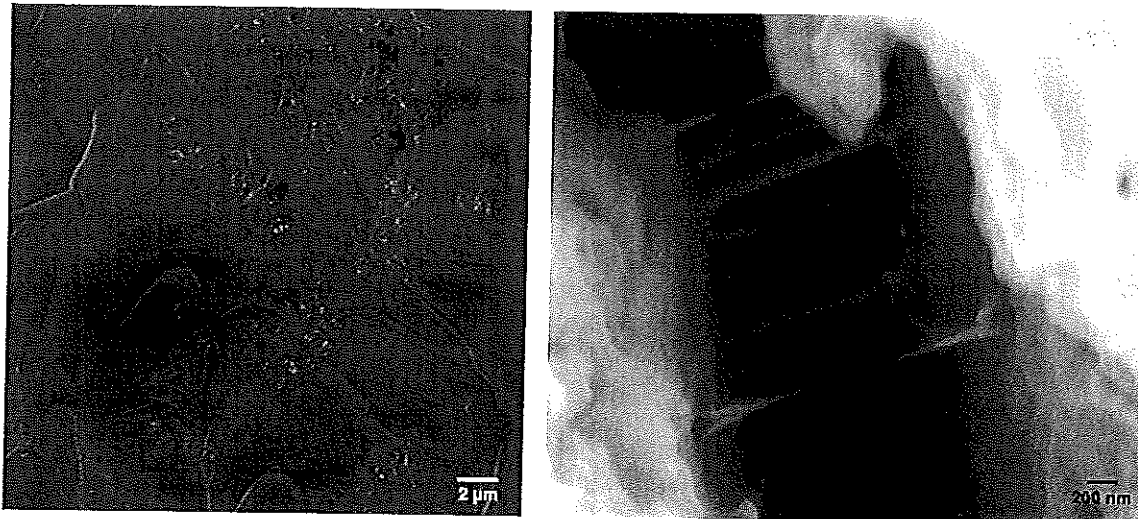
In conclusion, we observed a synergistic reinforcing effect of carbon nanotubes, in other words a simultaneous increase in tensile strength, Young's modulus and ductility, in the epoxy matrix. We assume the provided surface area, in combination with the specific mechanical properties of the nanofiller and the aspect ratio to be the determinant factors for the mechanical reinforcement of epoxy matrices by nanoparticles. However, a complete impregnation of the surface area has to be ensured, in order to enable an efficient load transfer between matrix and reinforcement. A chemical functionalisation of the CNT surface improves the dispersibility and the interfacial adhesion and can therefore be a useful tool in order to realize this impregnation. Presently, DWCNT-NH<sub>2</sub> reinforced epoxy shows the largest improvement of strength and stiffness under the given processing conditions. An even better improvement should be possible using functionalised SWCNTs. Realizing an appropriate dispersion and matrix adhesion by integration into the network structure, functionalised SWCNT provide a maximum surface and therefore exhibit the largest potential to improve the mechanical properties of polymers.

### 3.2 Fracture toughness

Recently, we published an overview on the influence of nanoparticles on the fracture toughness and the related micro-mechanical mechanisms<sup>23</sup>. In summary, the most important deformation and void nucleation, (ii) particle/fibre debonding, (iii) crack deflection, (iv) crack pinning, (v) fibre pull-out, (vi) crack tip blunting (or crack tip deformation), (vii) particle/fibre deformation or their rupture at the crack tip. Additionally, the overall size of the plastic deformation zone has to be considered.

Nanoparticles in general, and CNTs in special, possess a certain potential to improve the fracture toughness of epoxy systems due to their mechanical properties, the fibre-shaped structure (high aspect ratio) and the huge interface provided. The relatively best enhancement of the fracture toughness was obtained for a composite containing 0.5 wt.% DWCNT-NH<sub>2</sub> ( $K_{Ic} = 0.93 \text{ MPa}\cdot\text{m}^{1/2}$ ), which was 44% higher than the neat epoxy ( $K_{Ic} = 0.65 \text{ MPa}\cdot\text{m}^{1/2}$ ). The non-functionalised CNTs exhibited again a smaller effect on the toughness. For all mechanical characteristics, an exploitation of the theoretical surface area of the nanofiller as interface to the epoxy matrix is related to the dispersion and matrix impregnation. The interface is playing a major role concerning toughening of materials as well. According to the mentioned toughening mechanisms, we suggest a combination of individually separated dispersed nanotubes and well-impregnated small (sub-micrometer) agglomerates to be a favorable state of dispersion.

In case of a nano-scaled reinforcement we observe toughening mechanisms occurring at two different dimensional levels. A toughening of the epoxy by crack deflection at agglomerates, crack pinning, crack blunting and the extension of the plastic deformation zone in general, are (under consideration of the dimensions) micro-mechanical mechanisms. Other toughening mechanisms like inelastic matrix deformation and void nucleation, interfacial debonding, pull-out and crack-bridging do exist in macroscopic and microscopic scale, but according to the nano-sized structure of CNTs also in the nano-scale. Figure 3 illustrates two of the possible toughening nanoscaled mechanisms.



**Figure 3** – (left) SEM micrograph of a fracture surface of a CB/epoxy composite. The ellipsoid structure indicates void nucleation by generation of secondary cracks. This micromechanical mechanism is independent from the particle shape. (right) SEM micrograph of a fracture surface of a DWCNT/epoxy composite. The observed bridging mechanism can only occur with nanoparticles exhibiting a high aspect ratio.<sup>22</sup>

**Table 1**– Summary of the mechanical properties of all nanocomposites tested<sup>22</sup>

	Filler type / content [wt.%]	Young's Modulus [MPa]	Ultimate tensile strength [MPa]	Fracture toughness $K_{Ic}$ [MPa·m <sup>1/2</sup> ]
Epoxy	0.0	2599 (± 81)	63.80 (± 1.09)	0.65 (± 0.062)
Epoxy/CB	0.1	2752 (±144)	63.28 (± 0.85)	0.76 (± 0.030)
	0.3	2796 (± 34)	63.13 (± 0.59)	0.86 (± 0.063)
	0.5	2830 (± 60)	65.34 (± 0.82)	0.85 (± 0.034)
Epoxy/SWCNT	0.05	2681 (± 80)	65.84 (± 0.64)	0.72 (± 0.014)
	0.1	2691 (± 31)	66.34 (± 1.11)	0.80 (± 0.041)
	0.3	2812 (± 90)	67.28 (± 0.63)	0.73 (± 0.028)
Epoxy/DWCNT	0.1	2785 (± 23)	62.43 (± 1.08)	0.76 (± 0.043)
	0.3	2885 (± 88)	67.77 (± 0.40)	0.85 (± 0.031)
	0.5	2790 (± 29)	67.66 (± 0.50)	0.85 (± 0.064)
Epoxy/DWCNT-NH <sub>2</sub>	0.1	2610 (± 104)	63.62 (± 0.68)	0.77 (± 0.024)
	0.3	2944 (± 50)	67.02 (± 0.19)	0.92 (± 0.017)
	0.5	2978 (± 24)	69.13 (± 0.61)	0.93 (± 0.030)
Epoxy/MWCNT	0.1	2780 (± 40)	62.97 (± 0.25)	0.79 (± 0.048)
	0.3	2765 (± 53)	63.17 (± 0.13)	0.80 (± 0.028)
	0.5	*) 2609 (± 13)	*) 61.52 (± 0.19)	*)
Epoxy/MWCNT-NH <sub>2</sub>	0.1	2884 (± 32)	64.67 (± 0.13)	0.81 (± 0.029)
	0.3	2819 (± 45)	63.64 (± 0.21)	0.85 (± 0.013)
	0.5	2820 (± 15)	64.27 (± 0.32)	0.84 (± 0.028)

\*) High viscosity disabled degassing - composite contained numerous voids.

#### 4 ELECTRICAL PROPERTIES

The application of conductive nanoparticles to an isolating polymer matrix is expected to induce an electrical conductivity and also enhance the thermal properties at very low filler contents. In contrast to the realization of a mechanical reinforcement by CNTs, where a homogeneous dispersion, a good impregnation and a strong adhesion to the matrix is desired, the electrical conductivity is based on percolated pathways of conductive particles. Therefore, a good dispersion of the filler particles in the matrix and a controlled reagglomeration is a central requirement to achieve a low critical filler content to reach the percolation threshold.

In previous comprehensive studies the formation of percolated CNT-networks in epoxies, including the electrical properties of the composites, were investigated. Parameters influencing the composites conductivities, e.g. aspect ratio of the CNTs, shear-rate, temperature and curing conditions, as well as the application of an external electric field (AC and DC)<sup>13,24-26</sup> were evaluated. It could be shown that especially the cohesive interactions between particles and towards the matrix gain significant importance in the percolation behavior of particles at a nanometric scale, thus similarities to conventional colloid theories seem to be logical. The percolation threshold could be reduced to less than 0.005 wt.% MWCNTs, being the lowest critical filler contents reported so far. The reported critical filler concentrations for CNTs and also for carbon black<sup>27-30</sup> are by far lower than the theoretical prediction of the percolation theory, thus proving the dominance of interactions on a

molecular level influencing the network formation and showing the limitations of the percolation theory.

The aim of this part of the study was to find a correlation between the electrical conductivity and parameters as: aspect ratio, dispersibility and surface functionality of nanofillers, influencing the particle-particle and particle-matrix interactions<sup>31</sup>. The experimental results of the investigated samples are shown in Figure 4. This Figure shows the measured conductivity as function of the weight content.

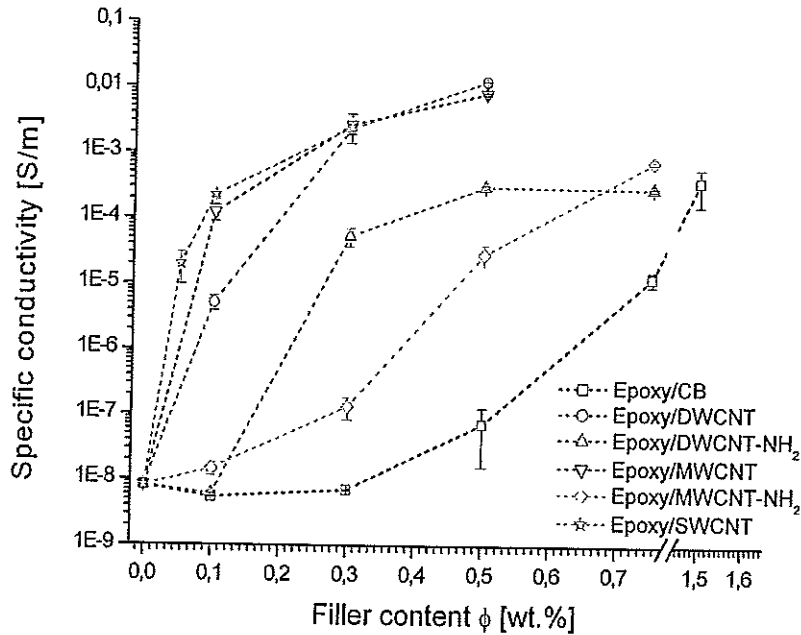


Figure 4 – Electrical conductivity of nanoparticle modified epoxy composites as function of the filler content [wt.%]<sup>31</sup>.

As expected, we generally observe the percolation threshold, being defined as the filler content to achieve a conductivity of  $\sigma \geq 10^{-6}$  S/m, to be lower for fibre-shaped fillers (high aspect ratio) than for spherical particles. The lowest percolation thresholds were observed for the non-functionalised CNTs, being in all cases below 0.1 wt.% CNTs, while 0.75 wt.% CB were required to achieve a similar conductivity. The overall conductivity of these composites turned out to be insignificantly influenced by the structural quality (graphitization) of the CNTs determined by Raman spectroscopy<sup>31</sup>.

The amino-functionalised CNTs show higher percolation thresholds, ranging between 0.1 and 0.3 wt.% for DWCNT-NH<sub>2</sub> and between 0.3 and 0.5 wt.% for MWCNT-NH<sub>2</sub>. The maximum conductivity of these composites is lower when compared to samples containing non-functionalised CNTs. An explanation for the observed behavior can be given by considering the functionalisation process. The functionalization via a ball-milling process in ammonia ruptures the CNTs, thus reducing their aspect ratio. According to this, the percolation threshold is shifted to higher filler contents. The reduction of the maximum level of conductivity is related to structural changes due to the functionalisation and the significantly improved affinity between epoxy and nanotube. The introduction of functional groups into a conjugated  $\pi$ -electron system is combined with the formation of  $sp^3$ -carbons. The  $sp^3$ -carbons interrupt the conjugation and induce a distortion of the graphitic layer. In terms of the electron conduction, these  $sp^3$ -carbons can be regarded as defects, reducing the maximum conductivity of the individual nanotube.

The reaction between the surface-groups located onto nanotubes and the epoxy matrix leads to the formation of an insulating epoxy layer. This layer prevents or suppresses direct contact between the CNTs, thus enhancing the contact resistance between the CNTs complicating

the electron conduction. The enhanced mechanical performance of composites containing amino-functionalised CNTs indicates an improved matrix adhesion to the epoxy. TEM-micrographs qualitatively proved the occurrence of such epoxy layers onto amino-functionalised CNTs<sup>20</sup>.

According to this, MWCNTs seem to have the highest potential of the investigated nanofillers to induce an electrical conductivity to an epoxy matrix. The relatively low SSA enables a good dispersibility and the incompatibility of the surface potential leads to the required reagglomeration. A functionalisation of the CNTs can be regarded as detrimental for the overall conductivity, due to the stabilization of the dispersion and the formation of an isolating epoxy layer around the nanotubes.

## 5 THERMAL PROPERTIES

The thermal conductivity of polymer composites is an important material property for many applications, but still widely unexplored. Due to the fact that most polymers exhibit a rather low thermal conductivity, it is of certain interest to obtain an improvement for some applications. Isolated carbon nanotubes can exhibit a high thermal conductivity if consisting of a perfect graphitic structure/lattice. The mentioned theoretical thermal conductivities of ~6600 W/mK for SWCNTs at room temperature<sup>32</sup> and the experimentally measured of 200 - 3000 W/mK at room temperature for MWCNTs<sup>33,34</sup>, led to the expectations of a certain enhancement of the thermal conductivity of polymer-based nanocomposites, by an incorporation of CNTs<sup>35</sup>.

The experimentally determined thermal conductivity of CNT/epoxy composites has been displayed as function of weight-content (Figure 5) and in relation to the provided interfacial area (Figure 6).

Generally we observed a slight enhancement of the thermal conductivity with increasing filler content (Figure 5). Our experimental data correspond to results obtained by Song et al.<sup>36</sup> on comparable CNT/epoxy composites. The non-functionalised nanotubes, except from the SWCNTs, led to the relatively strongest improvement of the thermal conductivity. In contrast, amino-functionalised CNTs do not significantly affect the thermal conductivity of the epoxy at these low filler contents.

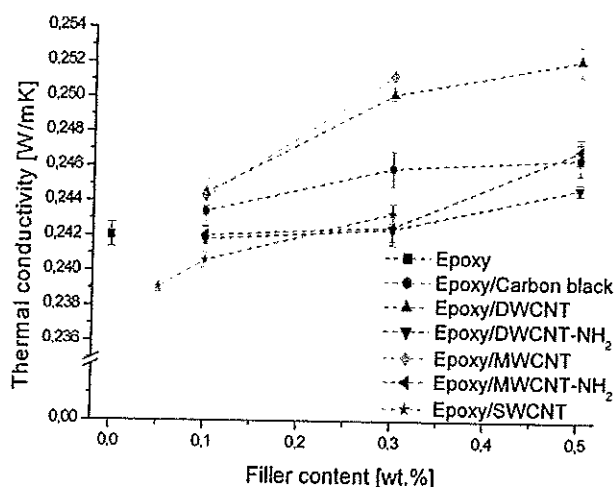
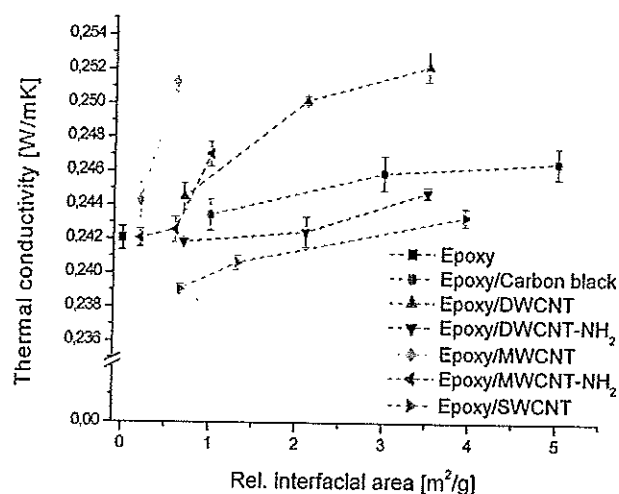


Figure 5 – Thermal conductivity as function of filler content in [wt.%]<sup>31</sup>.



**Figure 6** – Thermal conductivity as function of the relative provided interfacial area per gram composite [m<sup>2</sup>/g]<sup>31</sup>.

Carbon black filled epoxy exhibit thermal conductivities lying between the non-functionalised MWCNTs and DWCNTs and the amino-functionalised CNTs. The unusual behavior of nanocomposites containing low contents of SWCNTs, showing a lower thermal conductivity than the neat epoxy, is extensively discussed separately<sup>31</sup>. We found a correlation between the thermal conductivity and the provided interfacial area. Figure 6 shows the relative interfacial area per gram composite. The relatively largest improvement has been observed for non-functionalised CNTs, especially for the MWCNTs exhibiting the smallest SSA.

Assuming a phonon conduction mechanism inside the CNTs, the observed behavior can be explained by interactive forces between the nanofiller and the epoxy matrix, as well as the interfacial area and the type of CNT. According to the crystalline lattice structure of the CNT, they exhibit significantly higher thermal conductivity than the amorphous epoxy matrix. The phonon transport can be assumed to occur preferably through CNTs, due to higher free length of path in crystalline structures, which reduces the probability of scattering effects, e.g. Umklapp-scattering and lattice defect-scattering. A strong interaction between nanotube and epoxy matrix would lead to an intensive damping of the phonon at the CNT/epoxy interface. Consequently, a large interfacial adhesion and a huge interface between CNT and matrix would induce a strong damping of the flow of phonons, combined with an extensive interfacial boundary scattering. The experimental results substantiate this theory. The amino-functionalised CNTs, being integrated into the epoxy network, thus exhibiting the strongest interfacial adhesion, show relatively lower thermal conductivities when compared to the corresponding non-functionalised equivalents.

An unusual behavior has been observed for SWCNT/epoxy composites. The addition of highly thermal conductive particles to an epoxy resulted in composites, which exhibited a lower overall thermal conductivity than the neat matrix. At nanotube contents higher than 0.05 wt.% of SWCNTs, the expected enhancement was again observed. In a previous work, similar observations by Moisala et al.<sup>37</sup> on nanocomposites consisting of the same SWCNTs but with a different epoxy resin, which resulted in a decrease of the thermal conductivity at low filler contents as well. A detailed discussion on this special topic can be found elsewhere<sup>31</sup>.

A phonon transport by CNTs, providing a huge interfacial area, is hindered by the contact to the matrix and consequently the permanent coupling, which induces a high probability of boundary scattering. In contrast to SWCNTs, MWCNTs and DWCNTs exhibit a much smaller SSA and additionally the internal layers shield the conducted phonons, thus these nanotubes showed a relatively higher enhancement of thermal conductivity. A second effect reducing

the thermal conductivity is the transfer of phonons from nanotube to the nanotube. This transition occurs by direct coupling between CNTs, in case of improper impregnated ropes, CNT-junctions and agglomerates, or via the matrix by tunneling processes. In any case a transition occurs via an interface, thus the coupling losses can be related to an intense phonon boundary scattering.

In conclusion, we suggest thick MWCNTs with a high aspect ratio to be the most favorable type of nanotubes for an enhancement of polymer composites thermal conductivity. They provide the highest capacity due to the relatively small surface area, thus leading to the lowest interfacial boundary surface scattering and matrix coupling. Additionally, internal layers enable phonon conduction with a minimum of coupling losses. A functionalisation of the CNTs and especially a low aspect ratio reduces the relative enhancement of the thermal conductivity dramatically. However, in comparison to the electrical conductivity of epoxy-based composites, the authors regard a significant enhancement of the thermal conductivity by carbon nanotubes of  $\sim 5$  W/mK, which would be required for various applications, to be unlikely at filler contents, which do not negatively affect the mechanical performance.

## 6 SUMMARY & CONCLUSIONS

Nanocomposites consisting of a DGEBA-based epoxy matrix system and different types of carbon nanotubes were produced by calendering. The composites were investigated regarding the dispersibility of the CNTs in the matrix and the efficiency concerning an enhancement of the mechanical properties, as well as the electrical and thermal conductivity. The obtained data were discussed in terms of influencing parameters as (i) specific surface area (SSA), (ii) chemical functionalisation of the surface and (iii) particle shape and correlated to identified micro-mechanical mechanisms.

The potential of CNTs to improve strength and stiffness can be correlated to the specific mechanical properties, the aspect ratio and the SSA. Thus, the exploitation of the provided interface is playing a major role concerning the improvement of mechanical properties. The dispersion of the CNTs and the interfacial adhesion to the epoxy matrix are key issues in the development of nanocomposites. A chemical functionalisation of the CNT surface is certainly an important approach to improve both interfacial bonding and dispersibility. Small amounts of carbon nanotubes in epoxies lead to increased mechanical properties. The most significant improvements of strength (+10%), stiffness (+15%) and especially fracture toughness (+43%) were attained with amino-functionalised DWCNTs at 0.5 wt.% filler content under the given processing conditions.

Micromechanical mechanisms affecting the fracture toughness (e.g. plastic deformation of the epoxy matrix and nucleation of voids, crack deflection at agglomerates, etc.) were identified. These micromechanical toughening mechanisms observed were regardless the particle-shape. In addition to this, nanomechanical mechanisms, related to the fibre-shape of CNTs contribute to an enhancement of the fracture toughness. All nanotube/epoxy composites, particularly the amino-functionalised DWCNTs, being integrated in the epoxy network, show a significant contribution of the bridging mechanism to the fracture toughness.

Composites containing different types of CNTs were investigated concerning their electrical and thermal conductivity. The results were discussed in regard to the influence of particle content, provided interfacial area, the influence of a surface functionalisation and the aspect ratio. In contrast to the improvement of the mechanical properties of the epoxy resin by CNTs, where a huge surface area of the CNTs and good interfacial adhesion is necessary, a contradictive requirement has been found for the enhancement of these physical properties.

The occurrence of an electrical conductivity can be attributed to the formation of conductive pathways when the filler content exceeds a critical volume fraction. The aspect ratio of the filler, its dispersibility and the ability to conglomerate are crucial parameters for the realization of conductive composites at low filler contents. Consequently, MWCNTs exhibit the highest

potential for an efficient enhancement of the electrical conductivity, due to the relatively low surface area and high aspect ratio. Any kind of treatment, leading to a reduction of the aspect ratio (functionalisation, ultrasonication, etc.) result in a shifting of the percolation threshold.

The incorporation of CNTs into polymers resulted in a slight enhancement of the thermal conductivity. The overall size of the interface ( $\Rightarrow$  SSA), the aspect ratio and the interfacial adhesion were identified as parameters dominating the relative enhancement of the thermal conductivity. The nanometric size and the huge interface lead to strong phonons scattering at the interface. Thus, a relatively low interfacial area, weak interfacial adhesion and the existence of shielded internal layers promote the conduction of phonons and minimize coupling losses. According to this, MWCNTs seem to have the highest potential to improve the thermal conductivity of epoxies. However, regarding the achievements obtained within this study, CNTs seem to have a minor potential in this context. The theoretically predicted thermal conductivities of isolated tubes cannot be transferred to polymer-based composites in practice. The huge interface provided by CNTs lead to strong phonon boundary scattering. Additionally scattering at lattice defects minimizes the effective thermal conductivity. It has to be pointed out that CNTs and probably further nanoparticles, which provide a huge interfacial area, are not suitable for an enhancement of the thermal conductivity of polymer-based composites.

Under consideration of the obtained results, CNTs are a valuable chemical additive for the modification of epoxies and other polymers. Especially the combination with conventional fibre-reinforcements can be a promising approach for future perspectives in composite applications<sup>98</sup>

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