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Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites

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Abstract

Carbon nanotubes (CNTs) exhibit a high-potential for the reinforcement of polymers. The mechanical properties of potential matrices of fibre-reinforced polymers (FRP), such as epoxy resins, were significantly increased by low contents of carbon nanotubes (CNT) (tensile strength, Young's modulus and fracture toughness). Nano-particle-reinforced FRPs, containing carbon black (CB) and CNTs could successfully be manufactured via resin transfer moulding (RTM). A filtering effect of the nano-particles by the glass-fibre bundles was not observed. The glass-fibre-reinforced polymers (GFRP) with nanotube/epoxy matrix exhibit significantly improved matrix-dominated properties (e.g. interlaminar shear strength), while the tensile properties were not affected by the nano-fillers, due to the dominating effect of the fibre-reinforcement. The GFRP containing 0.3 wt% amino-functionalised double-wall carbon nanotubes (DWCNT-NH₂) exhibit an anisotropic electrical conductivity, whereas the conductivity in plane is one order of magnitude higher than out of plane.

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1. Introduction

Nano-particles are presently considered to be high-potential filler materials for the improvement of mechanical and physical polymer properties. The nanometric size, leading to huge specific surface areas (SSA) of up to more than 1000 m²/g, and their unique properties (of at least some of these nano-particles) have caused intensive research activities in the fields of natural and engineering sciences. Candidates in the collectivity of nano-particles with a high-potential for the enhancement of mechanical and physical properties of polymers are carbon nanotubes [1–3].

Their mechanical properties [4–7], a high aspect ratio and a high Young's modulus and tensile strength, in combination with an electrical and thermal conductivity

make them interesting materials for the use as nano-fillers in polymers and open up new perspectives for multi-functional materials, e.g. conductive polymers with improved mechanical performance.

Since the beginning of the research on CNT/polymer composites, scientists were able to utilise the potential of CNTs as conductive filler already at an early state. Until now, the percolation threshold had been further decreased to very low filler contents [8,9]. A controlled re-agglomeration of the CNTs, using either shearing or applying an electrical field, was the key to achieve percolation thresholds as low as 0.0025 wt% of multi-wall carbon nanotubes (MWCNTs) [10].

The mechanical reinforcement by the application of nano-particles as a structural element in polymers is more difficult to realise and still remains a challenging task. An efficient exploitation of the CNT properties in order to improve the materials performance is generally related to the degree of dispersion, impregnation with matrix and to the interfacial adhesion. The advantage of nano-scaled compared to micro-scaled fillers is their enormous surface area, which can act as interface for stress-transfer. However,

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a high SSA (for single-wall carbon nanotubes (SWCNTs) of $\sim 1300 \text{ m}^2/\text{g}$ [11]) and their cotton-like entanglement causes the formation of agglomerates. Agglomerates of SWCNTs, called nanoropes, are difficult to separate and to infiltrate with matrix. CNTs with a smaller SSA, e.g. MWCNTs, show a better dispersibility, although their efficiency towards mechanical reinforcement is lower than of SWCNTs. Double-wall carbon nanotubes (DWCNTs) with a SSA of $\sim 800 \text{ m}^2/\text{g}$, as used in this study, can be a good compromise. DWCNTs show a reduced tendency to agglomerate and a good dispersibility on account of their fairly high-SSA.

Another main issue in the realisation of mechanically reinforced CNT/polymer composites is the tuning of interfacial adhesion between the CNTs and the polymer. An experimental determination of the interfacial strength is still a difficult procedure, however, some progress has been made in this field, but most of the potential arises from theoretical predictions [12,13]. The stress-transfer from the matrix to the reinforcements has to be performed via the interface, which can be influenced by a chemical functionalisation of the CNT surface. A tailored functionalisation can lead to the formation of covalent bonds and/or additional dipole–dipole-interactions between CNTs and the polymeric matrix, resulting in a strengthened interface [14–16] and an improved wettability of the CNTs.

We recently reported about a new and efficient technique to disperse carbon-based nano-particles in epoxy resins [17]. The application of a mini-calander to disperse carbon nanotubes (and carbon black) became a very promising approach to reach a good state of dispersion and enabled to manufacture high volumes of nanocomposites. This method is an established and common technique to disperse micro-particles in different matrices, e.g. colour pigments for cosmetics or lacquers. A major advantage of this method is, besides the improved dispersion results, the efficient manufacturing of larger amounts of nanocomposites. The produced nanotube/epoxy composites exhibit a significant increase in fracture toughness, as well as an enhancement of stiffness already at low nanotube contents.

A replacement of FRPs by nanocomposites can be regarded as unrealistic, due to the highly developed and well-established conventional fibre-reinforcement of polymers and their still unmatched level of material properties. Nevertheless, the combination of a nanotube-modified matrix together with conventional fibre-reinforcements (e.g. carbon-, glass- or aramid-fibres), could lead to a new generation of multi-functional materials [3]. Besides electrical conductivity, which can be induced by the carbon nano-particles, an additional z -reinforcement can be expected. The fibre-orientation in structural components is usually in plane (x - and y -direction), leading to fibre-dominated material properties in these directions, whereas the z -direction remains matrix dominated. With regard on

the nanometric size, carbon nano-particles allow an infiltration between the micro-scaled fibres. The application of CNTs as reinforcing phase should increase the matrix properties, especially in z -direction, equivalent to improved interlaminar properties. Recently, Hsiao et al. [18] and Meguid and Sun [19] investigated the tensile and shear strength of nanotube-reinforced composite interfaces by single shear-lap testing. They observed a significant increase in the interfacial shear strength for epoxies with contents between 1 and 5 wt% of multi-wall nanotubes when compared to the neat epoxy matrix.

The present work describes the application of nano-particle reinforced epoxies as matrix for conventional glass-fibre-reinforcements (GFRP). The very first time an example of a GFRP in the dimension of a structural element is presented, consisting of a glass-fibre non-crimp fabric with a nano-particle modified matrix containing low weight fractions of DWCNT-NH₂ and carbon black (CB), respectively. The manufacturing via RTM and the investigation of the resulting tensile, interlaminar and electrical properties are described.

2. Experimental

2.1. Materials

The epoxy matrix used in this study consists of a modified DGEBA-based epoxy resin (L135i) with an amine hardener (H137i), supplied by Bakelite MGS Kunstharz-produkte GmbH, Stuttgart/Germany. This system, characterised by its extreme low viscosity ($\eta_{RT}=250 \text{ mPa s}$), and is a standard resin for infusion processes (e.g. RTM). The DWCNT-NH₂ were obtained from Nanocyl, Namur/Belgium and appear in an entangled and condensed form (Fig. 1a). These nanotubes consist of two graphitic shells and have an average outer diameter of 2.8 nm and a length of several micrometers.

In order to evaluate the potential of carbon nanotubes as nano-scaled reinforcement, the results were compared to nanocomposites containing similar contents of highly conductive carbon black (CB, Printex XE2 from Degussa/Germany). The CB consists of spherical primary particles with a diameter of 30 nm, which form aggregate/agglomerate structures (Fig. 1b). The nano-particle modified epoxies were used as matrix material for the glass-fibre-reinforced composite (GFRP).

2.2. Dispersion and processing parameters

In order to disperse CB and DWCNT-NH₂ in the epoxy resin, we manually added the nano-particles into the neat resin and added the resulting suspension batch-wise to a mini-calander for final high shear mixing. The gap size between the Alumina rolls (Al₂O₃) was 5 μm and speed was set to 20 (first roll), 60 (second roll) and 180 rpm (third roll),

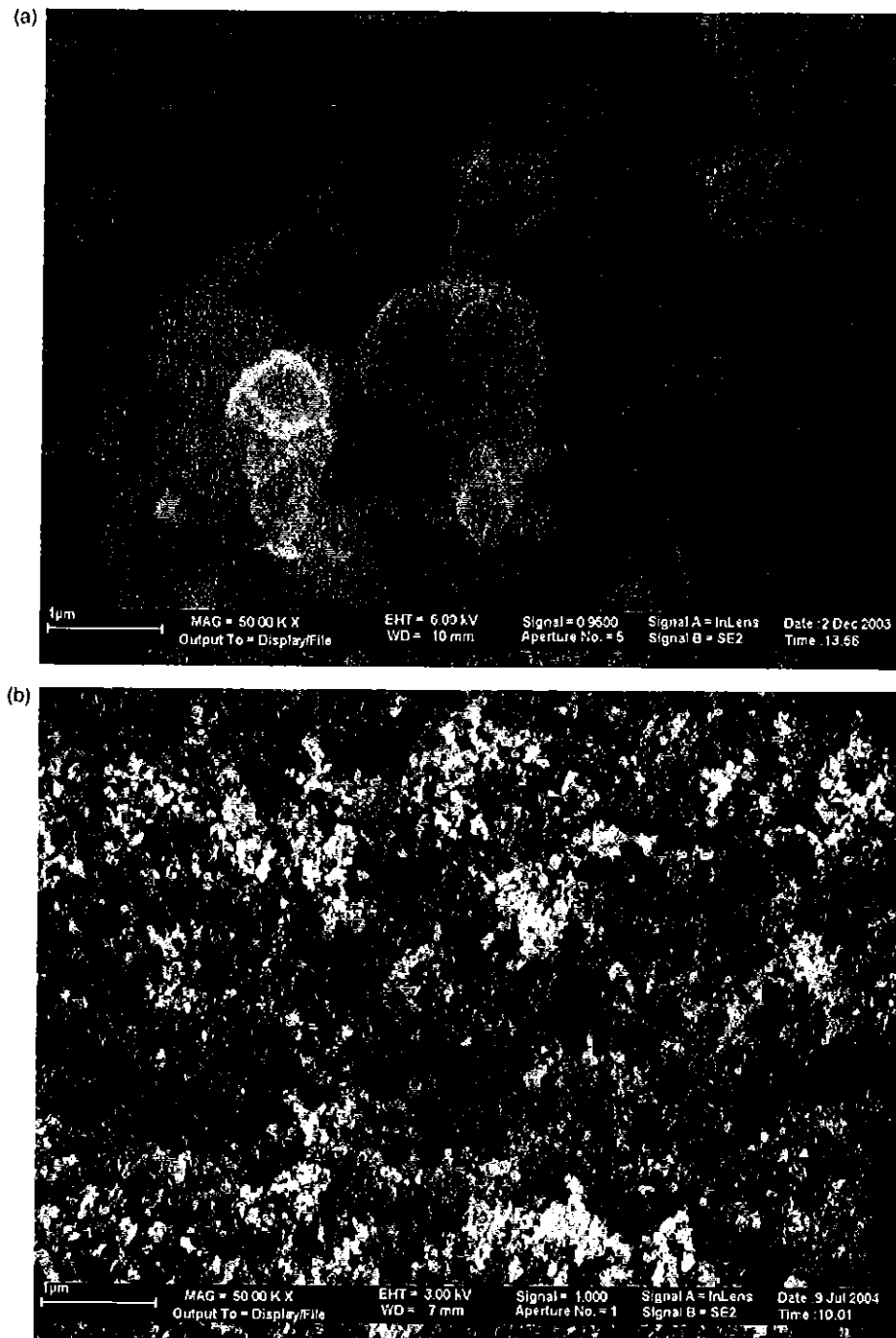



Fig. 1. SEM-images of DWCNT-NH₂ (1a) and carbon black (1b) used as nano-scaled filler in this study.

respectively. The dwell time of each batch of suspension rolls was approximately 2 min. A first primary dispersion of the agglomerates is performed in the knead-vortexes, whereas the final distribution of the nano-particles occurs in the thin gap between the rolls. The suspension was collected, mixed with the hardener for 10 min by intense stirring, cured for 24 h at room temperature (RT) and finally post-cured at 60 °C for 24 h.

2.3. Resin transfer moulding (RTM)

GFRPs were produced by RTM-technique, 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 Table 1. The resin was mixed with the amine hardener and degassed for 20 min in a previous step before injection. After infusion the final

Table 1
Schematic composition of the glass-fibre non-crimp fabric used in this study (Seartextex Wagner)

	Layer	Vol.-content (%)
	0°	48.7
	+45°	23.0
	90°	4.8
	-45°	23.0
	PET-binding yarn	0.5
	Glass-fibre content of the GFRP	~40

sample remained in the mould for curing. The curing conditions of the GFRPs were identical to those of the neat resin, as described previously, except the post-curing, which was elevated to 80 °C.

2.4. Mechanical characterisation

The tensile tests on the nanocomposite and the GFRPs were conducted according to DIN EN 527.1/2. The characterisation of the tensile properties of the plain polymer was performed with dog-bone specimens, 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. For the mechanical of the nanocomposites a minimum of eight specimens was tested for each sample. The quasi-static tensile tests of the GFRPs were carried out in 0°- and 90°-direction using a Schenk 63 kN-hydro pulser.

The interlaminar shear-strength was measured via three-point bending test using the short-beam method according to ASTM D 2344-84. The presented results are average values of 12 individually tested specimens for each sample.

The error bars in all graphs and tables correspond to the standard error.

2.5. Electrical characterisation

The investigation of the electrical conductivity of the GFRPs was performed by dielectric spectroscopy using a HP 4284a Impedance Analyser. All samples (five individual specimens) were investigated in 0, 90, $\pm 45^\circ$ and in z-direction in a frequency range between 10 Hz and 1 MHz, in order to detect a potential anisotropic behaviour of the composites. The samples were coated with a thin silver film to ensure a low contact resistance to the tips. The values obtained for 1000 Hz were plotted versus the filler content and the fibre-orientation, respectively, for the purpose of characterising the electrical conductivity.

2.6. Electron microscopy

The SEM-images were taken with a Leo FE-SEM 1530 at different acceleration voltages (1–1.5 kV). The samples were investigated without an additional coating to avoid a covering of the nano-scaled reinforcements. The dispersion was investigated by TEM, using a Philips EM 400 at 120 kV, on thin films (~ 50 nm) of nanocomposites. The films were obtained by ultra microtome cutting.

3. Results and discussion

3.1. Manufacturing of the nanocomposite, dispersion and matrix properties

The efficient exploitation of the potential reinforcing effect of carbon nanotubes can be referred to a large interfacial area between the CNT and the matrix, a strong interfacial adhesion and to a good impregnation of the CNTs with the matrix. The calendaring has turned out to be an effective method to disperse carbon-based nano-particles (carbon nanotubes and carbon black) [17].

This technique enables to manufacture several hundreds of gram of nanocomposite with constant level of dispersion. In order to accomplish the RTM-process, we had to produce at least ~ 600 g of CNT (CB)/epoxy. To analyse the state of dispersion we investigated samples by electron microscopy. Fig. 2 shows a TEM-image of a nanocomposite containing 0.1 wt% amino-functionalised DWCNTs. The nanotubes could be well separated and impregnated by the epoxy resin. The epoxy resin seems to have a strong ability to wet the functionalised CNTs, which is confirmed by the wetting angle.

The CNT/epoxy-nanocomposites showed an enhanced Young's modulus and fracture toughness in comparison to the neat epoxy [20]. The obtained mechanical properties of the applied matrices are summarised in Table 2. Already small amounts of carbon nanotubes led to an increase in

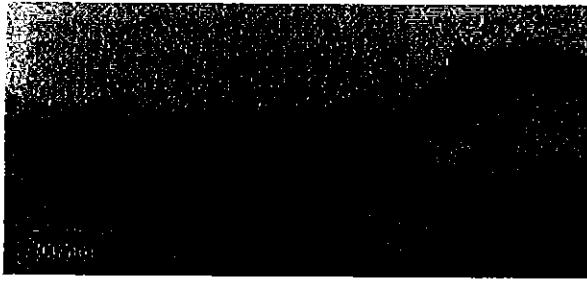


Fig. 2. TEM-image of a DWCNT-NH₂/epoxy-nanocomposite.

ultimate tensile strength (UTS), fracture toughness and Young's modulus, whereas similar contents of carbon black hardly affect strength and stiffness.

3.2. RTM-manufacturing

The nanotube-modified epoxy resin was used to manufacture GFRPs by RTM-technique. Despite the slight increase in viscosity, the production of GFRPs with a nanotube-modified epoxy resin containing 0.3 wt% DWCNT-NH₂ was possible. Nevertheless much higher filler contents of DWCNTs ($\phi_{\text{DWCNT}} > 0.5$ wt%) lead to processing problems due to a dramatically increasing viscosity, which have not been solved until now. It should be stressed out that the increase in viscosity is certainly related to the degree of dispersion and the SSA of the applied carbon nanotubes. Consequently, higher filler contents of MWCNTs, which have generally a smaller SSA than SWCNTs or DWCNTs, can be reached in an epoxy matrix with regard to the processibility.

The presented laminates, having a size of 21 × 36 cm², are the first examples of nanotube-reinforced FRP in the range of a structural component. Fig. 3 shows an optical micrograph of a manufactured FRP containing 0.1 wt% DWCNT-NH₂. Generally we could not see any filtering effect by the glass fibres. The nanotube concentration might be constant over the entire plate. The composite looks inhomogeneous due to an accumulation of matrix between the glass rovings and can partly be explained in terms of the formation of aggregate structures, on account of the re-agglomeration of the CNTs. The horizontal lines are

Table 2
Mechanical properties of (nano-)composites used as matrix for glass-fibre-reinforcement [20]

Filler type/content (wt%)	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Fracture toughness K_{IC} (MPa m ^{1/2})
Epoxy	2.59 ± 0.08	63.8 ± 1.03	0.65 ± 0.062
Epoxy/0.1% CB	2.75 ± 0.14	63.3 ± 0.85	0.77 ± 0.030
Epoxy/0.3% CB	2.79 ± 0.03	63.1 ± 0.59	0.86 ± 0.063
Epoxy/0.1% DWCNT-NH ₂	2.76 ± 0.09	63.6 ± 0.96	0.77 ± 0.058
Epoxy/0.3% DWCNT-NH ₂	2.94 ± 0.05	67.0 ± 0.48	0.92 ± 0.042

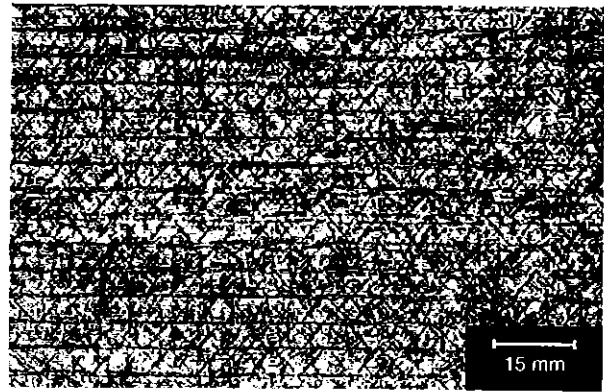


Fig. 3. Optical micrograph of a GFRP with CNT-modified epoxy matrix (0.1 wt% DWCNT-NH₂). Only the matrix-rich areas and the binding yarn become visible due to similarities of the refraction index of the glass fibres and the epoxy resin.

related to matrix-rich areas between the glass rovings in 0°-direction. An influence of the variation of matrix (fibre-) content on the electrical properties, or a potential orientation of the carbon nanotubes around the glass fibres, was described by measuring the electrical conductivity, as discussed in Section 3.4.

The matrix contains aggregates with a loose structure, which emerged through a re-agglomeration during degassing of the resin before injection (Fig. 4). This degassing leads to a foaming of the nanotube/epoxy-suspension and facilitated the re-agglomeration of the nano-fillers, as a result of the increasing surface area.

In order to suppress the re-agglomeration, it is necessary to stabilise 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, hinders the separation and dispersion and facilitates a re-agglomeration, though good stress-transfer via the enormous interface can be achieved. 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.

3.3. Mechanical properties of the GFRPs

The tensile properties of the composites were investigated by tensile testing in 0°- and 90°-direction, due to the differences in fibre-volume-content (0° ⇒ 48.7%; respectively, 90° ⇒ 4.8%). The determined tensile strengths and the Young's moduli for the FRP with epoxy and nanotube-modified epoxy matrix are shown in Fig. 5a and b, respectively. The CNT-reinforced FRP contained 0.1 wt% DWCNT-NH₂. We could not observe an influence of the carbon nanotubes on the strength. The tensile strength were

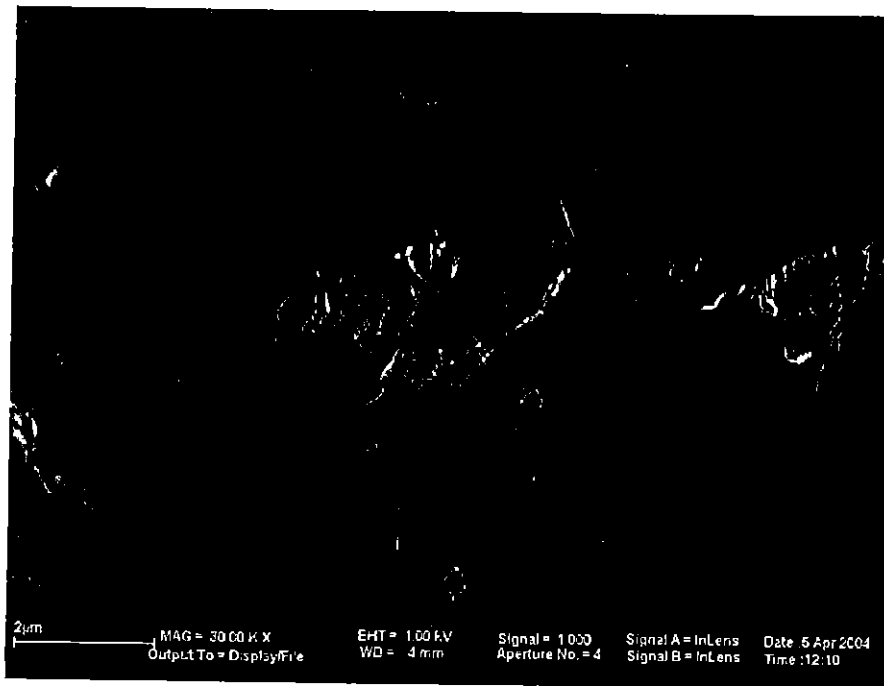


Fig. 4. SEM-micrograph taken from a fracture surface of a tested GFRP-specimen. Some small aggregates could be observed in the matrix-rich areas. The observed loose structure is caused by the re-agglomeration of the CNTs.

determined as $\sigma = 573 \pm 34$ MPa for the reference sample (GF-EP) and $\sigma = 536 \pm 28$ MPa for the nanotube-reinforced sample (GF-EP/CNT) in 0° -direction and $\sigma = 170 \pm 5$ MPa (EP-GF) and $\sigma = 170 \pm 13$ MPa (GF-EP/CNT) in 90° -direction, respectively. The variation in both cases is within the range of the standard errors. The Young's modulus seems also to be hardly influenced by the nanotube-reinforcement. Neither the obtained Young's moduli in 0° - [$E = 25.5 \pm 1.3$ GPa (GF-EP) and $E = 26.4 \pm 1.3$ GPa (GF-EP/CNT)], nor in 90° -direction [$E = 12.3 \pm 1.4$ GPa (GF-EP) and $E = 13.2 \pm 0.6$ GPa (GF-EP/CNT)] were significantly increased by carbon nanotubes. The FRPs show fibre-dominated behaviour of the tensile properties in the plane of the fibre-reinforcements.

The transverse and z-reinforcement of fibre-reinforced polymer composites is expected to be a potential area for the exploitation of carbon nanotubes as structural reinforcement. In order to analyse this potential, we performed ILSS-tests on GFRPs with (1) a neat epoxy matrix (EP) and a nano-modified epoxy containing (2) carbon black (EP/CB with 0.1 and 0.3 wt%) and (3) amino-functionalised double-wall carbon nanotubes (EP/DWCNT-NH₂ with 0.1 and 0.3 wt%). 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-NH₂/epoxy-nanocomposites in comparison to the GFRP with a neat epoxy matrix (Fig. 6).

The ILSS of the FRPs could be enhanced by the nano-modification with carbon nanotubes. In relation to the GFRP with the neat epoxy matrix (ILSS = 31.8 ± 1.7 MPa),

the nanotube-reinforced GFRP exhibit an improved ILSS of 36.8 ± 1.9 MPa at 0.1 wt% and 38.1 ± 1.4 MPa for 0.3 wt% CNT-content, corresponding to an improvement by 20%.

We observed a lower influence of the carbon black on the ILSS of the GFRP. The ILSS experimentally obtained for the sample containing 0.1 wt% CB was 32.7 ± 2.1 and 34.8 ± 1.8 MPa for 0.3 wt% CB, equivalent to an improvement by 9%.

Mainly two factors can explain the observed enhancement of the ILSS. On the one hand, the increased strength of the epoxy matrix caused by the nano-reinforcements, as shown in Table 2, can be regarded as the most important reason for the increased ILSS. However, a strengthened interface between the glass fibres and the nano-particles could be seen as another possible mechanism, which contributes positively to the ILSS. During the injection process, either carbon black or carbon nanotubes tend to aggregate around the fibre-reinforcements, as attested by conductivity measurements discussed in Section 3.4. Apart from the curing reaction of the epoxy matrix, additional cross-linking reactions occur between the amino-groups of the functionalised CNTs and the epoxy matrix on one hand and to the sizing of the glass fibres, which also contain epoxy-groups, on the other hand. These cross-links via the interface caused an increased interfacial strength, which could be interpreted as an evidence for the enhanced ILSS. The absence of functional groups, as in the case of carbon black leads to a weaker interface, which expresses itself in the less effective influence on the ILSS.

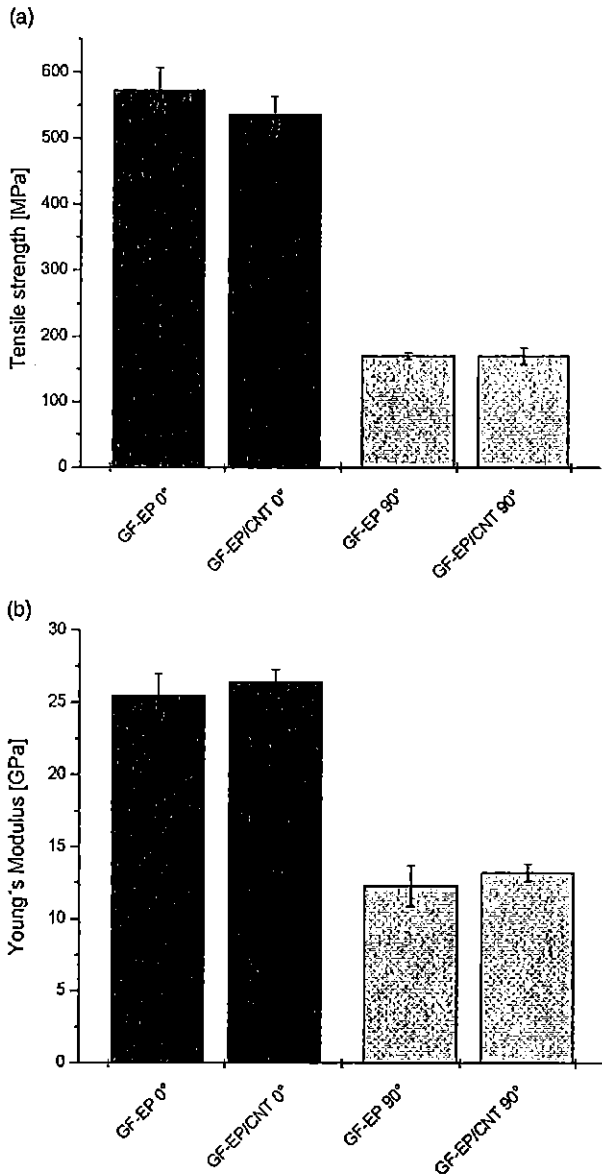


Fig. 5. Experimentally obtained tensile properties of the GFRPs (a) tensile strengths and (b) Young's modulus in 0°- and 90°-direction.

The less significant improvement of the composites containing 0.3 wt% nano-filler, compared to the lower filler content, can be also explained in terms of the increasing amount of agglomerates. These agglomerates indeed act as imperfections in a composite, which can induce an untimely failure, when the interfacial adhesion to the surrounding matrix is poor (Fig. 7a). The cross-linking cannot occur in the same way between the CB and the epoxy due to the absence of amino-groups in this filler. Nevertheless, the composites containing 0.3 wt% CB do also show an increased amount of agglomerates, as shown in Fig. 7b.

Although, the formation of covalent bonds between the nanotubes and the epoxy matrix can be regarded as a valuable tool to tailor the interfacial strength, enabling

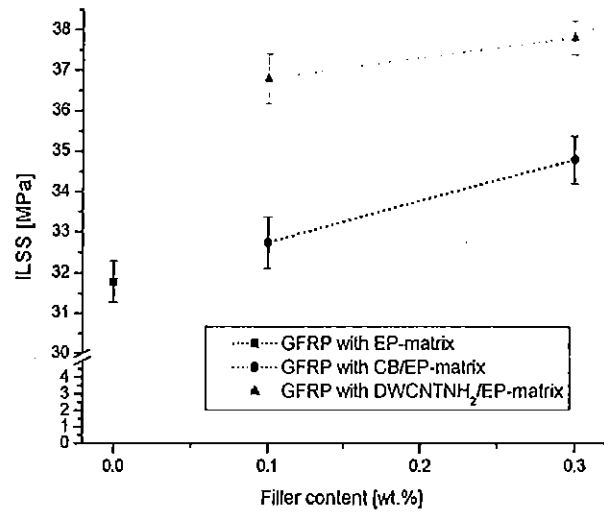


Fig. 6. Interlaminar shear strength (ILSS) of the (nano-reinforced) GFRPs.

a better stress-transfer between the matrix and the nanotubes and, therefore, controlling the matrix-dominated properties of a FRP.

Besides the negative effect of agglomerates on the mechanical properties, it was also possible to identify mechanisms by SEM for a positive influence of the CNTs on the matrix strength. Fig. 8 shows an SEM-image of a tested GFRP with 0.3 wt% DWCNT-NH₂.

The imaged DWCNT-NH₂ are located in a matrix rich area, on the edge of a shear-band. One can estimate from the formation of the observed shear-bands that the matrix in this region has been largely deformed. The orientation of the nanotubes indicates that the final failure occurred under pullout or rupture of the CNTs. The observed mechanisms consume energy and contribute to the increased matrix strength, also resulting in the increased ILSS. Furthermore, one can expect an increased toughness by dispersed DWCNT-NH₂ which are expected to decrease the stress concentration in the process zone ahead the crack tip by the induction of secondary cracks and crack-bridging, which has been identified previously [17].

3.4. Electrical properties

The application of conductive nano-particles to an isolating polymer matrix is supposed to induce an electrical conductivity, when the volume fraction exceeds the percolation threshold. The experimental results of the neat matrix materials are shown in Fig. 9. Generally, the percolation threshold is considered to be lower for fibre-shaped fillers (high aspect ratio) than for spherical particles. A re-agglomeration of nanotubes will lead to conductive paths at lower filler contents, depending on the aspect ratio and the mobility in the matrix. The non-functionalised DWCNTs have the highest tendency to re-agglomerate under formation of conductive paths. The percolation threshold has, therefore, been determined to be below 0.1 wt%.

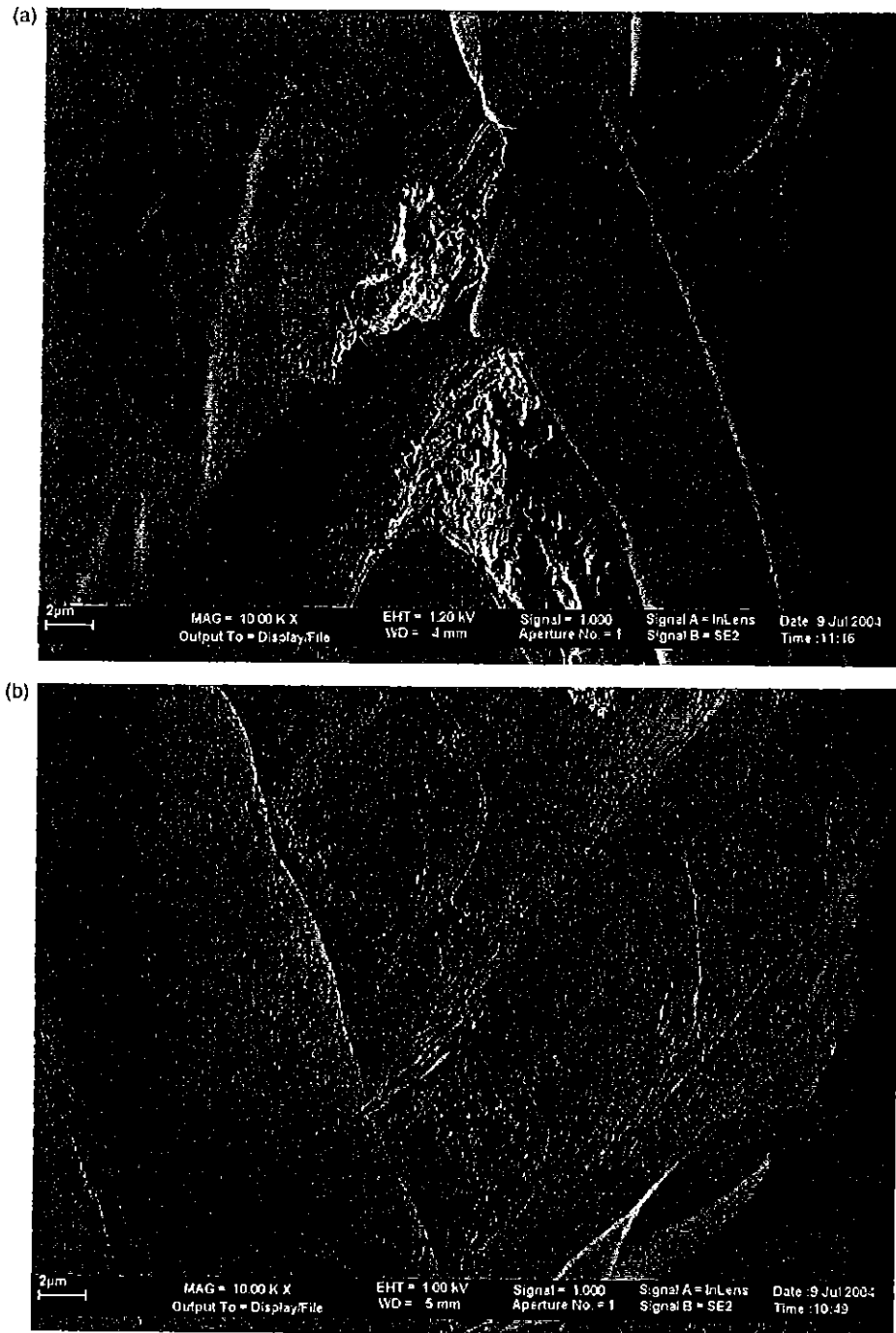


Fig. 7. (a) SEM-image of a tested FRP containing 0.3 wt% DWCNT-NH₂. The observed larger agglomerates decrease the efficiency concerning a mechanical reinforcement of the matrix. (b) SEM-image of a tested FRP containing 0.3 wt% CB. The matrix-rich areas between the glass-fibre do also contain an increasing amount of small agglomerates.

The obtained DWCNT-NH₂ were functionalised in a ball-milling process in an ammonia atmosphere. The functionalisation has led to a better and stabilised dispersion due to improved intermolecular interactions between the epoxy and the nanotube. The electrical conductivity is detrimentally influenced by a functionalisation of carbon nanotubes. This kind of treatment is always

connected to structural changes and, therefore, to a reduction of the electrical conductivity. As a result of this, the overall conductivity should be lower for DWCNT-NH₂ (-composites) than for DWCNTs (-composites). Additionally, the milling process will always lead to a rupture of the CNTs, resulting in a reduced aspect ratio [21]. As a conclusion of this the percolation threshold of particles with

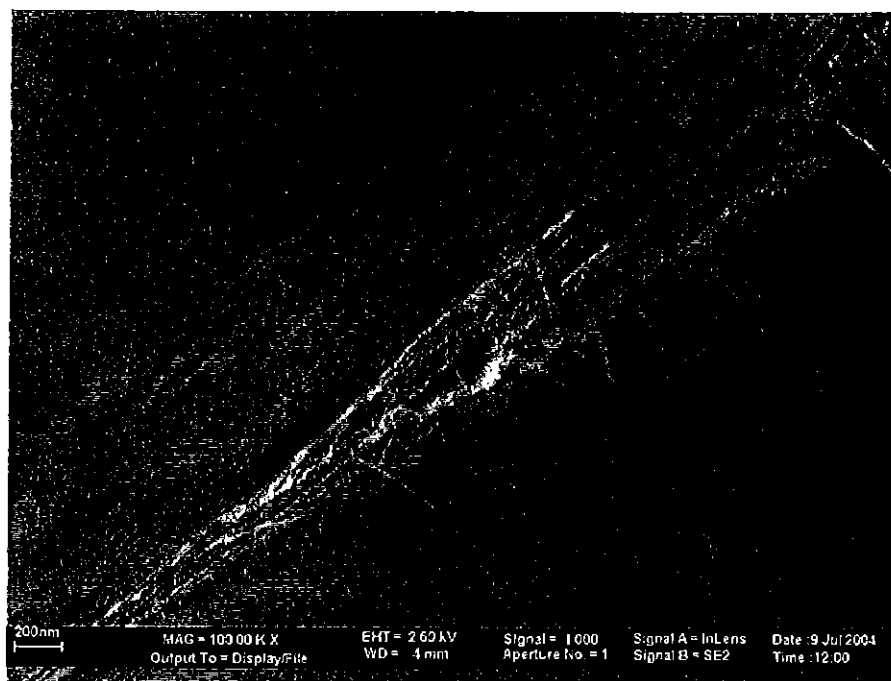


Fig. 8. SEM-image of isolated and impregnated DWCNT-NH₂ located in a matrix-rich area of large deformation.

a lower aspect ratio is shifted to higher filler contents. It has been determined to be between 0.1 and 0.3 wt% for DWCNT-NH₂ and above 0.5 wt% for CB, whereas primary particles have an aspect ratio of about one. However, the amino-functionalised DWCNTs were used for the nano-modification due to their better dispersibility and the reported improved mechanical properties.

Conductivity measurements have been performed on the FRPs with 0.3 wt% DWCNT-NH₂ (post-cured and non-post-cured) in 0, ±45, 90° and in z-direction in order to detect a possible dependence of the conductivity of the

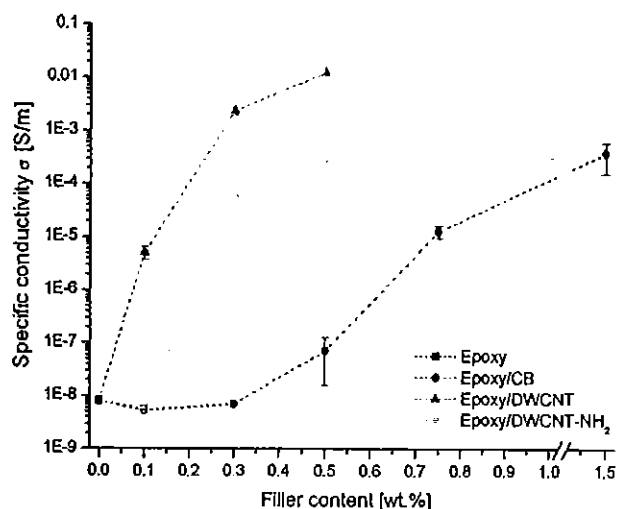


Fig. 9. Electrical conductivity of the nano-particle reinforced epoxy resin. Shown are the conductivities at $f=1000$ Hz.

composites on the fibre-orientation. Fig. 10 summarises the resulting conductivities of GFRPs with nanotube-modified epoxy matrix containing 0.3 wt% DWCNT-NH₂ as a function of the measured direction.

The electrical conductivity of the composites arises from conductive paths, formed by the CNTs, which can only be located in matrix channels between the glass fibres. The electrical conductivity in plane turned out to be more than an order of magnitude higher than out of plane. The fibre-reinforcement in plane precludes the formation of conductive paths, which explains the experimentally observed behaviour. Furthermore, it can be seen that post-curing

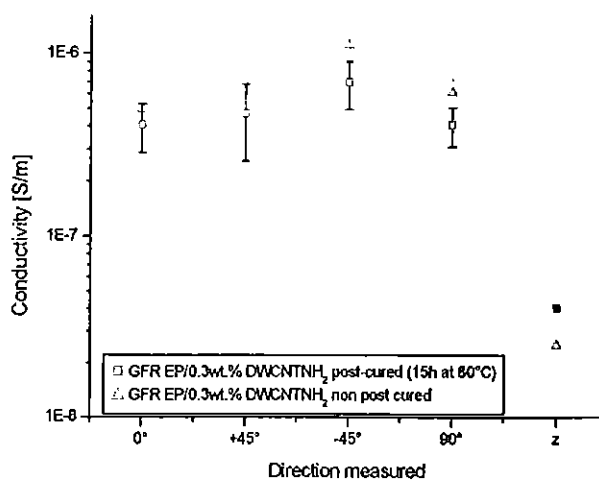


Fig. 10. Electrical conductivity of the nano-reinforced GFRP measured in different orientations.

reduces the overall conductivity. This effect can be explained in terms of a breaking of conductive paths while post-curing. The occurring shrinkage interrupts conductive paths to some extent, thus reducing the electrical conductivity of the GFRP [22]. A tuning of the CNT-content results in FRPs with improved interlaminar properties exhibiting only an in-plane conductivity for special devices, which could be utilised for structural components and 'life monitoring' [23].

4. Conclusions

A nano-modification of the epoxy matrix leads to novel FRPs with enhanced matrix-dominated mechanical properties and an anisotropic electrical conductivity. In order to efficiently exploit the potential of nano-particles, an appropriate dispersion and sufficient amounts of nano-modified epoxy are required. Both requirements can be fulfilled by the application of the introduced calendering method to manufacture the nanotube/epoxy-suspension.

The nanocomposites, reinforced with carbon nanotubes, exhibit an improved mechanical performance. Especially an influence of the CNTs on the fracture toughness could be observed.

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. Manufacturing of resins with nanotube contents of more than 0.5 wt% is still a challenge, due to the enormous surface area of CNTs and the resulting increase in viscosity.

The combination of conventional fibres (e.g. glass-, carbon-, aramid-fibres, etc.) and additional nano-phase reinforcement (e.g. carbon nanotubes) exhibits a high potential for structural applications. Minute amounts of carbon nanotubes (0.3 wt% DWCNT-NH₂) led to a significant increase of the matrix-dominated ILSS by 20%, while the tensile properties were not affected by the CNTs and still remain fibre-dominated. The addition of a similar amount of carbon black was less efficient concerning a mechanical improvement of the matrix material. Furthermore, some evidences for an increased glass transition-temperature by the DWCNT-NH₂ were given by DMTA-measurements on the neat nanocomposites. A further evaluation of this observation is part of the ongoing research.

The determination of the electrical properties yielded in an anisotropic behaviour. The electrical conductivity in-plane was more than an order of magnitude higher than in z-direction. A tuning of the CNT-content for a nanotube-modification of the epoxy matrix of FRPs could result in a new generation of materials with multi-functional properties, e.g. a combination of electrical and thermal conductivity together with improved mechanical performance.

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