

Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study

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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), and the relevance of a surface functionalisation are still to be answered. This first part of the study focuses on the evaluation of the different types of nanofillers applied, their influence on the mechanical properties of epoxy-based nanocomposites and the relevance of surface functionalisation. The nanocomposites produced exhibited an enhanced strength and stiffness and even more important, a significant increase in fracture toughness (43% at 0.5 wt% amino-functionalised DWCNT). 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.

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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) [1–4]. CNTs exhibit an exceptionally high stiffness and strength [5–8], a diameter dependent specific surface area (SSA) of up

to 1300 m²/g [9], 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 makes CNTs highly desirable candidates to improve the properties of polymers. Besides, the development of CNT/polymer nanocomposites opens new perspectives for multi-functional materials, e.g., conductive polymers with improved mechanical performance and with a perspective of damage sensing and “life”-monitoring.

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 fibres (e.g., short carbon fibres: SSA \ll 1 m²/g), leads to

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special challenges, which can be summarised in (i) an appropriate dispersion of the reinforcements in the matrix, (ii) a sufficient interfacial bonding and (iii) 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 behaviour. The SSA of CNTs is dependent on the diameter and the number of sidewalls [9], where a maximum is provided by SWCNTs. Additionally, SWCNTs have the largest aspect ratio compared to CNTs consisting of multiple layers. In order to minimise the SSA, SWCNTs form aggregates of bonded and aligned CNT bundles, called nano-ropes. These ropes, consisting of ten to hundreds of individual tubes, are difficult to separate and infiltrate with matrix.

The other extreme are MWCNTs. Having a much larger diameter and consisting of several concentric walls, these nanotubes provide a SSA of only 200 m²/g or less. Therefore, MWCNTs exhibit a much better dispersibility, but they provide smaller interface for stress transfer and a lower aspect ratio. Furthermore, the stress transfer between the concentric layers has to occur via interlayer shearing to be transferred by van der Waals forces, which are relatively weak. As a conclusion, MWCNTs can be considered to be less efficient concerning a mechanical reinforcement. We also have chosen to use DWCNTs for this study, possessing a SSA of 600–800 m²/g, giving a compromise between dispersibility and reinforcing potential.

Various methods to disperse nanotubes in polymer resins, such as stirring and sonication, have been reported in the literature [10,11]. Most of these methods are either limited in capacity or not powerful enough to separate the agglomerates into individual nanotubes. One common technique to distribute CNTs in epoxies is the sonication technique. A pulsed ultrasound separates the CNTs within agglomerates and disperses them in the matrix effectively. However, this method is only manageable for small batches due to the extreme reduction of the vibrational energy with increasing distance from the sonotrode. Another detrimental effect of this method is the reported rupture of the CNTs, caused by the local energy input [12–14], resulting in a reduction of the effective tube length.

Retaining a high aspect ratio of the CNTs, enabling an efficient load transfer to the nanotube, is of special interest towards an improvement of the mechanical performance of a CNT-reinforced polymer. The calendering method, introduced previously [15], 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. Therefore, we believe this

method to be a very promising approach to solve the issue of dispersion of nanoparticles for resin systems in the future.

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 interfacial bonding between CNT and matrix can be improved by functionalising the CNT-surface. 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 [16] and also experimentally proved by previous work [15,17,19].

The third main issue is a comprehensive knowledge about the integrity of the CNTs resulting in improved effectiveness on the mechanical and physical properties. According to the production techniques, as chemical vapour deposition (CVD), electric arc-discharge method, laser ablation and other catalytic processes, the nanotubes possess deviations of mechanical and physical properties. Influencing parameters are the defect-density and distribution (degree of graphitisation), the curvature, the aspect ratio, the length- and diameter distributions, the density and the purity. Furthermore, one will find numerous variations in CNT length and diameter and a distribution of different chiralities in one batch as well. As a conclusion, similarities can be drawn to polymers, where it is a common and established procedure to describe properties and structural features by the use of distributions (chain length, molecular weight, tacticity, etc.).

The function of CNTs as electrically conductive additive is generally understood and has already been commercially exploited. The reinforcing potential of CNTs on the other hand is still widely undeveloped and needs further basic research. Progress reported in the literature [15,17–29], can be summarised in that way, that there are still difficulties in achieving a reinforcing effect of CNTs in epoxy matrices, to prove their potential as structural modifier.

Allaoui et al. [18] investigated the influence of MWCNTs in a rubbery epoxy matrix. The addition of up to 4 wt% MWCNTs led to a significant increase in strength and Young's modulus. However, the suggested preparation method, using solvents (methanol), stirring and evaporation, did not lead to an adequate distribution. Agglomerates in the dimension of several tens of micrometers could still be detected by light microscopy. In this context, the authors would like to mention, that light microscopy may be a preliminary method in order to get an idea of the overall distribution of agglomerates,

but it is definitely not suitable to substantiate the discussion about the dispersion of CNTs, due to the limited resolution, insufficient for nanofillers.

The same group [19] reported an influence of length and aggregate size of MWCNTs on the improvement in mechanical and electrical properties of a standard DGEBA-based nanocomposite. Composites containing 0.5–4 wt% CVD-grown MWCNTs exhibited an increased Young's modulus, but a reduction in fracture strain. The reduction in fracture strain was explained in terms of the existence of agglomerates, leading to local defects enhancing early failure. Furthermore, a certain dependence of the mechanical behaviour on the aggregate size could be found.

Liao et al. [20] investigated the influence of SWCNTs on the thermo-mechanical properties of epoxy-based nanocomposites. The composites were produced by the use of sonication and the application of solvents and surfactants to disperse the nanotubes. A dependence of the achieved dispersion on the relative improvement of the mechanical properties was observed. The preparation route was considered to be an effective method in order to disperse CNTs. However, in their case, the incorporation of SWCNTs led to a reduction of the glass transition temperature, being explained by a reduction of the interfacial adhesion due to the use of a surfactant and the mentioned solvent.

Miygawa and Drzal [21] reported an increase in the storage modulus of epoxy-based nanocomposites containing fluorinated SWCNTs. A linearly decreasing glass transition temperature with increasing filler content was also observed. This result could indicate that a fluorination of CNTs may not be a suitable functionalisation to significantly improve the interfacial adhesion. A correlation of fluorinated SWCNTs to PTFE- or other matrix incompatible particles could be drawn, which would induce a similar behaviour.

The influence of oxo-fluorination of MWCNTs on the fracture toughness of epoxy matrix nanocomposites has been investigated by Park et al. [22]. A certain increase in fracture toughness by SENB-testing (single edge notch bending) was shown. The results were related to the modified surface polarity of the CNTs, leading to an improved bonding to the matrix by polar interactions. In contrast to the neat fluorination, this functionalisation generates additional hydroxyl groups on the CNT surface, enabling hydrogen bonds to the epoxy matrix.

Promising results, concerning a mechanical reinforcement of epoxy resins by the use of CNTs were recently reported by Zhu et al. [23,24]. They showed a significant progress in improving the CNT dispersion and matrix adhesion by adding 1 wt% alkylamino-functionalised SWCNTs to an epoxy matrix thus, resulting in an increased strength and Young's modulus. The presented functionalisation assimilates the polarity and directly

incorporates the SWCNTs into the epoxy network. Their results were in agreement with our results [15,17,25] using smaller quantities of amino-functionalised CNTs. In addition to the improvement in strength and stiffness, an increased glass transition temperature was observed. This substantiates previous results [25,26], reporting a similar influence of the direct incorporation of CNTs into the matrix by covalent bonding. Tailored functional groups induce the formation of covalent bonds to the matrix material. We would like to point out that the surface chemistry of carbon nanotubes (introduction of functional groups), could be regarded as the most important aspect in efficiently exploiting the benefits of CNTs for a mechanical reinforcement.

This brief description shows the diversity of possible variables in developing CNT/epoxy nanocomposites. A comparison of results reported is often difficult, due to the usage of different epoxy matrices, with different processing techniques and parameters, as well as the choice of CNTs with different pre-treatments (e.g., functionalisation), from various sources with again different types and qualities. Presently, CVD is regarded as the most relevant manufacturing process for CNTs, due to the high production capacity fulfilling technical and in the near future industrial demands as well [27,28].

In this part of the study, we describe the influence of different types of CVD-grown CNTs (single-, double- and multi-wall CNTs) on the mechanical properties of epoxy-based nanocomposites. We produced nanocomposites using identical processing conditions, by systematically varying CNT-type, filler content and surface functionality. All results are compared to reference materials, as the neat epoxy matrix and a nanocomposite containing carbon black. Keeping most variables constant, it was the aim of this study to compare the influence of these different types of CNTs on the mechanical properties and to appraise the real potential of CNTs as structural modifiers of epoxy-based composites. The modification of the electrical and thermal conductivity by CNTs will be presented separately [32].

2. Experimental

2.1. Materials

2.1.1. Epoxy matrix system

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 Kunstharzprodukte GmbH, Stuttgart/Germany. This epoxy system is a standard resin for infusion processes (e.g., RTM – resin transfer moulding) and it is characterised by its low viscosity ($\eta_{RT} = 250$ MPa s).

2.1.2. Carbon nanotubes

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

(a) Single-wall carbon nanotubes

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.

(b) Double-wall carbon nanotubes (purified and amino-functionalised)

The DWCNT ($-\text{NH}_2$) 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.

(c) Multi-wall carbon nanotubes (purified and amino-functionalised)

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 μm . The functionalisation process was similar to the one described for DWCNTs.

2.1.3. Carbon black

We used nanocomposites containing highly conductive carbon black (CB) as reference material. The CB, Printex XE2 from Degussa/Germany, is highly graphitised and commonly used as conductive filler for anti-static applications or as colour 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. Carbon black, being common and cheap nanoparticles, has extensively been investigated in the past. We used CB as reference in order to appraise the effect of the particle-shape on the achieved improvements concerning the mechanical properties and, therefore, to obtain information on the real potential of CNTs as mechanical reinforcement for epoxy matrices.

2.2. 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 for final high shear mixing. The gap size between the ceramic rolls of the mini-calander (Al_2O_3) was 5 μm and the speed was set to 20 (1st roll), 60 (2nd roll) and 180 rpm (3rd roll). The dwell time of each batch of suspension was ≈ 2 min. 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 $^\circ\text{C}$ for 24 h.

2.3. Mechanical characterisation

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. The sharp incipient crack was introduced by carefully hammering a sharp razor blade into the notch, whereas a crack initiates in the zone of stress concentration in front of the blade. A minimum of 6 specimens of each sample was tested for statistical evaluation.

2.4. 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.

3. Results and discussion

3.1. Influence of SSA and surface functionalisation of the CNTs on the dispersibility in epoxy resin

Dispersing nanoparticles in a chosen matrix system is a challenging process. As already mentioned in the introduction, nanoparticles exhibit a SSA, which is several orders of magnitude larger than that of conventional fibre-reinforcements (e.g., SWCNT: SSA ~ 1300 m^2/g).

In order to homogeneously disperse nanoparticles in the epoxy and to properly impregnate the potential surface area of the nanofiller, a huge energy input has to be ensured to overcome the nanotube–nanotube adhesion by van der Waals-forces. A local introduction of the required energy, as performed by sonication, will lead to a damage of the nanotube structure and to a reduction of the effective length [12–14]. We could prove that the application of a mini-calander is an effective method to disperse CNTs and CB in epoxy matrix systems [17], thus, all nanocomposites investigated in this study were manufactured using this method. Presently, TEM is the only method to attain qualitative information concerning a distribution of nanoparticles in a polymer matrix. Therefore, we investigated the produced composites by TEM. In Fig. 1(a)–(f), representative TEM micrographs of the achieved dispersion for the investigated CNTs are shown.

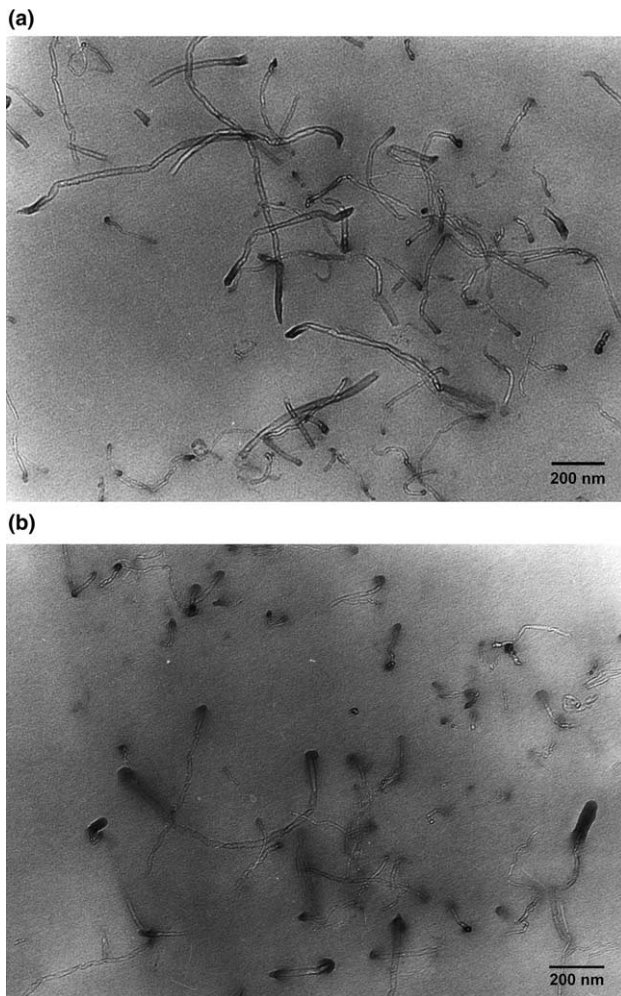


Fig. 1. TEM-images of the manufactured composites. Achieved state of dispersion for: (a) epoxy/MWCNT; (b) epoxy/MWCNT–NH₂; (c) epoxy/DWCNT; (d) epoxy/DWCNT–NH₂; (e) epoxy/SWCNT; (f) epoxy/CB.

As it can be seen from Fig. 1(a) and (b), both MWCNT and MWCNT–NH₂, respectively, exhibit a high dispersibility in the epoxy matrix. The homogeneous dispersion in the matrix was achieved by calandering with only very few agglomerates remaining. The MWCNTs exhibit the smallest SSA (~200 m²/g) of the investigated tubes, tantamount to the lowest attractive forces and agglomeration behaviour.

The amino-groups seem to stabilise the CNT-dispersion by stronger interactions with the epoxy matrix. This can be attributed to the increased polarity of the CNTs by the functional groups and the possible reaction of the amino-groups with the epoxy resin, forming covalent bonds. Fig. 1(b) indicates a very good matrix adhesion of the amino-functionalised MWCNTs. Some of the imaged CNTs, stick out of the plane of the prepared films. These CNTs have not been cut by the diamond blade, but pulled out. However, the remaining epoxy layer coating the nanotubes indicates a very strong matrix adhesion.

The described effects were also observed for the DWCNTs. According to the larger surface area of 700 m²/g, the interactive forces between the DWCNTs are significantly larger, thus, requiring more energy to disperse the aggregated nanotubes in the epoxy matrix. The achieved dispersions are shown in Fig. 1(c) and (d). The two different types of DWCNTs, non-functionalised DWCNTs (Fig. 1(c)) and amino-functionalised DWCNTs (Fig. 1(d)) show a mixed structure of broken-up agglomerates and isolated nanotubes. The alignment of the DWCNTs to be seen in Fig. 1(c) and (d) could be caused either by ultra-microtome cutting, as reported by Ayajan et al. [29] for similar epoxy/CNT-nanocomposites, or by the induced shearing.

The achieved dispersion for SWCNTs in the epoxy matrix is shown in Fig. 1(e). The TEM-micrograph shows a mixture of separated SWCNTs, as well as mostly small agglomerates with a diameter of 50–300 nm. Furthermore, few larger agglomerates exhibiting a diameter of about two micrometer were observed.

A further improved dispersion should be possible for all CNTs using this calandering method, but a detailed parameter study is required in this case. So far the question concerning the favourable state of dispersion, it is still unsolved. Do we have to achieve a structure of completely separated CNTs homogeneously dispersed in the epoxy matrix or not? Fact is, that a good impregnation of the nanofillers is the prerequisite for an efficient exploitation of the potential benefit from CNTs as structural reinforcement. A combination of impregnated agglomerates and isolated nanotubes can be considered to be a favourable state of dispersion for at least some purposes. A detailed discussion on this topic is accomplished in Section 3.3.

Fig. 1(f) is a TEM-micrograph of the reference material containing carbon black. As it can be seen in the

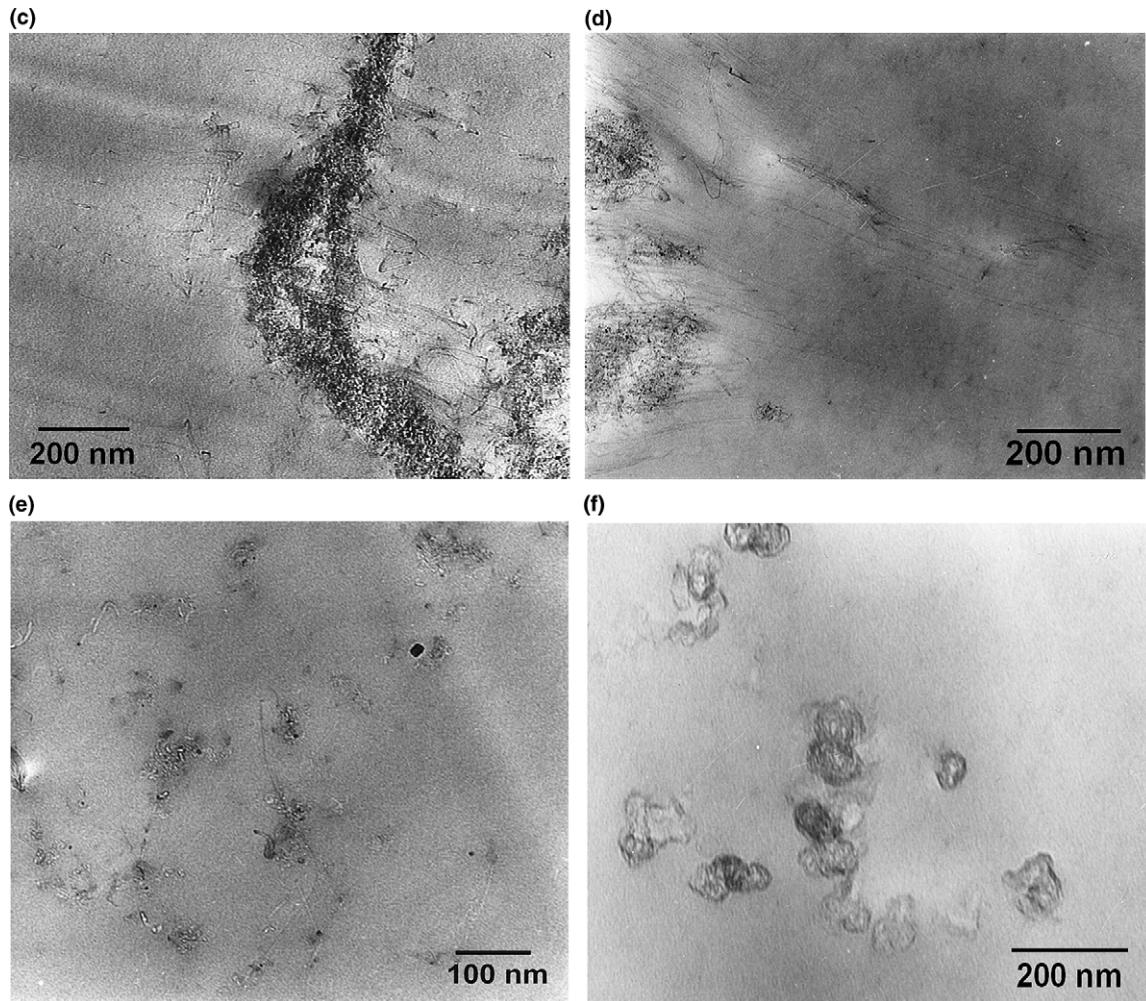


Fig. 1 (continued)

micrograph, the CB was separated into the aggregate structure. These aggregates are homogeneously dispersed in the matrix system. The generation of high shear forces during the calendering process reflects itself in the separation of primary particles from the aggregates, frequently observed by TEM.

The achieved dispersion reveals the applicability of a calendering technique to efficiently disperse various nanoparticles in epoxies and probably also in other liquid polymers and polymer solutions.

3.2. Evaluation of the mechanical properties of CNT/epoxy composites

The reinforcement potential of the CNTs can only be activated if an effective load transfer from the surrounding epoxy matrix into the nanotube and reverse is possible. Therefore, a good impregnation with the matrix, together with a strong interfacial adhesion has to be ensured. According to the fact that a stress transfer can only occur via the outermost layer of a nanotube, one

can conclude a maximum potential of SWCNTs concerning mechanical reinforcement. However, the larger the provided interface, the more serious the dispersion conditions, thus, aggravating the impregnation. Alternatives could be CNTs exhibiting a smaller SSA, which led to a better dispersibility.

In this section, we compare the results of the mechanical testing and discuss parameters influencing the mechanical reinforcement by CNTs. The results of the neat epoxy and the analogous composites containing the same filler contents CB as those of the CNTs are shown as reference in all of the following figures. All mechanical properties are summarised in Table 1.

Fig. 2 shows the ultimate tensile strength (UTS) of the nanocomposites containing non-functionalised (Fig. 2(a)) and functionalised CNTs (Fig. 2(b)) as function of filler content, respectively. The UTS of the neat epoxy matrix is shown in the form of the dashed line for comparison.

In general one can say, that the addition of small amounts SWCNTs and DWCNTs increases the UTS

Table 1
Mechanical properties of nanoparticle reinforced composites

	Filler type/content (wt%)	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Fracture toughness K_{Ic} (MPa m ^{1/2})
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 ₂	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) ^a	61.52 (0.19) ^a	^a
Epoxy/MWCNT–NH ₂	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)

^a High viscosity disabled degassing – composite contained numerous voids.

moderately, whereas MWCNTs lead to a slight reduction. CB, as reference material, does not significantly influence the UTS of the epoxy matrix at very low filler contents.

The relatively large improvement in UTS by SWCNTs compared to the other nanofillers can be explained by the high specific mechanical properties and the highest aspect ratio of the SWCNTs. Combined with the high SSA, SWCNT do not have inactive internal layers, they exhibit the highest potential to improve the strength of materials. DWCNTs consisting of two concentric layers, exhibit a smaller SSA and lower aspect ratio, but do not agglomerate as pronounced as SWCNTs. The composite containing 0.3 wt% DWCNT exhibits a maximum UTS (67,8 MPa), which did not further increase with higher tube loadings.

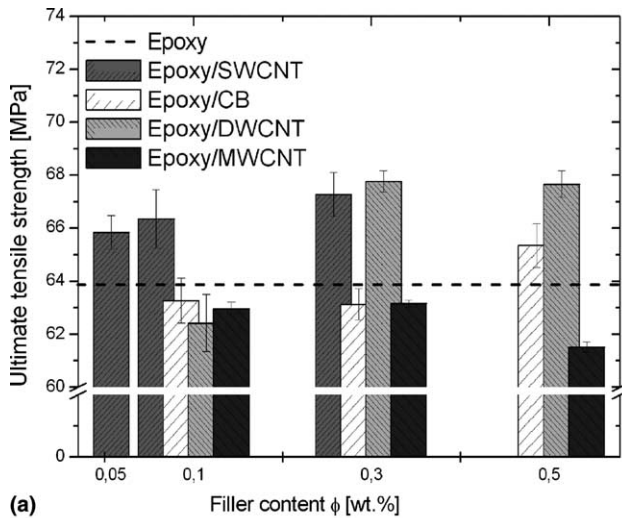
Neither the addition of small amounts of MWCNT, nor MWCNT–NH₂, do significantly affect the UTS of the epoxy resin. An explanation for the observed behaviour can be found by considering the concentric structure of MWCNTs. Due to the absence of stress transfer to internal layers, only the outermost layers of MWCNTs contribute to the mechanical reinforcement. Based on geometrical calculations, it is possible to show for an imaginary nanotube with an outer diameter of 15 nm, an inner diameter of 4 nm and a layer distance of 0.32 nm, an effective surface area of only 9% of the total weight contributes to the reinforcement of the epoxy matrix. The slight reduction of the UTS by MWCNTs compared to the neat epoxy matrix and the relatively lower increase for SWCNTs and DWCNTs

at higher filler contents can be attributed to an increasing amount of improper impregnated agglomerates, acting as imperfections in the composite, inducing early failure.

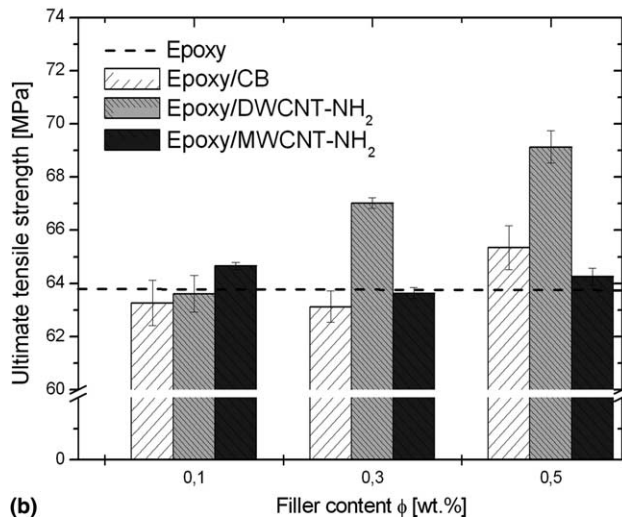
The UTS of composites containing amino-functionalised CNTs is summarised in Fig. 2(b). The amino-functionalisation of the CNTs improves the dispersibility by increasing the surface polarity and induces an incorporation of the nanotubes into the matrix network, thus, resulting in a generally larger improvement of the UTS. A content of 0.5 wt% DWCNT–NH₂ led to an increase in UTS from 63.7 MPa (epoxy) to 69.2 MPa (+10%). The UTS of the composites containing MWCNT–NH₂ remains on the level of the neat epoxy. The more efficient improvement of the UTS by functionalised CNTs proves the importance of a chemical surface functionalisation to integrate the CNTs by covalent bonding in the network structure of the epoxy matrix. This is an effective method to significantly improve the interfacial adhesion, making functionalisation to a key issue in the development of CNT-reinforced epoxy composites.

Fig. 3 illustrates the corresponding Young's moduli of composites containing non-functionalised (Fig. 3(a)) and amino-functionalised CNTs (Fig. 3(b)).

The addition of any kind of nanofiller increases the stiffness of the matrix material, as long as a proper impregnation with the matrix and a sufficient adhesion is ensured. The neat epoxy matrix exhibits a Young's modulus of 2599 MPa. The present results for SWCNT/epoxy composites show an almost linear



(a)



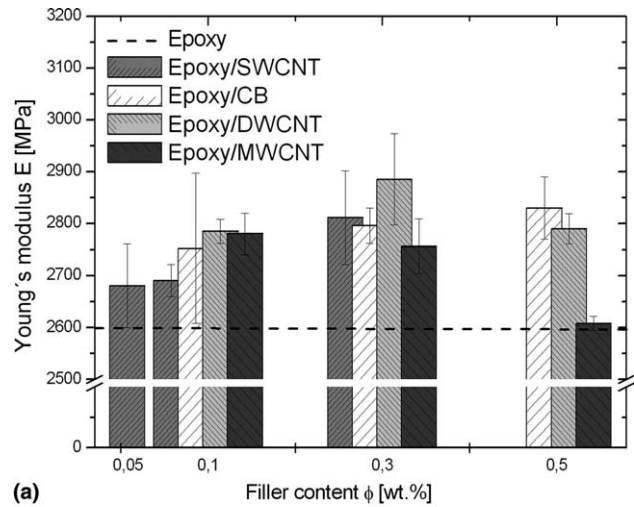
(b)

Fig. 2. Ultimate tensile strength of epoxy-based composites containing (a) non-functionalised and (b) amino-functionalised nanoparticles.

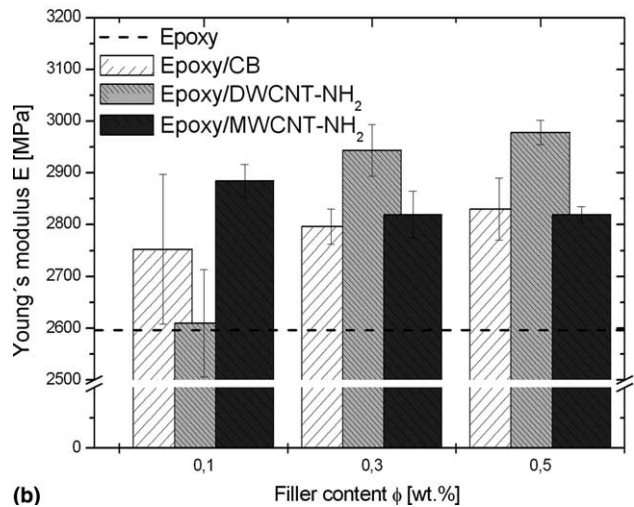
increase of the Young’s modulus in relation to the filler content, yielding in a maximum of 2812 MPa at 0.3 wt% under the given processing conditions.

The Young’s modulus of MWCNT/epoxy composites increases at contents of 0.1 wt% MWCNT and decreased later for higher MWCNT loadings. A possible explanation can be given for this behaviour by assuming a similar state of high quality dispersion for all nano-composites after the calendaring process. An increasing amount of agglomerates in the cured composites was observed for the CNT/epoxy composites above filler contents of $\phi > 0.1$ wt%. We propose these agglomerates to be a result of reagglomeration. According to the smaller number of particles in MWCNT/epoxy composites, compared to SWCNTs, a reagglomeration of MWCNTs does reduce the Young’s modulus more significantly.

DWCNT showed stronger improvements in the mechanical properties, yielding in a maximum Young’s



(a)



(b)

Fig. 3. Young’s modulus of epoxy-based composites containing (a) non-functionalised and (b) amino-functionalised nanoparticles.

modulus of 2885 MPa (+11%) at 0.3 wt% DWCNTs, but decreasing again for higher filler contents. This effect can again be attributed to the reagglomeration, but due to the larger number of particles we observe a shift to higher filler contents.

The amino-functionalised nanotubes turned out to be more efficient concerning an improvement of the Young’s modulus, thus again proving the relevance of surface functionalisation. Amino groups located onto the CNT surface will react under formation of covalent bonds with the epoxy, thus, resulting in a significantly enhanced interfacial adhesion. We observed a maximum increase of the Young’s modulus for a composite containing 0.5 wt% DWCNT–NH₂ (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.

A similar behaviour, when compared to non-functionalised MWCNTs, was observed for MWCNT–NH₂. These composites showed a stronger enhancement of the Young's modulus, but stagnating on the achieved level at higher filler contents. The decreasing efficiency can again be related to the reagglomeration, which was less intensive as for the non-functionalised MWCNTs.

An estimation of the relative improvement of strength and stiffness by any kind of filler should be performed according to its volume fraction. However, the density of CNTs is dependent on the CNT-diameter and, therefore, required for a determination of the volume fraction. Thostensen and Chou [5] suggested an approach which considers the inner- and outer diameter of CNTs and its distributions, as well as possible defects in the CNT structure. Unfortunately, reliable and statistically validated data (length, diameters, etc.) are difficult to obtain due to the nanometric dimensions.

The effect of a surface functionalisation becomes visible by directly comparing the stress–strain (σ/ϵ -) curves of the tested samples. Fig. 4 shows representative σ/ϵ -curves of the epoxy resin and two composites containing each 0.3 wt% of DWCNTs and DWCNT–NH₂, 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. Regarding the area under the σ/ϵ -curves as the fracture work of the composites, first evidences were given for improved fracture toughness. A detailed discussion is accomplished in the following section.

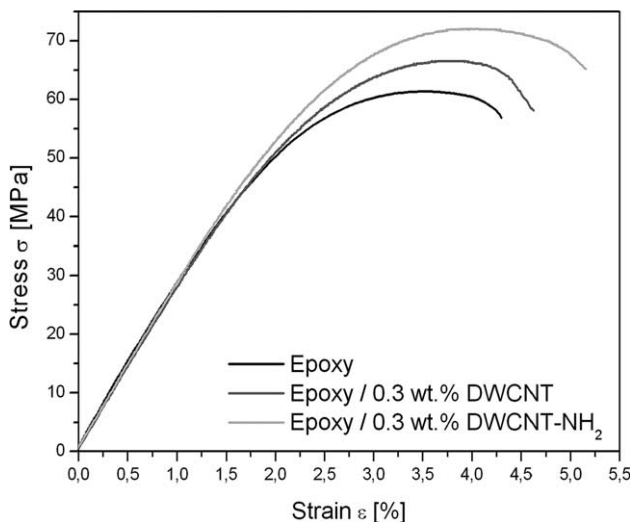


Fig. 4. Comparison of the stress/strain-behaviour of the neat epoxy and nanocomposites containing 0.3 wt% DWCNTs and 0.3 wt% DWCNT–NH₂.

In conclusion, 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 realise this impregnation. Presently, DWCNT–NH₂ 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. Realising 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.

3.3. Potential of CNTs to improve the fracture toughness of an epoxy matrix

Epoxy resins are favourable and commonly used matrix systems for a huge variety of applications. They provide a high strength and stiffness, good thermal stability, high thermo-mechanical stability and good resistivity against chemicals, but a relatively low toughness. The fracture toughness of polymers, tantamount to an improved resistivity against crack propagation, thus a higher damage tolerance, is a crucial and limiting factor for the design of structural components, especially with regard to the long-term behaviour (fatigue) [30]. Therefore, an improvement of the fracture toughness of epoxies is a desirable goal of research activities.

A comprehensive knowledge about the influence of nanoparticles on the micromechanics is required in order to explain the observed toughening effect of nanoparticles. Recently, we published an overview over the influence of nanoparticles on the fracture toughness and the related micro-mechanical mechanisms [31]. In summary, the most important mechanisms leading to an increase in fracture toughness are: (i) localised inelastic matrix 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.

The fracture surfaces of composites give first information about fracture mechanisms and the influence of particle modification on the fracture behaviour. Fig. 5(a) and (b) shows SEM images of fracture surfaces of the neat epoxy resin (Fig. 5(a)) and a representative

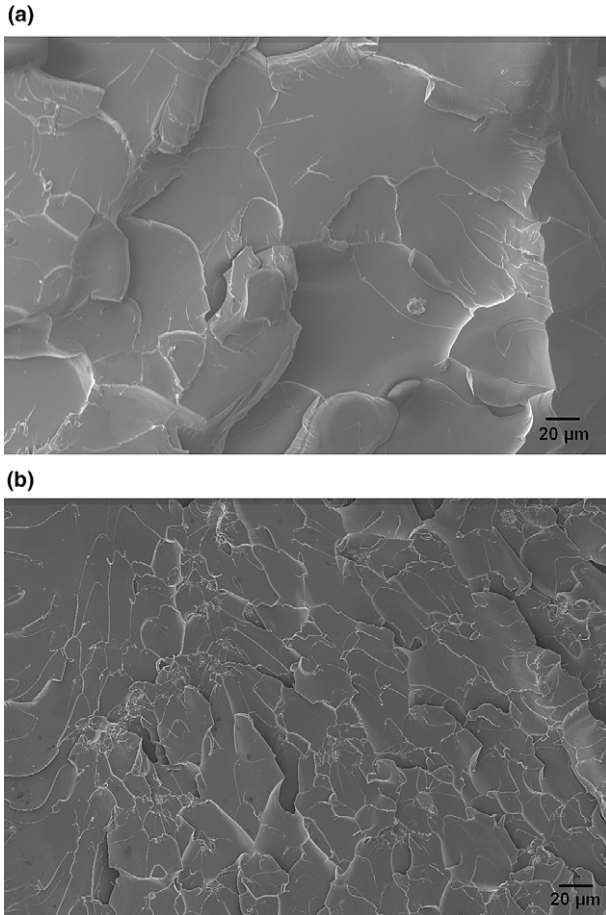


Fig. 5. SEM-micrographs of a fracture surfaces at low magnifications (1000 \times), showing (a) the epoxy and (b) a DWCNT-NH₂/epoxy composite. The composite containing CNTs exhibits a significantly rougher fracture surface compared to the neat epoxy, indicating a toughening effect of the nanoparticles.

nanocomposite containing 0.1 wt% DWCNT-NH₂ (Fig. 5(b)). The imaged fracture surfaces were taken from similar areas of the failed specimens. The general toughening effect of (nano-) particles reflects itself in a significantly larger roughness of the fracture surface of the sample containing CNTs. A similar effect has been observed for all nanofillers, indicating this effect being related to the general existence of particle reinforcements.

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 [13]. In this section, we present the results of fracture-toughness-tests performed on CT-specimens. The results are displayed in Fig. 6, and will be discussed in correlation with the identified micro-mechanical mechanisms.

The neat epoxy resin has a fracture toughness of $K_{Ic} = 0.65 \text{ MPa m}^{1/2}$. Non-functionalised nanoparticles generally increase the fracture toughness of the epoxy

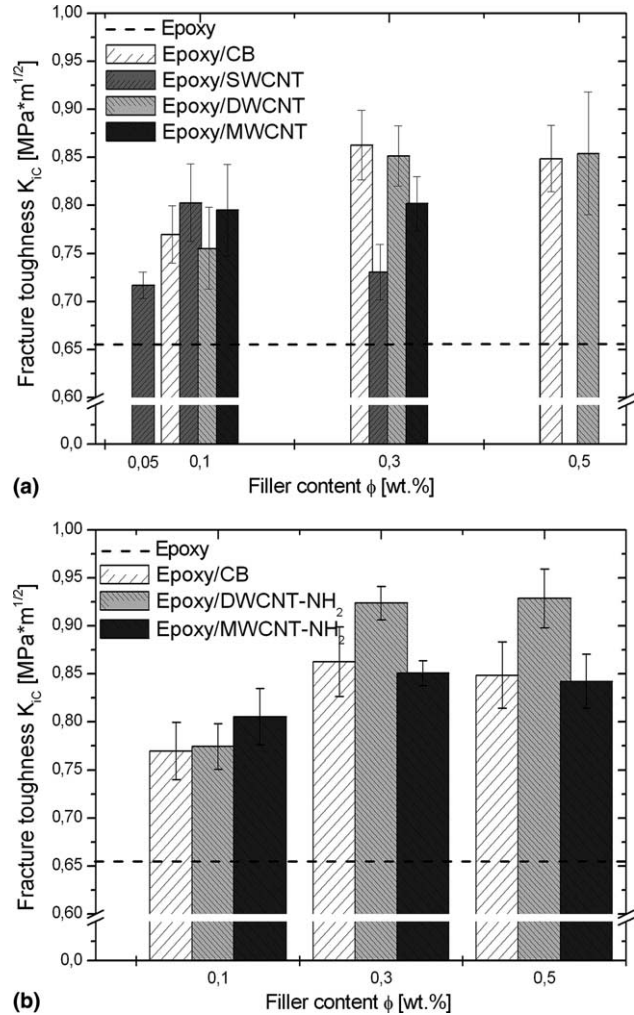


Fig. 6. Experimentally obtained fracture toughness of epoxy-based composites containing (a) non-functionalised and (b) amino-functionalised nanoparticles.

matrix significantly at very low filler contents, as shown in Fig. 6(a). The relative improvement of the K_{Ic} -value is not dependent on the particle-shape and, therefore, the main fracture mechanical mechanism leading to the enhanced fracture toughness could be related to the huge surface area of the nanoparticles. As discussed in Section 3.1, we observed a partly agglomerated dispersion for all nanofillers, which leads to the conclusion that the localised inelastic matrix deformation, void nucleation and crack deflection at the agglomerates are the dominating toughening mechanisms.

A certain dependence of the provided surface area of the nanofillers on the toughening capacity could be found. In tendency, large surface areas lead to a more efficient improvement of fracture toughness. The decrease in fracture toughness (e.g., SWCNT at 0.3 wt%), observed at higher filler contents, is related to the reagglomeration. 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. Thus, the interface is playing a major role concerning toughening of materials. 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 favourable state of dispersion.

The amino-functionalisation of CNTs improves their dispersibility (see Section 3.1) and increases the interfacial adhesion, leading to a higher effective interfacial area in the composite. However, a too strong interfacial adhesion between matrix and reinforcement negatively affects the toughness by suppressing interfacial failure, which is prerequisite for many toughening mechanisms.

Our experimental results, displayed in Fig. 6(b), prove a positive influence of an amino-functionalisation of the CNT surface on the fracture toughness. The measured fracture toughness of the composite containing 0.3 wt% DWCNT-NH₂ ($K_{Ic} = 0.92 \text{ MPa m}^{1/2}$) was 42% higher than the neat epoxy ($K_{Ic} = 0.65 \text{ MPa m}^{1/2}$).

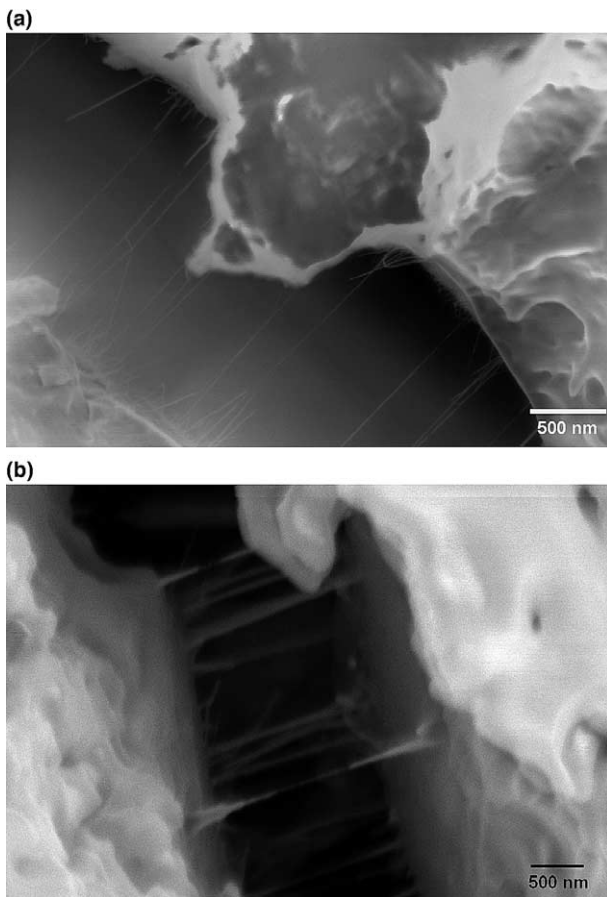


Fig. 7. SEM-micrographs of DWCNT(-NH₂)/epoxy composites. A crack, induced by etching, is bridged by (a) amino-functionalised and (b) non-functionalised double-wall carbon nanotubes. Crack-bridging is one micro-mechanical mechanism leading to the observed increase in fracture toughness. The bridged gap length is about 500–1000 times the average diameter of the nanotubes.

Besides the improved dispersibility and impregnation of the surface, we also relate this effect to the integration of CNTs into the epoxy-network structure. The relation of amino-groups to the number of surface carbon atoms of the CNTs is about 1/100, according to the information of the manufacturer. Furthermore, it was shown that these functional groups appear in localised domains onto the surface, thus, locally bonding the CNT to the matrix. The localisation of functional groups, especially at the ends of the CNTs, is a result of the functionalisation process. A ball milling, as used in our case, will break the CNTs and generate highly reactive ends, which immediately react with the surrounding solvent (amines). The situation described allows certain mobility and reorientation in the matrix under stress situations, which consumes more energy in case of interfacial failure, due to the additional rupture of the covalent bonds to the epoxy-molecules. The high strain to failure of CNTs [6,7] in relation to the epoxy enables a huge deformation of the nanotube, which is several times that of the epoxy matrix. This also allows a crack bridging of

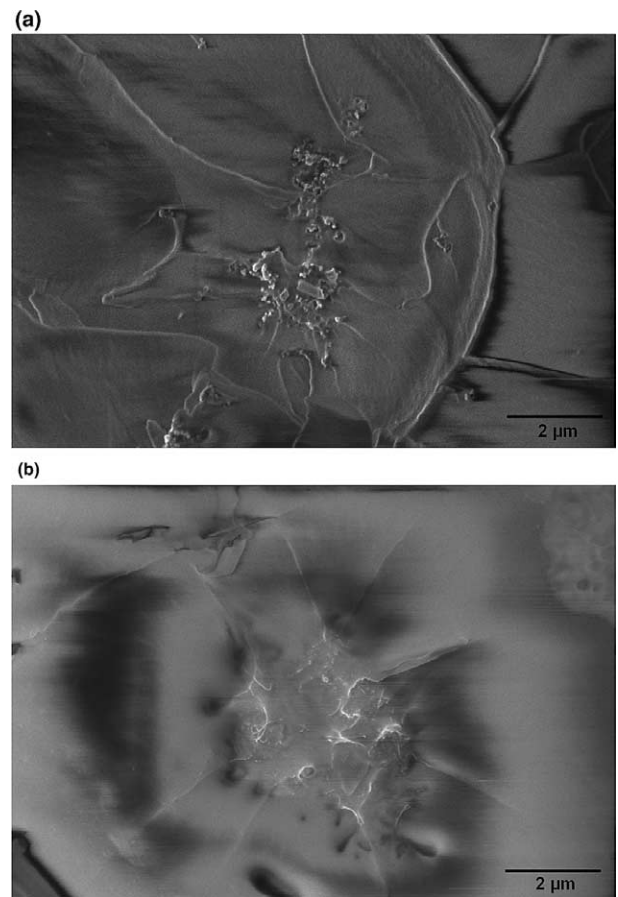


Fig. 8. SEM-micrographs showing small agglomerates of (a) carbon black/epoxy and (b) DWCNT(-NH₂)/epoxy composites. Shear-bands around the agglomerates indicate a major contribution of plastic matrix deformation and void nucleation to the fracture toughness of nanoparticle filled epoxy. This mechanism is independent from the particle shape.

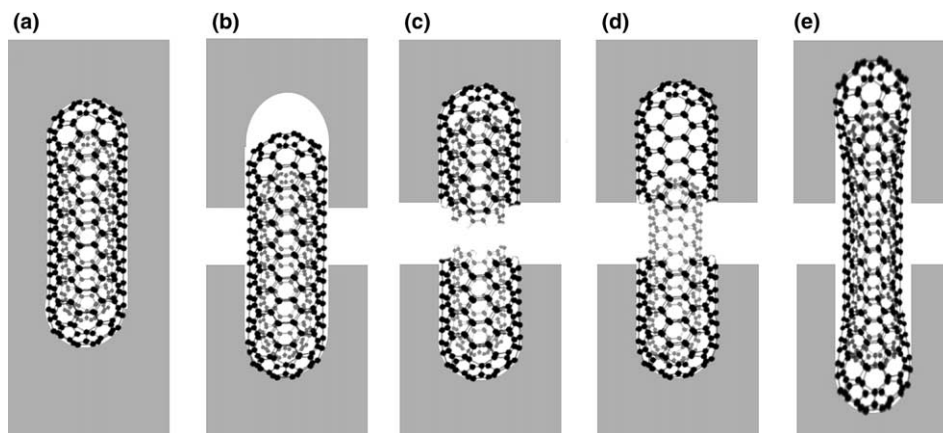


Fig. 9. Schematic description of possible fracture mechanisms of CNTs. (a) Initial state of the CNT; (b) pull-out caused by CNT/matrix debonding in case of weak interfacial adhesion; (c) rupture of CNT – strong interfacial adhesion in combination with extensive and fast local deformation; (d) telescopic pull-out – fracture of the outer layer due to strong interfacial bonding and pull-out of the inner tube; (e) bridging and partial debonding of the interface – local bonding to the matrix enables crack bridging and interfacial failure in the non-bonded regions.

functionalised DWCNTs (Fig. 7(a)), as well as non-functionalised DWCNTs in the epoxy (Fig. 7(b)), as observed by SEM.

The imaged cracks were induced into the composite by stresses due to the drying of the composite after surface etching with sulphuric acid. The imaged surface cracks were not directly formed during etching, due to the short etching time of only 60 s. We could instead observe the generation of the surface cracks inside the SEM as a result of vacuum drying and thermal stresses. This method allows the investigation of the composite by SEM underneath the surface.

A comparison to the CB-containing epoxy composites underlines the advantage of fibrous over spherical particles. Toughening mechanisms like localised inelastic matrix deformation and void nucleation, interfacial debonding and crack deflection at agglomerates are accessible for all particles, regardless the particle shape. These mechanisms could be identified by SEM investigations on the nanocomposites (Fig. 8(a) and (b)). We observed shear-bands around the agglomerates of CB (Fig. 8(a)) and DWCNT-NH₂ (Fig. 8(b)), thus, indicating void nucleation caused by plastic deformation of the matrix to be a major toughening mechanism.

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 and additionally further mechanisms are possible, illustrated in Fig. 9.

A reliable quantitative description is presently difficult. It is yet not clear whether mathematical approximations based on macro-/microscopic approaches are also valid to explain nano-mechanical processes or not. Therefore, Fig. 9 schematically describes possible processes and mechanisms, explaining the deformation and failure of CNTs bridging a crack.

The initial situation of the CNT in an ideal case (Fig. 9(a)) is a completely impregnated and isolated embedded in the matrix. In case of a crack the mechanisms Fig. 9(b)–(e) can occur, depending on the interfacial adhesion and the mechanical properties of the CNTs. In case of a weak interfacial bonding simple pull-out of the CNT from the matrix occurs (Fig. 9(b)). In contrast, a very strong bonding between CNT and matrix will lead to a complete rupture of the CNT (Fig. 9(c)) or to fracture of the outer layer and a telescopic pull-out of the inner tube(s) (Fig. 9(d)). A spatial bonding of the reactive groups at the interface, as suggested in our case, enables a partial debonding of the interface, but allows a crack bridging (Fig. 9(e)). This bridging suppresses a further crack opening. However, increasing stresses would finally lead to a failure of the CNT, according to Fig. 9(c) and (d).

4. Summary and conclusions

Nanocomposites consisting of a DGEBA-based epoxy matrix system and different types of carbon nanotubes were produced by calandring. The composites were investigated regarding the dispersibility of the CNTs in the matrix and the efficiency concerning a mechanical reinforcement. 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.

CNTs in general exhibit a certain potential to improve the mechanical properties of the tested epoxy matrix systems. A correlation between the provided surface area and the dispersibility was found. The dispersibility turned out to be more difficult, the larger the SSA of the CNTs. A functionalisation with amino-groups improved the dispersibility in all cases and stabilised the CNT-suspension, thus, reducing the reagglomeration. This effect was attributed to an assimilated polarity of the surface and to a possible reaction between the introduced amino-groups and the epoxy resin, thus, integrating the CNTs into the epoxy-network structure.

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.

Micro-mechanical 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 micro-mechanical 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. We suggest mechanisms explaining the increased fracture toughness of epoxy-based composites, despite a strong matrix bonding of the amino-functionalised CNTs. Commonly a very strong interfacial bonding is a adverse to an enhancement of the fracture toughness by using macro- and microscopic particles.

In conclusion, carbon nanotubes enable the development of a new generation of materials with multi-functional properties, such as a combination interesting physical properties [32] together with improved mechanical performance. 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 [33–35].

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