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Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites☆

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Abstract

Nanostructured modification of polymers has opened up new perspectives for multi-functional materials. In particular, carbon nanotubes (CNTs) have the potential to realise electrically conductive polymers with improved or retaining mechanical performance. This study focuses on the evaluation of both, the electrical and thermal conductivity of nanoparticulate filled epoxy resins. We discuss the results with regard to the influence of the type of carbon nanotube (SWCNT, DWCNT and MWCNT), the relevance of surface-functionalisation (amino-functionalisation), the influence of filler content (wt% and vol%), the varying dispersibility, the aspect ratio and the specific surface area.

Keywords: Carbon nanotubes; Thermal conductivity; Nanocomposite

1. Introduction

The development of polymer composites with nanoscaled modifiers has become an attractive new subject in materials science. Utilisation of electrically conductive nanoparticles to impart electron conduction in polymers has been investigated over the last two decades. The discovery of carbon nanotubes (CNTs) [1–3] has caused special attention in this context. CNTs exhibit, besides good mechanical properties [4], a high electrical and thermal conductivity [5] due to their graphite-like structure. These properties, in combination with an aspect ratio of up to several thousands, enables the development of electrically conductive polymers using only very low filler contents, such that the composites retain or even improve on mechanical performance of the matrix. Additionally, these nanomaterial filled composites should show an enhanced thermal conductivity.

Presently, a range of nanotube types is available (e.g. single-wall nanotubes (SWCNT), double-wall nanotubes (DWCNT) and multi-wall nanotubes (MWCNT)). These CNTs possess a diameter dependent specific surface area (SSA) of up to 1300 m^2/g (SWCNTs) [6] and can be produced by different techniques. Furthermore, their surfaces can be functionalised with a variety of surface groups to improve their dispersibility. Given these numerous variables, this study aims to investigate and discuss the influence of SSA, aspect ratio, surface functionalisation and interfacial interactions between nanotubes and epoxy matrix on the electrical and thermal conductivity of the composite.

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 realisation of a mechanical reinforcement by CNTs, where a homogeneous dispersion, a good impregnation and a strong adhesion to the matrix is desired [7–9], the electrical conductivity is based on percolated pathways of conductive particles. Electrical conductivity can be explained by the established percolation theory [10], with an onset of the conductivity when a critical filler concentration, commonly named percolation threshold, is reached to form conductive pathways. This critical filler content has been predicted to be 16 vol% for randomly oriented spherical particles. The percolation theory was originally developed for spherical particles, thus having limited validity for rod-like fillers. Rod-shaped particles (e.g. chopped carbon fibres, carbon nanofibres and nanotubes), possess a high aspect

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ratio, a ($a = l/d$ = length/diameter), with $a \gg 1$, and are generally advantageous over spherical particles ($a \sim 1$) with regard to the filler content required to achieve percolation. An advanced percolation theory has been developed by Celzard and Munson–McGee [11,12], which includes the aspect ratio of particles in determining the critical volume fraction required to achieve a conducting, percolated network. The percolation threshold for rod-like particles with aspect ratios of >100, was calculated to be 0.24–1.35 vol% [12]. The divergence from experimentally obtained results, which find lower percolation thresholds, can be explained by the restriction of their model to volumetric effects. For example, Brownian motion of the fillers and any cohesive forces (particle–particle- or particle–matrix interaction), induced by van der Waals- and dipole–dipole interactions (Coulomb-forces) were not considered in their approach.

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) [13–16] were identified. It could be shown that especially the cohesive interactions between particles and towards the matrix gain significant importance in the percolation behaviour 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 content reported so far. The reported critical filler concentrations for CNTs and also for carbon black [17–20] 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 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. Carbon nanotubes exhibit a high thermal conductivity, due to their consistence of carbon atoms assembled in a graphitic structure/lattice. Consequently theoretical thermal conductivities of $\sigma \sim 6600$ W/mK for SWCNTs at room temperature [5] have been predicted. Experiments on isolated MWCNTs showed values of $\sigma \sim 200$–3000 W/mK at room temperature [21,22]. According to this, a certain enhancement of the thermal conductivity of polymer-based nanocomposites, by an incorporation of CNTs can be expected and have also been reported for CNT/polymer nanocomposites [23,24]. However, the observed effects of CNT-incorporation into polymers and the influence of interfacial area, aspect ratio and interfacial adhesion on the thermal conductivity is yet not completely understood.

This study aimed to investigate the influence of the different nanotube types on the electrical and thermal conductivity of epoxy-based composites. The experimentally obtained conductivities will be discussed with regard to the type of CNTs and their aspect ratio, surface area and surface functionalisation. This paper considers the potential of the various CNTs and gives perspectives about which type of nanotube is favourable to be applied as modification to enhance the electrical and thermal conductivity of epoxy resins.

2. Materials and experimental procedure

2.1. Epoxy matrix

The produced nanocomposites consisted of a modified DGEBA-based epoxy resin (L135i) cured with an amine hardener (H137i), supplied by Bakelite/MGS Kunstharzprodukte GmbH, Stuttgart/Germany. This standard epoxy system is commonly used for resin infusion processes (RTM and VARTM), due to its low viscosity of $\eta_{RT} = 250$ mPa s.

2.2. Carbon nanotubes

All nanotubes used as nano-structured modifiers were produced by the chemical vapour deposition (CVD) process. The basic data of the investigated nanofillers such as supplier, length, diameters and graphitisation are given in Table 1 and typical micrographs of their structure are given in Fig. 1. The geometric data, supplied by the manufacturers, were used to

Table 1
Specification of nanoparticles applied in the studies

Type of nanofiller	Diameters (nm)	Length (μm)	Density ρ_{CNT} (g/cm^3) (calculated)	Graphitisation G (%)	Manufacturer/ TEM-image
Carbon black (CB)	$d_{primary} \sim 30$ nm	–	2.25	46.30	Degussa
Printex XE 2	$d_{Aggrte.} \sim 150$			±0.36	Fig. 1(a)
SWCNT	$d_{isol.} < 2$ nm	Up to 10 μm	0.86	92.12	Th. Swan Ltd and Co.
Elicarb				±0.85	Fig. 1(b)
DWCNT	$d_{inner} \sim 2.1$ nm	Up to 10 μm	0.98	85.97	Nanocyl
	$d_{outer} \sim 2.8$ nm			±1.91	Fig. 1(c)
DWCNT-NH$_2$	$d_{inner} \sim 2.1$ nm	Undefined	0.98	79.57	Nanocyl
Amino-funct. (~1%)	$d_{outer} \sim 2.8$ nm	500 nm–5 μm		±3.65	Fig. 1(d)
MWCNT	$d_{inner} \sim 4.0$ nm	Up to 50 μm	2.09	49.01	Nanocyl
	$d_{outer} \sim 15$ nm			±0.73	Fig. 1(e)
MWCNT-NH$_2$	$d_{inner} \sim 4.0$ nm	Undefined	2.09	48.25	Nanocyl
Amino-funct. (~1%)	$d_{outer} \sim 15$ nm	500 nm–10 μm		±0.22	Fig. 1(f)

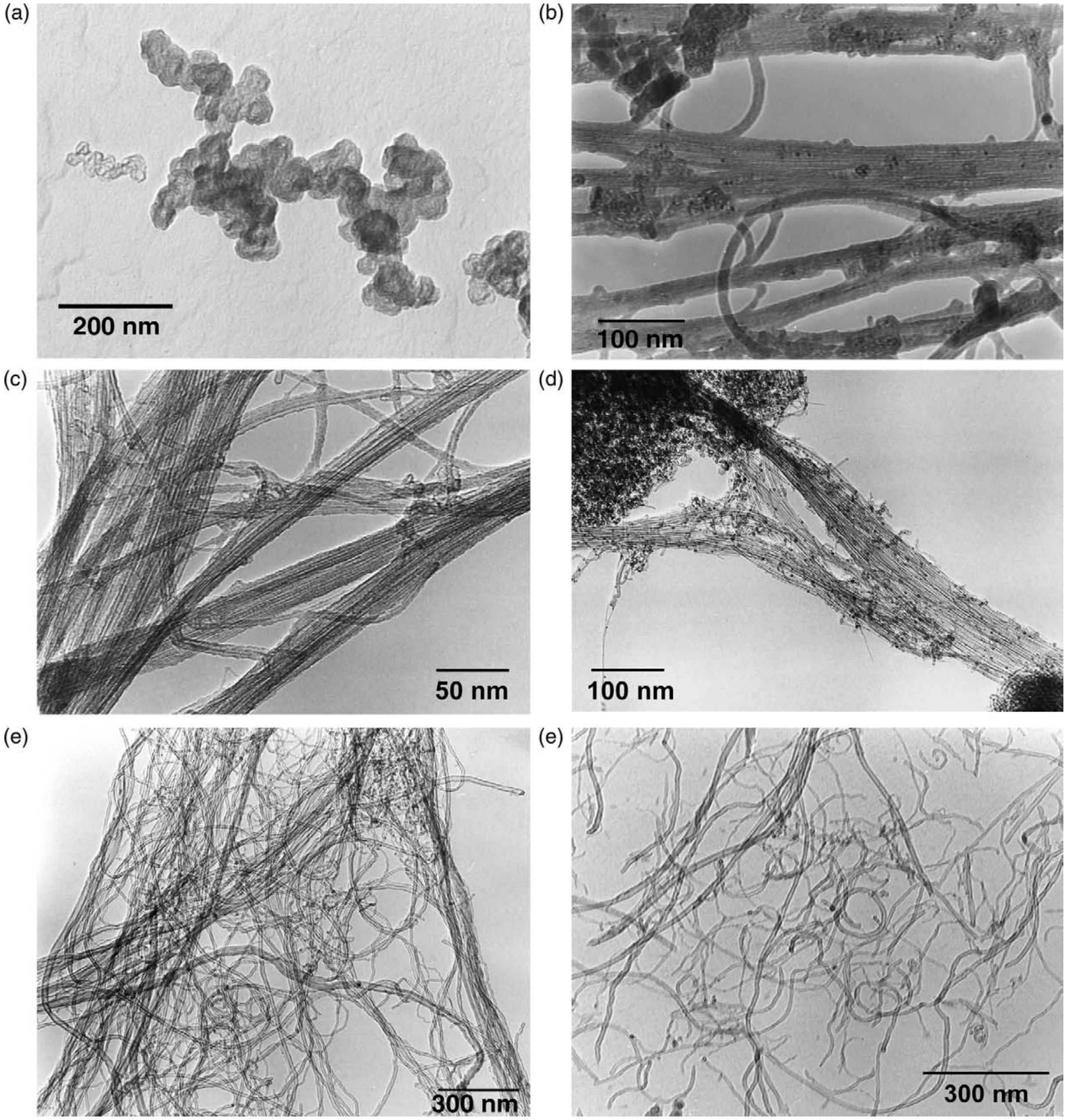

Fig. 1. TEM-images of the investigated nanofillers: (a) carbon black (CB), (b) single-wall CNTs (SWCNT), (c) double-wall CNTs (DWCNT), (d) amino-functionalised double-wall CNT (DWCNT–NH_2), (e) multi-wall CNTs (MWCNT), (f) amino-functionalised multi-wall CNT (MWCNT–NH_2).

calculate the densities, as discussed in Section 3.1. The degree of graphitisation, G, was determined by Raman-spectroscopy and calculated from the observed intensities of the G- (I_G) and D-band (I_D), using the following equation $G=I_G/(I_G+I_D)\times 100\%$. ($G$ will increase with a decreasing number of defects and edges present in the sample).

2.3. Dispersion and processing parameters

The nanoparticles were dispersed in the epoxy matrix by a three-roll mill (mini-calander), as we reported previously [8,9]. The composites were produced using identical processing conditions by varying filler type and content. The roller speed (20, 60 and 180 rpm) and the dwell-time of the batches ($t=120$ s) were kept constant. The suspensions were collected, mixed with the amine hardener for 10 min at 500 rpm, cured for 24 h at room temperature (RT) and post-cured for another 24 h at 60 °C.

2.4. Thermal conductivity measurement

The thermal conductivity was measured using a Hot Disk thermal analyser (Hot Disk AB, Uppsala/Sweden), which is based upon a transient technique. A minimum of eight individual measurements was performed on bulk specimens ($20\times20\times6\ \mathrm{mm}^3$) with the sensor (3 mm diameter) being placed between two similar slabs of material. The sensor supplied a heat-pulse of 0.03 W for 20 s to the sample and the associated change in temperature was recorded. The thermal conductivity of the individual samples was obtained by fitting the data according to Gustavsson et al. [25].

2.5. Electrical conductivity measurement (AC)

The electrical conductivity was measured by dielectric spectroscopy using a HP 4284a impedance analyser. The samples (each five specimens) were tested with voltage amplitude of 1.0 V in a frequency range between 20 Hz and 1 MHz. The conductivity σ was calculated from the complex impedance (Z^*) according to $\sigma(\nu)=1/|Z^*(\nu)|t/A$, where t is the sample thickness and A is the cross sectional area.

2.6. Electron microscopy

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 and allowing a contrast imaging of the fracture surfaces (Section 3.2). The TEM-images were taken using a Philips EM 400 at 120 kV. Ultra thin films of the composites (~50 nm) were obtained by ultra-microtome cutting.

3. Results and discussion

3.1. Electrical properties of CNT/polymer composites

The addition of carbon nanotubes to the epoxy induces an electrical conduction even at low CNT concentrations, which can be explained by the occurrence of conductive pathways at a critical filler concentration. However, the pure percolation theories exhibit only limited validity in case of high aspect ratio nanoparticles, as previously discussed. We tried to find a correlation between the electrical conductivity and the aspect ratio, dispersibility and/or surface functionality of nanofillers, since these factors influenced the particle–particle and particle–matrix interactions. The experimental results of the investigated samples are shown in Fig. 2 as function of the weight content.

As expected, the percolation threshold, defined as the filler content to achieve a conductivity of $\sigma \geq 10^{-6}$ S/m, occurred 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 (graphitisation) of the CNTs determined by Raman spectroscopy (Table 1).

The amino-functionalised CNTs show a higher percolation threshold than the untreated nanotubes, with the threshold ranging between 0.1 and 0.3 wt% for DWCNT–NH_2 and between 0.3 and 0.5 wt% for MWCNT–NH_2. The shifting of the percolation threshold was attributed to the functionalisation process. The amino-groups were introduced by ball-milling the tubes in ammonia, which ruptures the CNTs and thus reduces their aspect ratio. The overall length of the CNTs is difficult to determine, however, the remaining aspect ratio of the CNTs occurred to be in the range around 100 according to the specification of the manufacturer (Table 1) [26]. Therefore, the percolation threshold, which is dependent on the aspect ratio, is shifted to higher filler contents. A second effect, the disturbance of the graphitic structure, which can be related to the treatment, also reduced the conductivity of the tubes, since the introduction of functional groups into a conjugated π-electron system, as in the case of graphite structures, is combined with the formation of sp^3-carbons. The structural changes 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. Finally, the amino-functionalisation significantly improved the affinity between the epoxy and the nanotubes. The reaction of the epoxy resin with the nanotubes' surface-groups formed an electrically insulating epoxy layer, which increases the distance between individual tubes, making the tunnelling of electrons from tube to tube harder. This improved adhesion of the matrix to the nanotubes was confirmed by enhanced mechanical performance of composites containing amino-functionalised CNTs and by TEM-micrographs [27].

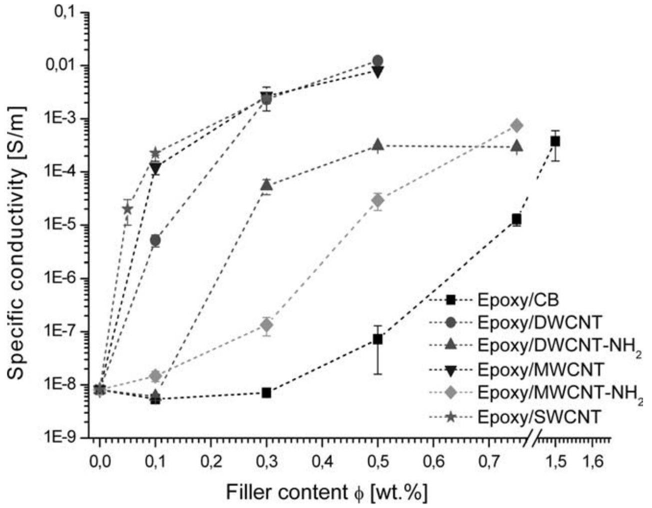

Fig. 2. Electrical conductivity of the nanocomposites as function of filler content in weight percent.

The formation of percolated networks is a volumetric effect and thus the volume content of the different nanotubes needs to be considered as well. However, the volume content of CNTs is difficult to determine due to the dependence of the nanotubes' density on the diameter distribution and defects. Eq. (1) shows an approach suggested by Thostenson et al. [28] to determine the density of CNTs.

$$\rho_{\mathrm{CNT}} = \frac{\rho_{\mathrm{g}}(d_{\mathrm{a}}^2 - d_{\mathrm{i}}^2)}{d_{\mathrm{a}}^2} \qquad (1)$$

The equation considers the inner- and outer diameter of the CNTs (d_i = inner diameter and d_a = outer diameter) and puts them into relation to the density of graphite (ρ_g). It is obvious, that an increasing nanotube diameter is connected to a higher density, limited by the density of graphite. Thin nanotubes (e.g. SWCNTs) consequently exhibit a much lower density than thicker ones (MWCNTs). However, within one batch of CNTs, one will always find diameter distributions consequently influencing the density. A consideration of diameter distributions of the CNTs concerning the density can be achieved by expanding the calculations with a corresponding term. Here, we used a simplified approach, which can be used in order to sufficiently approximate the volume content of the different nanotube types for a qualitative discussion of our results, by using the average diameters given by the manufacturer. The electrical conductivities of the nanocomposites as a function of the calculated volume content are shown in Fig. 3.

It was found that the increase in conductivity with weight percent loading of nanotubes was virtually independent of type of non-functionalised nanotubes (Fig. 2). However, when volume fraction is considered, the nanoparticles with the highest densities show the lowest percolation thresholds. Therefore, MWCNTs seem to have the highest potential of the investigated nanofillers to induce an electrical conductivity to an epoxy matrix. This effect is indirectly related to the relatively low SSA of MWCNTs, which enables a good dispersibility. In order to achieve the conductive network, the incompatibility of the surface potentials of CNTs and epoxy, leads to the required reagglomeration. A functionalisation of the CNTs, which enhances the compatibility to the epoxy matrix and reduces the aspect ratio, can be regarded as detrimental for the overall conductivity. It leads to a stabilisation of the dispersion and the formation of an isolating epoxy layer around the nanotubes in an unlikely case.

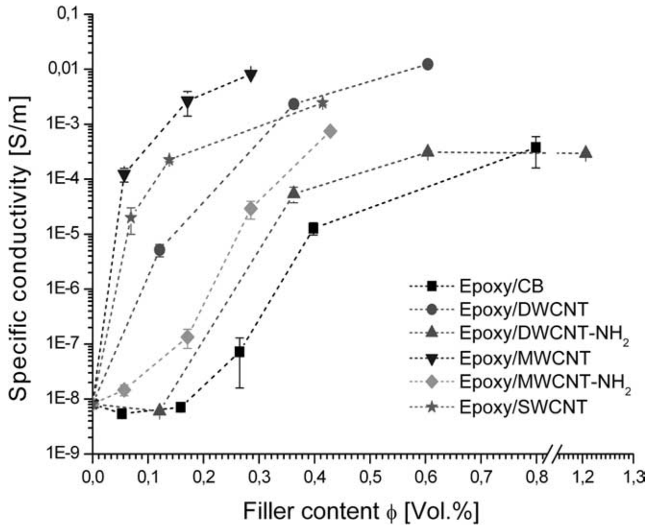

Fig. 3. Electrical conductivity of the nanocomposites as function of filler content in volume percent.

3.2. Contrast imaging of conductive filler networks by SEM

Presently, a visualisation of conductive networks of nanoparticles is difficult. Most of the recent publications used optical microscopy to visualise the formation of microscopic pathways. However, the limitation of magnification and resolution of optical microscopes does not allow an investigation of sub-micrometer structures in the range of individual nanotubes and thin ropes. Recently, Loos et al. [29] reported a powerful technique to visualise CNT-structures embedded in polystyrene using SEM. The differences in charge contrast of conductive filler and isolating matrix has been utilised to image the nanoscaled pathways of percolated filler-particles. We used a similar technique at lower acceleration voltages, thus the penetration depth of the electrons was much smaller, only detecting CNTs onto and slightly under the surface. Fig. 4 shows SEM-micrographs of composites containing 0.1 wt% MWCNTs (Fig. 4(a)) and 0.1 wt% MWCNT–NH_2 (Fig. 4(b)). The surface is bright due to the build up of charge while the dark lines correspond to carbon nanotubes, which provide an electrical earth, thus the conductive pathways become visible.

As it can be seen from the length of the dark lines, non-functionalised CNTs (Fig. 4(a)) exhibit a much larger aspect ratio when compared with the amino-functionalised CNTs (Fig. 4(b)). The reduction of the aspect ratio was attributed to the functionalisation process. Comparing these

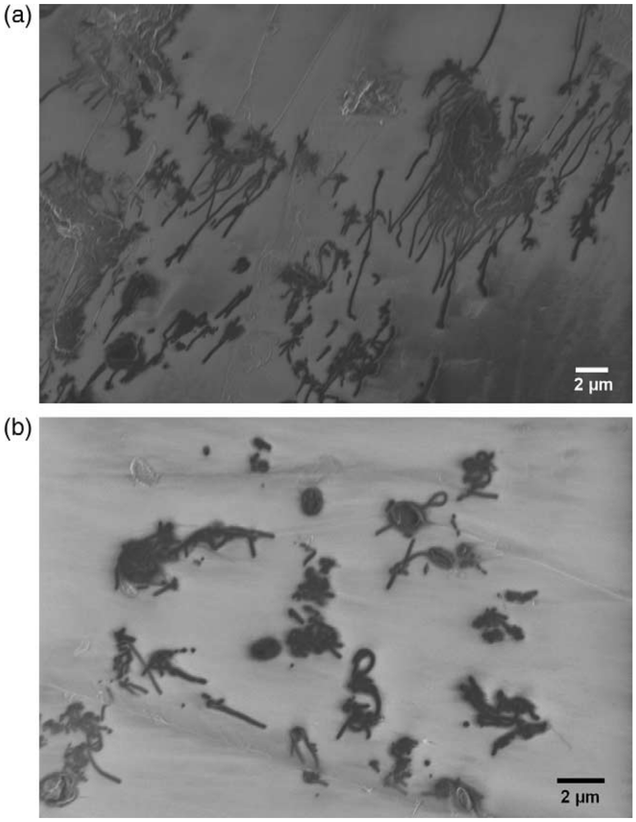

Fig. 4. Scanning electron fractography of a nanocomposite containing 0.1 wt% MWCNTs (a) and MWCNT–NH_2 (b). The conductive pathways of MWCNT (–NH_2) in the epoxy matrix underneath the surface become visible by contrast imaging of the conductive filler.

two micrographs, it is obvious that the critical filler concentration of non-functionalised CNTs to form conductive pathways is lower than for the amino-functionalised CNTs. The MWCNT/epoxy composite, shown in Fig. 4(a), exhibits an electrical conductivity, while the percolation threshold of the MWCNT–NH_2 has not been reached at the same filler concentration.

3.3. Thermal conductivity of CNT/epoxy-composites

The transport of thermal energy in CNTs can be related to a phonon conduction mechanism. The phonon conduction in nanotubes is influenced by numerous processes such as the number of phonon active modes, the boundary surface scattering, the length of the free path for the electrons and phonons and inelastic Umklapp-scattering. Thus, a theoretical description of the phonon conduction mechanisms is non-trival [30]. This study tries to experimentally identify and describe general parameters influencing the thermal conductivity of CNT/epoxy composites. Therefore, we do not refer to the phonon conduction mechanism inside a CNT, and simplify the heat conduction mechanism by assuming a general phonon mechanism.

A correlation of electrical and thermal conductivities with each other leads to further information on the thermal conduction mechanism in CNT/epoxy composites. Phonon conduction by a percolated network of CNTs, would lead to a simultaneous increase in both, thermal and electrical conductivity by several orders of magnitude, when the critical filler content to form the percolated network is reached. Fig. 5 shows the electrical conductivity of the nanocomposites as a function of the thermal conductivity. While the electrical conductivity increases with increasing CNT-content, the thermal conductivity seems to be unaffected. Therefore, a direct correlation between the electrical conductivity, which is based on a percolation mechanism and the thermal conductivity, is not observed on first view. However, a correlation of the experimental data with those attained by theoretical models, indicate some correlation between thermal and electrical conductivity.

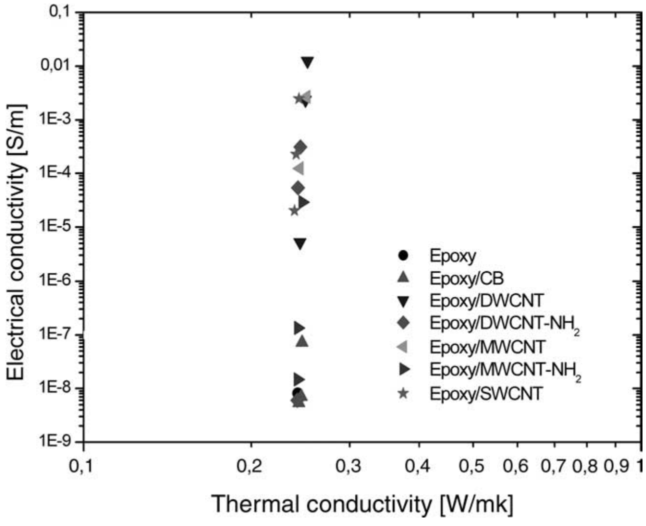

Fig. 5. Electrical conductivity of the nanocomposites as function of their thermal conductivity.

The experimentally determined thermal conductivities, displayed as a function of weight-, volume content and relation to the provided interfacial area per mass unit are shown in Figs. 6–8.

A slight enhancement of the thermal conductivity with increasing filler weight-content was observed (Fig. 6) with our experimental data correlating to results obtained by Song et al. [24] on comparable CNT/epoxy composites. The non-functionalised nanotubes, except from the SWCNTs, led to the strongest improvement of the thermal conductivity, while amino-functionalised CNTs do not significantly affect the thermal conductivity of the epoxy at these low filler contents. Carbon black filled epoxy exhibit thermal conductivities lying between the non-functionalised MWCNTs and DWCNTs and the amino-functionalised CNTs. The unusual behaviour of nanocomposites containing low contents of SWCNTs, showing a lower thermal conductivity than the neat epoxy, will be discussed separately.

There was a correlation between the thermal conductivity and the interfacial area per unit mass (Fig. 7) and the volume content of the nanofillers (Fig. 8). The largest improvement has been observed for non-functionalised CNTs, especially for the MWCNTs exhibiting the smallest SSA.

In order to understand the differences in the behaviour, one has to consider the conduction mechanism of thermal energy. Assuming a phonon conduction mechanism inside the CNTs, the observed behaviour can be explained in terms of interactive forces between the nanofiller and the epoxy matrix, as well as processes occuring at the interfacial area.

According to the crystalline lattice structure of the CNTs, they exhibit significantly higher thermal conductivity than the amorphous epoxy matrix. The phonon transport can be assumed to occur preferably through CNTs, due to the higher number of phonon vibrational modes and the higher free length of path in the crystalline graphite structures, compared to amorphous structures.

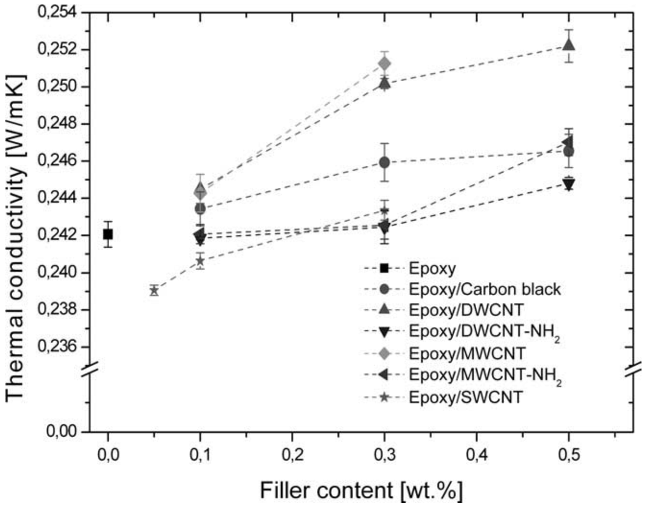

Fig. 6. Thermal conductivity as function of filler content in (wt%).

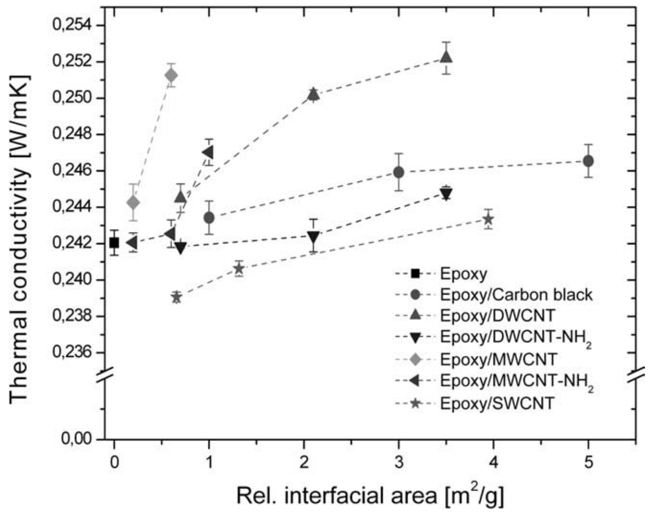

Fig. 7. Thermal conductivity as function of the relative provided interfacial area per gram composite (m^2/g).

Real CNTs are characterised by a large aspect ratio, a huge surface area (interface) and a defected graphite lattice structure.

The phonon conduction of thermal energy in materials is dominated by scattering effects (interfacial boundary- and defect scattering). In addition, the damping of the phonons' vibrational amplitude exhibits some relevance in the same context.

The probability of scattering events is proportional to the number of defects and the overall size of the provided interface and defines the efficiency as thermal conductor. The higher the defect density and the larger the provided interface, the lower the efficiency as thermal conductor. The potential of CNTs and other nanoparticles can, therefore, be considered as limited due to the tremendous surface area, which acts as interface in polymer composites. The dominance of interfacial boundary scattering becomes obvious in Fig. 7. As SWCNTs exhibit the largest SSA, they show the lowest enhancement, followed by DWCNTs (intermediate SSA). Largest improvements are observed for MWCNTs, with the smallest SSA (Fig. 7). Therefore, CNTs with a small SSA have to be favoured to enhance the thermal conductivity of epoxy matrix composites. The influence of phonons being conducted by internal layers may be considered as a superimposing effect as well. Internal layers in MWCNTs cannot interact with the epoxy matrix, thus enabling phonon conduction with a minimum of coupling losses. DWCNTs, exhibiting only one internal layer, show therefore, a relatively lower enhancement than MWCNTs. However, the achieve enhancements can be considered as insignificant.

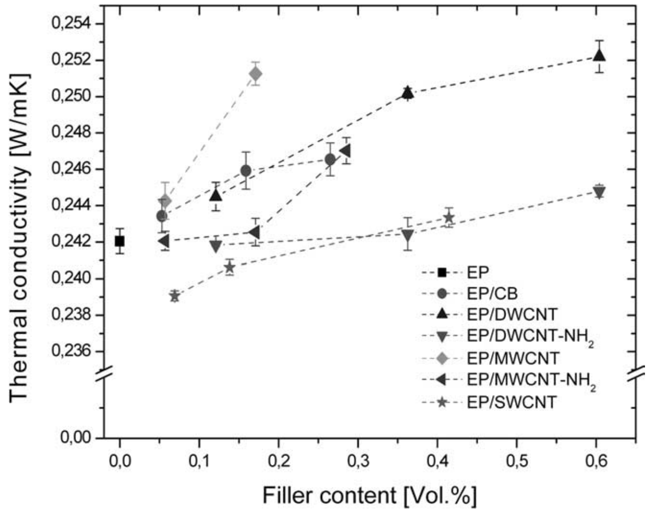

Fig. 8. Thermal conductivity as function of filler content in (vol%).

The aspect ratio of filler-particles acting as thermal conductors in polymers is of certain importance as well, especially when oriented. A high aspect ratio of highly thermal conductive fillers allows a conduction of phonons over a long distance without any transitions from particle to particle. Some evidences were given by the experimental results. However, the influence of the aspect ratio of nanoscaled filler is of minor importance. The large size of the interface dominates the thermal conduction (⇒ interfacial boundary scattering), and thus the interface being the limiting factor of nanoparticles concerning an enhancement of the thermal conductivity of polymers. The aspect ratio will gain importance with reducing the interfacial area as for conventional fillers (e.g. chopped carbon fibres).

The interfacial adhesion between filler and polymer influences the phonon conduction as well, by affecting the damping behaviour of the phonons' vibrational amplitude at the interface. The stronger the interactions between nanotube and epoxy matrix the more intensive the coupling of the highly thermal conductive CNTs with the polymer matrix, being is a poor conductor. A weak interface reduces the coupling effect and, therefore, enhances the efficiency of CNTs as thermal conductor in polymers. Consequently, a strong interfacial adhesion pronounces a damping of the phonons amplitude and has to be avoided in respect of an enhancement of the thermal conductivity by CNTs. The experimental results substantiate the requirement of a weak interfacial adhesion, since the composites containing amino-functionalised CNTs show relatively lower thermal conductivities compared to the corresponding composites with non-functionalised nanotubes. The amino-functionalisation leads to integration of the CNTs into the epoxy network and thus these nanotubes exhibiting the strongest interfacial adhesion.

An unusual behaviour 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. Similar observations of a decrease in the thermal conductivity at low filler contents were made by Moisala et al. [31] in a previous work on SWCNTs–epoxy composites made with a different surface treatment, manufacturing process and resin system, thus proving a systematic effect.

SWCNTs have a potentially higher thermal conductivity than MWCNTs due to a high number of phonon vibrational modes, being even higher compared to graphite structures [32] and additionally a low defect density and thus a low probability of phonon-scattering from lattice defects. It is suggested that the reduced thermal conductivity of SWCNT/epoxy composites is related to the dimensions (diameter) of the nanotubes being closer to the dimension of the duromers than the other investigated nanofillers, which results in a strong interfacial interaction. The phonon conduction will preferably occur through the CNTs, due to higher free lengths of paths in the crystalline graphite lattice compared to the epoxy. A phonon transport in the amorphous epoxy is unlikely, due to its significantly smaller number of phonon vibrational modes.

Phonon transport by SWCNTs will be hindered by the contact to the matrix and consequently the permanent coupling, which induces a high probability of boundary scattering. MWCNTs and DWCNTs, in contrast to SWCNTs, exhibit a much smaller SSA. Importantly, the internal layers shield the conducted phonons, thus these nanotubes showed a relatively higher enhancement of thermal conductivity. Another effect reducing the thermal conductivity is the transfer of phonons from nanotube to nanotube. This transition occurs by direct coupling between CNTs, in case of the improper impregnated ropes, CNT-junctions and agglomerates, or via the matrix. In all these cases, the transition occurs via an interface and thus the coupling losses can be assorted to an intense phonon boundary scattering.

Thick MWCNTs with a high aspect ratio are suggested to be the most favourable type of nanotube for an enhancement of a polymer composite's thermal conductivity. Such nanotubes provide the highest increase for a given volume fraction due to their small surface area and lowest interfacial boundary surface scattering and matrix coupling. Additionally, internal layers enable phonon conduction with a minimum of loss due to a negligible coupling with the matrix. Functionalisation of CNTs and low aspect ratios reduce the relative enhancement of the thermal conductivity dramatically. However, in comparison to the electrical conductivity of epoxy-based composites, the author states that a significant enhancement of the thermal conductivity by carbon nanotubes of $\sigma \sim 5$ W/mK, which would be required for various applications, is unlikely at filler contents which do not affect the mechanical performance negatively.

The thermal conductivity found for the MWCNT(–NH$_2$)/epoxy composites were fitted to theoretical models to understand the mechanisms involved. We chose two simple first-order models, the first was based on the formation of an internal network of the conductive filler within the composite (rule of mixtures) Eq. (2) and the second one assumed the composite material was homogenous and thus the filler particles being isolated in the matrix (parallel electric circuit model, Eq. (3)).

$$\frac{k_c}{k_m} = \phi_m + \frac{k_f \phi_f}{k_m} \tag{2}$$

$$\frac{k_c}{k_m} = \frac{1/k_m}{(\phi_m/k_m + \phi_f/k_f)} \tag{3}$$

k_c thermal conductivity composite
k_m thermal conductivity matrix
k_f thermal conductivity filler
ϕ_m volume fraction matrix
ϕ_f volume fraction filler

A third model to calculate the thermal conductivity of composites, developed by Hatta et al. [33,34], is based on the equivalent inclusion method from Eshelby [35]. We chose this more complex method because of the consideration of the aspect ratio and the averaging of the thermal conductivities of matrix and filler. The final equations for the calculation of the thermal conductivity of short fibre filled composites with a random orientation are given in Eqs. (4)–(7). The thermal conductivity of the MWCNTs was taken as $k_f = 200$ W/mK as given in the literature [21]. This value is lower than the theoretical predictions [5], but we regard this it as more realistic due to the fact that the theoretical values assume structurally perfect CNTs.

$$\frac{k_c}{k_m} = 1 + \phi \frac{[(k_f - k_m)(2S_{33} + S_{11}) + 3k_m]}{J} \tag{4}$$

$$J = 3\frac{(1-\phi)(k_f - k_m)S_{11}S_{33} + k_m[3(S_{11} + S_{33}) - \phi(2S_{11} + S_{33})]}{(k_f - k_m)} \tag{5}$$

$$S_{11} = \frac{1/D}{2\left[(l/D)^2 - l\right]^{3/2}} \left\{ \left(\frac{l}{D}\right) \left[\left(\frac{l}{D}\right)^2 - l \right]^{1/2} - \cos \mathrm{h}^{-1} \left(\frac{l}{D}\right) \right\} \tag{6}$$

$$S_{33} = 1 - 2S_{11} \tag{7}$$

l length of the filler
D diameter of the filler

S_{11} and S_{33} are tensors for the thermal conductivity of anisotropic composites. In the case of isotropic composites,

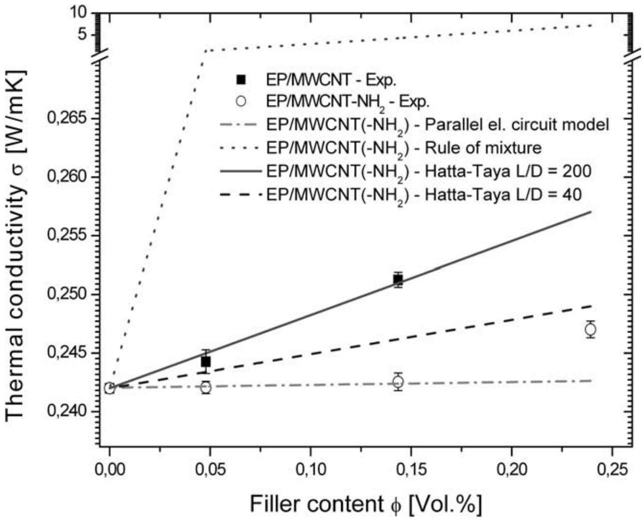

Fig. 9. Correlation of the experimentally obtained thermal conductivities for MWCNT(–NH$_2$)/epoxy composites with theoretical models.

as for a random distribution of fillers, the *S*-tensors are reduced to scalar terms exclusively.

The experimentally obtained thermal conductivities for MWCNT ($-NH_2$)/epoxy composites and the fitted data are shown in Fig. 9. The rule of mixtures calculates the thermal conductivity of the composite, according to the volume fraction of each component, which is regarded as separate phases and neglects interactions between these phases. The separate contribution of the two phases to the thermal conductivity of the composite maximises the effect of the minor phase, which leads to an overestimation of the thermal conductivity by this model. Therefore, this model will give an upper bound for the thermal conductivity. The second model, estimating an isolated state of the conductive filler in the matrix, leads, therefore, to thermal conductivities, which can be regarded as lower bound.

A realistic description of the experimental data of the MWCNT/epoxy composites is obtained applying the Hatta–Taya model (for randomly distributed short fibres). The results for the thermal conductivity are in good agreement with the experimental data.

However, according to the fitted aspect ratio ($l/D=200$), it can be concluded, that the potential of MWCNTs is yet not fully exploited. Further enhancement of the thermal conductivity can be expected by consideration of the length of the MWCNTs ($l\sim 50$ μm) [26], which results in a maximum aspect ratios of up to $l/D\sim 3000$. The observed difference of the maximum and fitted values for the aspect ratio result from an agglomerations of CNTs, their waviness and any shortening that occurs during the calandering process.

A description of the results of the amino-functionalised MWCNTs is more difficult. The best fitting of the conductivities for the two low filler contents was attained for the simple 1st order model given in Eq. (3). It assumes the absence of a conductive network, which is given for this case because the percolation threshold was found to be at higher filler contents, thus the particles can be regarded as isolated [33].

At filler loadings above the percolation threshold, as for the composite with the highest content of MWCNT–NH_2, the thermal conductivity was described by the Hatta–Taya model. This composite exhibits a percolated network, as proved by the electrical conductivity, thus the 1st order model loosing its validity. The fitting aspect ratio of $l/D=40$ is lower when compared to the non-functionalised MWCNTs. This demonstrates again the detrimental effect of functionalisation process, which was observed to rupture the CNTs and a reduction of the effective length.

The thermal conductivity of our CNT/epoxy composites correlates well to the Hatta–Taya model, when the CNT-content exceeds the electrical percolation threshold. We suggest this effect to be related to a reduced distance between the percolated CNTs. This network facilitates phonon conduction by reduced boundary scattering losses. Composites containing CNTs at volume fractions below the percolation threshold, the filler behaviour can be described as an isolated phase, thus the results correspond to simple first order model of a parallel electric circuit.

4. Conclusions

The electrical and thermal conductivities of composites containing different types of CNTs were investigated. The results were discussed in regard to the influence of particle content, interfacial area, influence of surface functionalisation and 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 the electrical and thermal 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 realisation 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.) correspondingly increases the percolation threshold.

An imaging of conductive pathways inside a composite was achieved by contrast imaging using SEM. This new technique can be a useful tool for mechanistic investigation and provides higher resolutions than LM, allowing investigations on a nanoscale. Furthermore, a transparency of the samples is not required, not limiting the filler contents of the samples to be investigated.

The incorporation of CNTs into polymers resulted in a slight enhancement of the thermal conductivity. The overall size of the interface (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 phonon-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 minimises 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 large interface provided by CNTs lead to strong phonon boundary scattering. Additionally scattering at lattice defects minimize the effective thermal conductivity. It has to be pointed out that CNTs and probably further nanoparticles, which provide large interfacial areas, are not suitable for an enhancement of the thermal conductivity of polymer-based composites.

A correlation of the experimental data with theoretically calculated thermal conductivities based on the Hatta–Taya model was obtained, when the filler concentration exceeds the percolation threshold. It could be shown, that the formation of a percolated network of CNTs also had certain influence on the heat conduction. That implied either a certain contribution of electron conduction to the heat transport in CNT/epoxy composites when the filler content exceeds the percolation threshold, or more probable the reduced distance between the CNTs facilitates the phonon conduction by a reduced boundary scattering.

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