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Titania-doped multi-walled carbon nanotubes epoxy composites: Enhanced dispersion and synergistic effects in multiphase nanocomposites

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ABSTRACT

Multi-walled carbon nanotube-epoxy composites are modified with titania nanoparticles in order to obtain multiphase nanocomposites with an enhanced dispersion of carbon nanotubes. The dispersion is monitored using rheological and electrical conductivity measurements. An increase in dispersion quality can be correlated to an increased storage shear modulus of the uncured suspensions and to a decreased electrical conductivity in the bulk nanocomposite. The newly formed microstructure is revealed using transmission electron and optical microscopies. Due to chemical interactions between both types of nanoparticles an attractive potential is generated leading to a significant rearrangement in the particle network structure. Besides an enhanced dispersion, the hybrid structure leads to synergistic effects in terms of the glass transition of the nanocomposites. Although a decrease of the glass transition temperature (T_g) is observed for the nanocomposites containing only one type of filler, the combination of titania and carbon nanotubes into a hybrid structure reduces the decrease of T_g, thus demonstrating the potential of such hybrid structures as fillers for multi-functional epoxy nanocomposites.

1. Introduction

It is well known that nanoparticles posses the potential to significantly modify the properties of a polymeric matrix. This potential depends strongly on the physical nature of each type of particle. Inorganic particles such as montmorillonite, fumed silica or metal-oxide particles mostly affect the mechanical, thermal and functional properties of thermoset polymers [1–6]. In case of titania nanoparticles, optical properties (UV-resistance and transparency) of polymers can be adjusted and they also posses photo-catalytic properties [7–10]. Among all types of nanoparticles carbon nanotubes gained high interest in the last 15 years due to their unique combination of good mechanical and electrical properties [11]. Depending on the processing route and type of carbon nanotubes, percolation thresholds could be found below 0.1 wt.% in epoxy matrix systems [12–14]. Corresponding to inorganic nanoparticles carbon nanotubes also offer the potential for increasing mechanical properties in polymers such as the fracture toughness [15]. An increase of up to 45% could be observed for only small amounts of double-walled carbon nanotubes in an epoxy matrix [16]. Since carbon nanotubes are unique and novel nanoparticles the comprehension and exploitation of these potentials are far from being complete.

The control of carbon nanotube dispersion and its improvement still remains a great challenge. A sufficiently good dispersion is one of the key factors for the transfer of the properties of carbon nanotubes into nanocomposite systems. Their very high specific surface area (up to 1300 m^2/g) leads to high attractive forces which have to be overcome by a dispersion process. Commercially available carbon nanotubes are often in an entangled state, additionally complicating dispersion. Among other reasons, a lack of industrial applications for carbon nanotube-epoxy composites can be directly related to inadequate dispersion methods. Three major approaches have been conducted so far in order to improve the dispersion quality: improved mechanical distribution, chemical functionalisation of carbon nanotubes and the application of dispersing aids.

First, high shear mixing processes are a promising approach to increase the separation of carbon nanotubes. Conventional stirring techniques are often insufficient to disperse carbon nanotubes effectively but they are cost effective and upscaleable to the industrial level. In recent works we described a highly effective shear mixing process, involving a three-roll-mill, in order to produce nanocomposites with a superior dispersion of nanoparticles in an epoxy matrix [6,12,13]. Depending on the processing conditions the electrical properties, e.g., the percolation threshold, can vary significantly [12–14,17].

Secondly, a chemical functionalisation can result in improved dispersion due to improved interactions between the epoxy matrix and carbon nanotubes [18,19]. Additionally, the mechanical properties can be increased because of an enhanced interfacial load

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transfer [9,15,20–22]. Nevertheless, the structure of the nanotube can be destroyed and the length can be shortened which leads to reduced electrical properties [12,23].

The third approach for an enhanced carbon nanotube dispersion is the application of dispersing agents [19,24]. Some work was done using SDS and other surfactants, enhancing the dispersion in organic solvents [23]. Regarding epoxy nanocomposites, only little work was done using commercially available dispersing agents. Typical dispersing agents for epoxy systems are based on block copolymers which may lead to degraded mechanical properties [25,26].

In this work, we describe a new approach for an enhanced carbon nanotube dispersion by the addition of a second type of nanoparticle, which constitutes a third phase. One major advantage of such multiphase systems is the enhanced dispersion combined with advanced physical properties due to synergistic effects. Synergistic effects can often be related to a change of the state of dispersion of one or both types of particles. Depending on the type of filler, interactions between fillers and/or matrix can also vary. Conventional multiphase systems are based on microscale particles with a hybrid structure. For example, synergistic effects were found regarding elastic moduli in rubber systems which already reached industrial application level [27,28]. Interestingly, only few studies were conducted so far in multiphase nanocomposites compared to binary nanocomposites. Ma et al. found an improved state of dispersion in carbon nanotubes/nanoclay in an ABS resin system [29]. The particle combination leads to synergistic effects in elastic modulus and flame retardancy [29,30]. Peeterbroeck et al. found comparable results in EVA-based systems [31]. The combination of carbon black and nanoclay in polyamide can also cause an altered state of dispersion, inducing changes in the electrical percolation behaviour [32]. Liu and Grunlan propose synergistic percolation behaviour for SWCNT/nanoclay epoxy composites with decreasing percolation threshold [33]. Similar results were found in previous studies for carbon nanofibre/clay epoxy composites [34]. Increased electrical conductivities were found in epoxy nanocomposites when blending carbon black and silica [35] or carbon nanotubes and graphite nanoplatelets [36].

2. Experimental

The used polymer matrix consists of a DGEBA-based epoxy resin (Araldite® LY 556), an anhydride hardener (Aradur® CH 917) and an accelerator (DY 070), provided by Huntsman®, Basel/Switzerland. The resin system provides good mechanical and thermal properties ($T_g = 140–150\ ^\circ C$) and is certificated for aeronautic applications. The multi-walled carbon nanotubes (MWCNTs, Graphistrength C100®) have an outer diameter of about 15 nm with lengths up to 10 μm and were supplied by Arkema®, France. The titania nanoparticles (Hombitec RM110®) were supplied by Sachtleben®, Germany. The titania is nanosized with length of about 10 nm. Both types of nanoparticles provide comparable specific surface areas of about 450 m^2/cm^3.

Binary (one type of particle and matrix) and ternary (both types of particles and matrix) nanocomposites were produced using a highly effective shear mixing process including a three-roll-mill as mentioned earlier [6,12,16]. For the binary systems the volume content of the fillers was varied from 0.01, 0.1 to 0.3, respectively. For the multiphase systems the volume content was held constant for one type of filler and varied for the other one as mentioned before, e.g., 0.01 vol.% MWCNT plus 0.01 vol.% titania. Additionally, binary systems with 0.6 vol.% filler content were produced as references. Table 1 shows the resulting matrix of the produced systems.

After dispersion of the nanoparticles with the three-roll-mill and mixing with hardener and accelerator in a vacuum dissolver, dispersion analysis was conducted by rheological investigations on the uncured samples. The rheometer used in this study (Rheologica Stress Tech HR®) offers the possibility of in situ optical microscopy. Frequency sweep tests were conducted at 50 °C with a constant shear stress of 1 Pa. After curing (4 h at 80 °C and 8 h at 140 °C) in an aluminium mould, samples were prepared for impedance spectroscopy. In order to obtain information about the dispersion in the cured state, the AC electrical conductivity was measured in the frequency range between 20 Hz and 1 MHz. The electrical conductivity values used for comparison were taken at 1000 Hz.

Table 1
Overview of the produced nanocomposites

[vol.%]		TiO_2		
		0.01	0.1	0.3
MWCNT	0.01	0.01 + 0.01	0.01 + 0.1	0.01 + 0.3
	0.1	0.1 + 0.01	0.1 + 0.1	0.1 + 0.3
	0.3	0.3 + 0.01	0.3 + 0.1	0.3 + 0.3

Thermal analysis was performed with a Seiko® SCC 5200 differential scanning calorimeter (DSC). After curing of the epoxy nanocomposites in the DSC chamber, following the recommended curing cycle (4 h at 80 °C and 8 h at 140 °C), the samples were heated to 200 °C and cooled down to room temperature. The glass transition temperature (T_g) was determined in a second heating scan. Each cycle was performed at a rate of 10 °C/min. In order to investigate the dispersion of the cured nanocomposites, light and electron microscopies were conducted. The light micrographs were taken in transmission mode at a magnification of 50 with a standard Leitz® light microscope. Samples were prepared by grinding and polishing with resulting thickness of about 200 μm. Transmission electron micrographs were taken using a Philips EM 400 at 120 kV. Ultra thin films of the composites ($w = 50$ nm) were obtained by ultramicrotome cutting.

3. Results and discussion

In principle, the dispersion of carbon nanotubes can be adjusted at two different stages of the production route. First, the initial dispersion can be affected by mixing conditions, functionalisation of carbon nanotubes or dispersing agents. Furthermore, the curing conditions strongly affect the reagglomeration process in epoxy matrices [13,37]. These curing conditions include the curing time and temperature, the way of temperature input and the chemical constitution of the matrix (e.g., amine or anhydride hardener). In order to reveal information at which stage of the production process the presence of titania influences the MWCNT dispersion, cured and uncured samples were compared.

3.1. Rheological analysis

Fig. 1 shows the storage shear modulus (G′) of the uncured binary MWCNT suspensions. Newtonian flow behaviour can be found for the reference and the suspension with 0.01 vol.% MWCNT. The frequency dependence follows a power law with a slope of two. An increase in filler content leads to a significant increase in storage shear modulus for low frequencies which can be correlated with the rheological percolation [38]. Fig. 2 displays the storage shear modulus as a function of filler content of titania at 0.5 Hz oscillation frequency. The addition of titania at a filler content of 0.01 vol.% MWCNT does not lead to any changes in the storage shear modulus. The elastic properties are still dominated by the resin for volume contents below the rheological percolation threshold. For MWCNT contents at or above the percolation threshold the addition of titania leads to changes in the rheological response of the

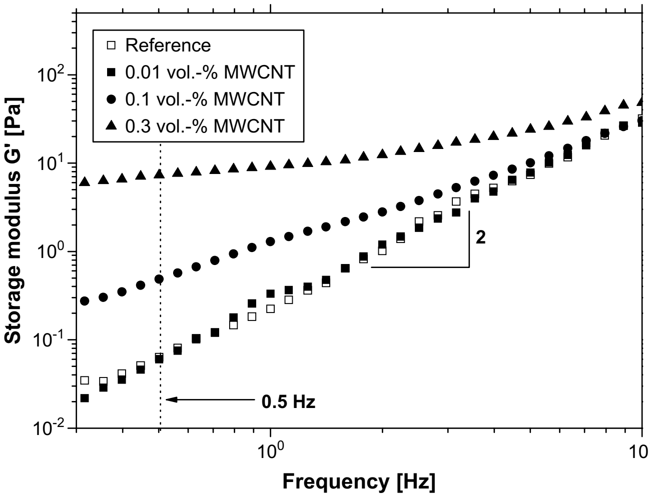

Fig. 1. Storage modulus of the MWCNT suspensions as a function of oscillation frequency.

suspension. In case of the high filled MWCNT systems with 0.3 vol.% the addition of only 0.01 vol.% titania leads to an increase of one order of magnitude in storage modulus, followed by a decrease with increasing content of titania back to the level of the binary MWCNT system. Analogue results can be found for the systems with 0.1 vol.% MWCNT. Here, the addition of 0.01 vol.% titania decreases the storage modulus about half an order of magnitude.

Optical micrographs reveal an improved dispersion quality of MWCNTs due to the presence of titania in the uncured resin system at a filler content of 0.01 vol.% MWCNT. At the end of the oscillation test the MWCNTs tend to form shear induced agglomerates (Fig. 3a) [13]. Titania particles lead to a stabilization of the fine dispersed MWCNT structure achieved after the three-roll-mill dispersion process (Fig. 3b). It has to be mentioned that the revealed changes in microstructure in Fig. 3 cannot be monitored by changes in the rheological response due to the low MWCNT content. Conversely, the described changes in the rheological behaviour for the higher filled systems cannot be monitored in optical micrographs since the transparency of the suspensions is too low. Nevertheless, the storage shear modulus can be directly correlated to the described changes in the microstructure of the uncured resin and turns out to be an appropriate tool to evaluate the dispersion quality.

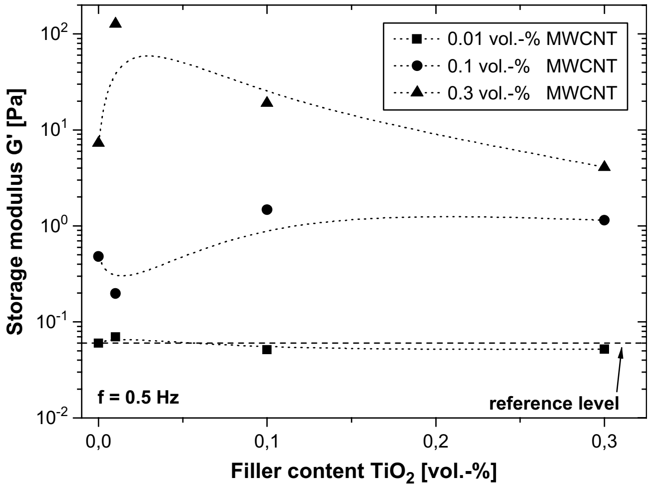

Fig. 2. Storage modulus of the MWCNT/TiO_2-suspensions at 0.5 Hz as a function of filler content of titania. The dotted lines are inserted only for improved visualisation and do not represent a fit of the data.

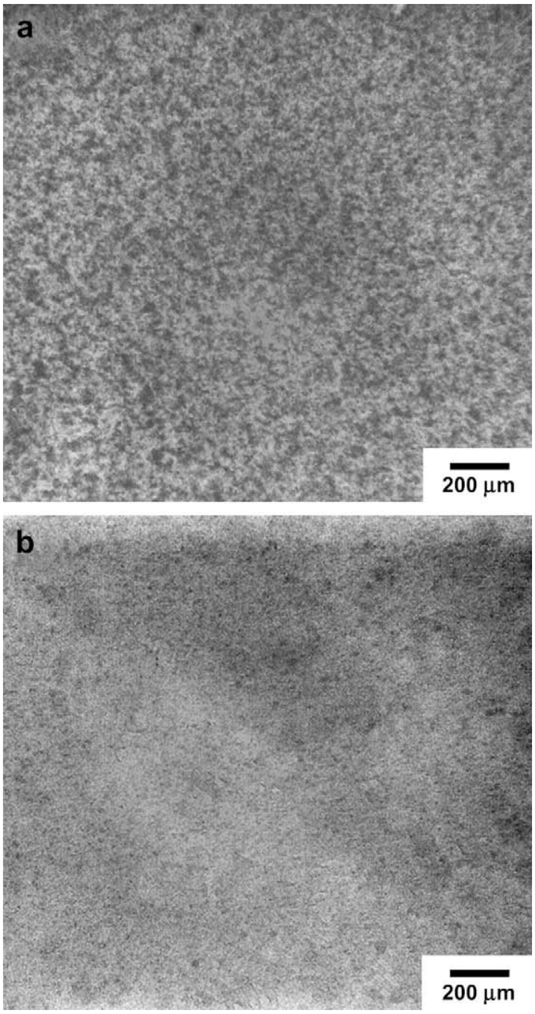

Fig. 3. Optical micrographs of the suspensions taken at the end of the frequency sweep tests. (a) 0.01 vol.% MWCNT, (b) 0.01 vol.% MWCNT plus 0.01 vol.% titania.

3.2. Electrical conductivity

The electrical conductivity is shown in Fig. 4. Analogue to the rheological response, carbon nanotubes exhibit an electrical percolation behaviour which is characterised by an abrupt and sharp increase in electrical conductivity by orders of magnitude since a network of carbon nanotubes is built up [13,39]. The addition of 0.01 vol.% MWCNT leads to a conductivity of around 10^{-7} S/m, which is one order of magnitude higher than the neat resin (10^{-8} S/m). At a filler content of 0.1 vol.% MWCNT the conductivity rises to 3×10^{-4} S/m, well above the percolation threshold. The increase in MWCNT content to 0.3 vol.% leads to a further increase in conductivity up to 10^{-2} S/m.

The formation of such a network is strongly dependent on the type of filler, functionalisation, dispersion process and curing conditions [17]. Thus, the presence of titania decreases the electrical conductivity because of an improved state of dispersion of MWCNTs which is achieved for these ternary nanocomposites. For the ternary nanocomposites containing 0.01 vol.% MWCNT the electrical conductivity values level off as the titania load is increased. A similar trend was observed for the ternary nanocomposites containing 0.1 vol.% MWCNT. If the amount of titania (0.3 vol.%) exceeds the amount of carbon nanotubes (0.1 vol.%) a decrease of several orders of magnitude was observed. Other works reported similar results. The presence of an optimum ratio

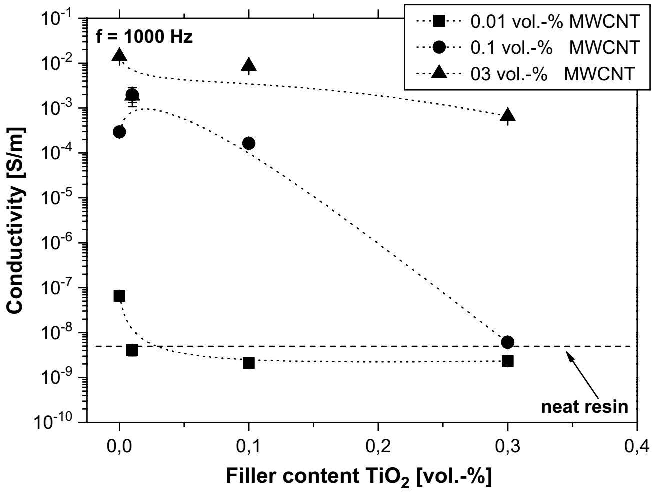

Fig. 4. Conductivity of the cured nanocomposites as a function of titania filler content. The dotted lines are inserted only for improved visualisation and do not represent fitted data.

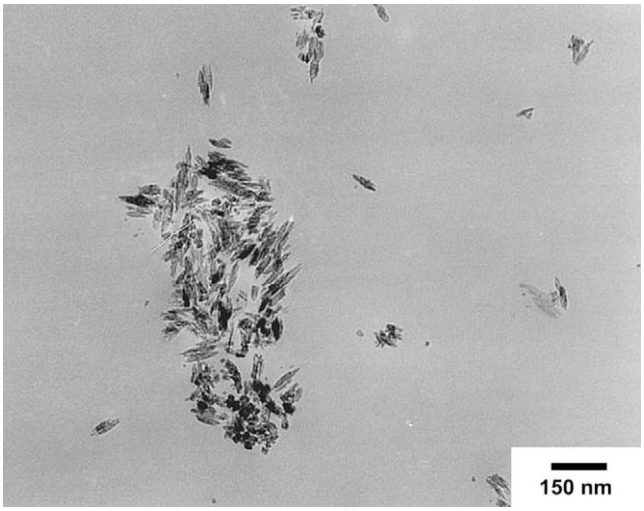

Fig. 5. Transmission electron micrograph of a binary titania nanocomposite (0.1 vol.%).

between conductive and non-conductive fillers seems to exist. Below that critical concentration the conductivity is increased followed by a decrease [35].

Conversely, an almost titania-independent conductivity was found for the ternary systems with 0.3 vol.% MWCNT. Here, the addition of titania only leads to a maximum decrease to 10^{-3} S/m. In principle, systems containing higher amounts of carbon nanotube do not react as sensitive to the addition of titania as the low filled systems. On the account of a pronounced percolated network the amount of titania which is necessary to interrupt these network contacts and thus increases the tunnelling distance increases with increasing MWCNT content. Thus, the percolation threshold is shifted to higher values on account of the addition of titania. It has to be denoted that also contradictionary results were found in the literature: the introduction of nanoclay leads to improved electrical conductivities [33,34]. In this work, we used titania as a third phase which may have a different effect on the carbon nanotube network formation. In the present work, the superior state of dispersion of carbon nanotubes leads to a further increase in dispersion quality with the addition of titania. In contrast, the work by Liu and Grunlan [33] deals with a more agglomerated state of dispersion. Here, the introduction of foreign particles leads also to an enhanced dispersion but is correlated to increased electrical conductivities.

3.3. *Dispersion and distribution of MWCNTs*

Optical and electron micrographs were taken in order to correlate the findings for electrical conductivity with the spatial distribution of the fillers. Fig. 5 shows transmission electron micrographs of a binary system containing 0.1 vol.% titania nanoparticles. Unlike carbon nanotubes, titania does not build up any network or fractal-like structures, since their interparticle interactions are weak compared to MWCNTs [5]. Thus, titania is dispersed homogeneously in the matrix with isolated agglomerates or even isolated primary particles. This fact can also be explained in terms of chemical reactions between the anhydride hardener and the titania nanoparticles. Anhydride hardener molecules might be promptly adsorbed at the surface of titania. Previous studies concerning the adsorption of maleic anhydride onto titanium dioxide suggest that the anhydride ring is opened by the structural defects of TiO_2, which are constituted by five-coordinated Ti^{+4} [40]. Since the amount of such structural defects in nanosized titania is reported to be much higher than bulky titania particles [41], this

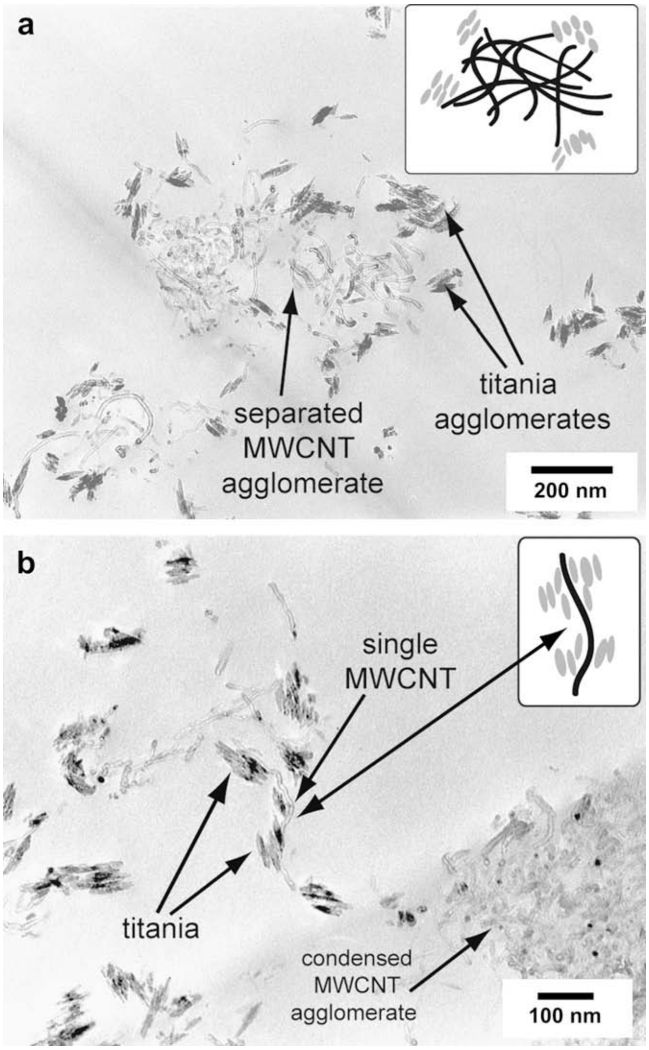

Fig. 6. Transmission electron micrograph of a ternary MWCNT plus titania nanocomposite: (a) MWCNT agglomerate is surrounded by titania, (b) titania covers a single MWCNT. Titania particles appear as short and dark needles while the MWCNTs appear as more light and hollow tubes.

interaction might play an important role on the dispersion of titania nanoparticles in anhydride-containing epoxies.

In multiphase systems, primary particles of titania cover the surfaces of single nanotubes (see Fig. 6b). Agglomerates of titania surround agglomerates of MWCNTs (see Fig. 6a). In Fig. 6 MWCNTs tend to appear shorter than their original length of 10 μm due to the small thickness of the ultramicrotome films. The hybrid structure is mostly independent on the filler concentration, thus Fig. 6 shows representative structures. It has to be mentioned that only fully separated agglomerates can be interpenetrated by titania nanoparticles. Some agglomerates which derive from the previous CVD-production process are condensed and physically entangled (see Fig. 6b). They can neither be separated by the high shear mixing process nor by the incorporation of titania. Therefore, titania can act only as a dispersing aid to free movable MWCNTs. Nevertheless, the strong affinity of titania to aromatic rings (graphite-like structure) [42] can cause the hybrid structure. In previous studies, the attachment of nano-titania on the surface of carbon nanotubes was also found in PAN fibres [43], indicating the importance of this interaction mechanism. Another important effect of such interactions between MWCNTs and titania is related to the zeta-potential (i.e. the surface charge) of the titania nanoparticles. Previous studies on adsorption of polyelectrolytes at the surface of titania demonstrated that the zeta-potential at pH 7 is negative, and decreased even further due to the reactions between the carboxylic acids from these polyelectrolytes and the titania surface [44–46]. Accordingly, titania should be negatively charged after the adsorption of the anhydride hardener and carboxylic acids produced during the curing process. Since MWCNTs are known to have a positive zeta-potential in organic solvents [47,48], it seems likely that the negatively charged titania nanoparticles have a tendency to be attracted by the positively charged surface of MWCNTs. Therefore, this titania-assisted dispersion of MWCNT in the epoxy resin may be explained by electrostatic interactions between the titania and the MWCNT nanoparticles.

The formation of a hybrid structure can lead to an altered state of dispersion, not only in the uncured systems (see Fig. 3) but also in the cured systems. Fig. 7 shows the development of the agglomerate distribution for the ternary systems with 0.01 vol.% MWCNT and titania. The attachment of titania at the surface of MWCNTs is weakening the electrostatic interactions between carbon nanotubes due to less free surface area of MWCNTs. Additionally, the reagglomeration during curing is suppressed due to a steric stabilization (compare Fig. 7a and b) of the nanotube distribution by the titania particles. Further increases in titania content do not lead to changes in the microstructure (Fig. 7c and d) since the MWCNTs are already dispersed well in the matrix. The decrease in transparency does not stem from a further improved dispersion of the MWCNTs but more due to the addition of titania. Thus, the electrical conductivity subsequently decreases as described earlier.

For the systems with 0.1 vol.% MWCNT the effect of titania is less distinguished. In case of the 0.01 vol.% titania system the agglomerate distribution is coarsened, which is in line with the higher electrical conductivity observed for this nanocomposite. For the ternary system with 0.1 vol.% MWCNT and 0.1 vol.% titania a finer structure can be observed. In case of 0.3 vol.% titania the structure is also coarser than the binary MWCNT system but the bulk conductivity decreases by orders of magnitude (compare Fig. 8a and d). Therefore, titania does not only change the distribution of MWCNTs and their agglomerates but also the number of conductive pathways is reduced. Finally, the main controlling effect of the decrease in electrical conductivity can be derived from an increase in tunnelling distance due to a covering of the MWCNTs by titania. The tunnelling distance turns out to be key factor for the development

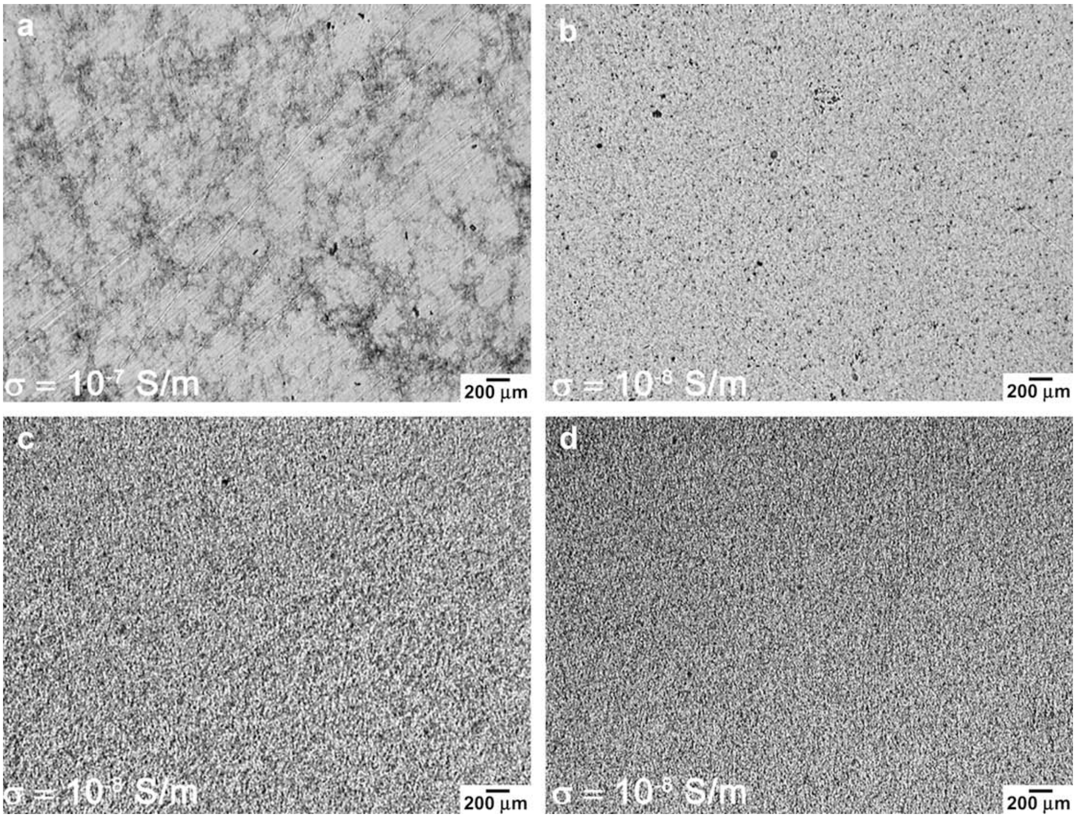

Fig. 7. Transmission light micrograph (50×) of: (a) 0.01 vol.% MWCNT, (b) 0.01 vol.% MWCNT plus 0.01 vol.% titania, (c) 0.01 vol.% MWCNT plus 0.1 vol.% titania, (d) 0.01 vol.% MWCNT plus 0.3 vol.% titania.

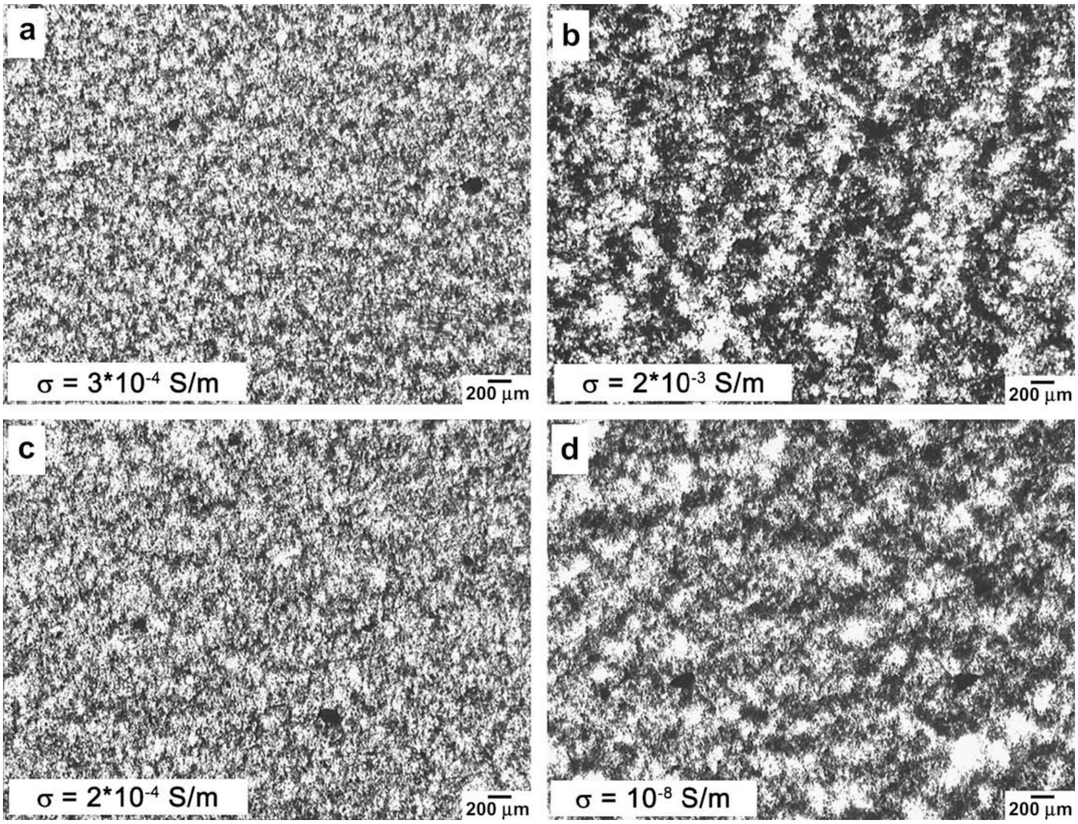

Fig. 8. Transmission light micrograph (50×) of: (a) 0.1 vol.% MWCNT, (b) 0.1 vol.% MWCNT plus 0.01 vol.% titania, (c) 0.1 vol.% MWCNT plus 0.1 vol.% titania, (d) 0.1 vol.% MWCNT plus 0.3 vol.% titania.

of an electrical conductivity in isolating matrices [13]. The coarsening of the microstructure in Fig. 8b probably does not rise from the addition of titania, since the amount turns out to be very small (0.01 vol.%). It is known, that near the percolation threshold effects of curing conditions can have a significant influence on the formation of the percolated network [17], although special efforts were undertaken to keep production conditions constant. Nevertheless, during curing in the mould local inhomogeneities in curing dynamics lead to convection cells in the epoxy, which can cause the coarse structure in Fig. 8b. Thus, at filler concentrations near the percolation the dispersion effect of titania may be counterbalanced due to instable reagglomeration dynamics. In Fig. 8d titania could cause the coarser structure of MWCNTs. Unlike the structure of the low MWCNT filled systems (Fig. 7a and d) the network of MWCNTs is already quite dense and can be even more densified due to higher amounts of titania (0.3 vol.%). In conclusion, if the amount of titania exceeds the amount of MWCNTs an even more agglomerated structure may be found in higher filled MWCNT systems.

3.4. Synergistic effects in glass transition behaviour (T_g)

The hybrid structure in titania/MWCNT multiphase systems and their effect on the state of dispersion leads to synergistic physical effects, e.g., the glass transition temperature (T_g). Fig. 9 shows the T_g of the produced samples. The addition of MWCNTs subsequently decreases the T_g up to 10 °C compared to the neat resin. A similar behaviour is found for the binary systems with titania. Here, the addition of 0.6 vol.% titania leads to a decrease of 16 °C. Increasing volume contents of nanoparticles decrease T_g. The behaviour of the ternary systems differs significantly from the binary systems and is strongly dependent on the filler concentrations of each type of particle. For the ternary systems with

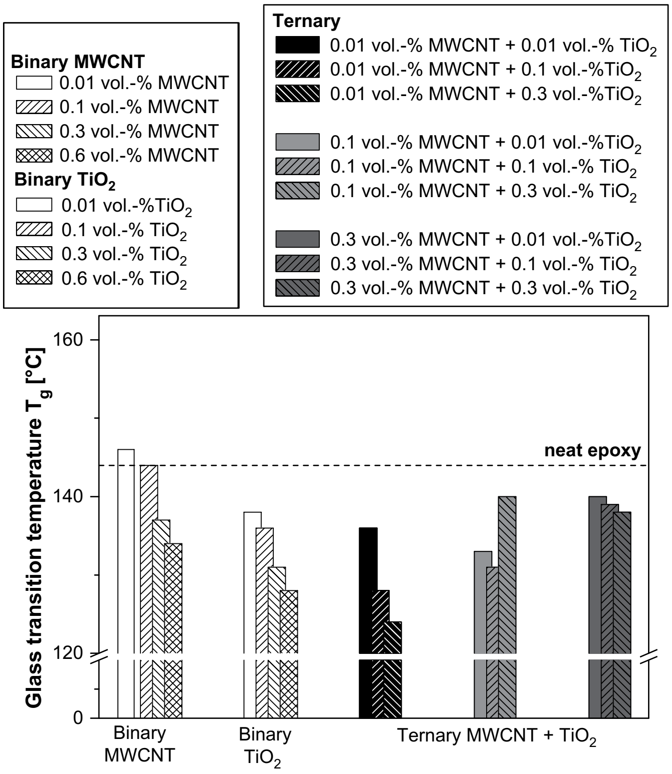

Fig. 9. Glass transition temperatures obtained from DSC scans after curing.

0.01 vol.% MWCNT the decrease is mainly attributed to the addition of titania since the volume content of MWCNT is low. Thus, the behaviour does not differ much from the binary titania systems.

In case of the ternary systems with 0.3 vol.% MWCNT the negative influence of titania is almost vanished (Fig. 9 right columns), since a decrease of T_g with increasing titania content cannot be observed. The T_g of the all ternary systems with 0.3 vol.% MWCNT remains at or above the level of the corresponding binary system. Considering now the overall volume fractions, the ternary systems exhibit a lower decrease in T_g. For example, the ternary system including a total volume fraction of 0.6 (0.3 vol.% MWCNT and 0.3 vol.% titania) exhibits a decrease of only 6 °C, the binary systems with 0.6 vol.% a decrease of 10 °C for the MWCNTs and 16 °C for titania, respectively.

Independent of the titania loading, an increasing MWCNT content leads to an increase in T_g in ternary systems. In contrast, binary MWCNT systems exhibit a decreasing T_g with increasing filler content.

Changes in T_g in nanocomposites are mainly attributed to the formation of an influenced matrix region in the vicinity of the nanoparticles, the so-called interphase. The size and properties of the interphase are strongly dependent on the matrix polymer, the interface chemistry of matrix and particles, and the state of dispersion by means of the effective interfacial area between particles and matrix. Beside its actual importance as a physical parameter, the glass transition temperature is a sensitive parameter to evaluate qualitatively the interphase properties [49].

In thermoplastic polymers the motion of long molecular chains can be altered effectively by adding carbon nanotubes giving rise to increasing T_g [50,51]. In epoxy systems the effect of carbon nanotubes on the structure is more complicated, since the cross-link density can be varied in the interphase by small molecule migration [49,52]. Changes in T_g are small compared to thermoplastics due to the cross-linking, which controls the relaxation processes. The literature does not report any distinguished trend in the thermo-mechanical behaviour, whether positively or negatively. It seems more likely that the chemical structures of matrix and particles and their compatibility are mainly responsible for changes in T_g. Some works describe strong increases in T_g [2,22,53,54] since some other works exhibit almost no or negative influences [1,55–58]. It has to be mentioned that improvements were often found in low property resins with low cross-linking degree or they can be correlated to solvent-assisted production processes. Negative influences were often reported either in highly cross-linked systems or in anhydride cured systems as the one used in this work.

Beside changes in the state of dispersion, we believe that possible interactions between particles and hardener/resin cause changes in the stoichiometry of resin and hardener in the interphase region, and thus a decrease in T_g is observed. In the present study, the epoxy resin is based on DGEBA, which contains aromatic (benzene) rings. These rings can interact strongly with the graphitic layers of MWCNTs, leading to a selective adsorption of the resin since the anhydride hardener does not contain any benzene-like structure [59,60]. In other words, in the vicinity of MWCNT surface there might be a higher concentration of DGEBA molecules as of the anhydride, and an interphase with lower cross-linking degree (due to the excess of resin at the surface of MWCNT) is expected to be formed [52]. Additionally, the cross-linking density tends to be more inhomogeneous.

If titania is dispersed in the epoxy system and the curing reaction once started, it is known that carboxylic acids and their salts are formed as intermediates for the curing process [61,62]. The most common reaction between these acids and titania is the proton-transfer from the carboxylic acid to the titania surface yielding Ti–OH groups and carboxylate anions [63]. Another reaction often reported is the formation of chelate complexes involving the carboxylate anions formed in the first process [61]. Therefore, the nanosized titania might de-activate the anhydride and change the molecular structure of the epoxy system giving rise to materials having a lower cross-linking density due to the incomplete curing reaction. It must be acknowledged that adsorption of carboxylic acids at titania surfaces takes place even after the entire surface of this oxide is covered by covalently bonded carboxylate anions. These reactions might affect the cross-linking density of the cured resin, since the anhydride hardener is expected to be de-activated by the titania, and thus leading to a decrease in T_g.

In ternary systems the chemical interactions between the particles and the matrix are less due to interactions which take place between MWCNTs and titania themselves as described earlier. A significant part of the surface area of the particles is covered by the second type of particle. Thus, the overall surface area of the particles is reduced and leads to less interactions with resin or hardener due to a reduced effective filler content. Thus, the stoichiometry is kept more constant which leads to the best thermal performance in terms of the glass transition temperature for the ternary nanocomposites with an overall volume fraction of 0.6. Besides this geometrical issue, both interactions of particles with the matrix can be compensated by each other. MWCNTs can adsorb resin molecules whilst titania can adsorb the anhydride hardener. Since both types of particles exhibit a tendency for attraction, a more homogeneous cross-linking density in the interphase can be expected.

4. Conclusions

Ternary nanocomposites containing multi-walled carbon nanotubes and titania nanoparticles were successfully produced. The revealed microstructures were characterised by various direct (light and electron microscopies) and indirect (rheometry, electrical conductivity) methods. Synergistic effects were found by means of the glass transition temperature in DSC analysis. Due to intrinsic chemical interactions between the MWCNTs and the titania nanoparticles a hybrid structure is formed without any additional functionalisation of the nanoparticles, characterised by an attachment of titania nanoparticles at the surface of MWCNTs and a covering of MWCNT agglomerates by titania agglomerates, leading to an improved state of dispersion for low filled MWCNT nanocomposites (0.01 vol.%). Rheological investigations combined with in situ optical microscopy can be correlated to changes in the dispersion quality. An increase in the dispersion quality can be monitored by an increase in the elastic response (G'), and thus an increase in viscosity which may affect the processing conditions. In the cured condition, the reagglomeration of MWCNTs can be suppressed by the titania and leads to an exceptional good state of dispersion for low filled MWCNT systems. The increase in the state of dispersion can be directly correlated to a decrease in electrical conductivity, since conductive pathways are destroyed and tunnelling distances are increased by the incorporation of titania nanoparticles in the MWCNT network. Rheometry and electrical investigations turned out to be appropriate tools for the determination of the state of dispersion in MWCNT-epoxy composites. The decrease in the glass transition temperature could be reduced or kept constant in the ternary systems since interactions between matrix and particles, which affect the interphase and thus the T_g negatively, are reduced due to interparticle interactions between both types of particles. Multiphase nanocomposites are a promising approach to improve the dispersion of carbon nanotubes because foreign nanoparticles can act as dispersing agents. Since titania is known to improve mechanical properties of polymers, titania turns out to be advantageous compared to conventional dispersing agents such as block copolymers. Furthermore, highly filled nanocomposites can be produced without worsening the dispersion. The combination of nanoparticles could be one approach to improve thermal stability (T_g) of high performance epoxy nanocomposites, since it turns out to be a crucial issue for the industrial application.

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