European Polymer Journal 47 (2011) 2069–2077

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Combined electrical and rheological properties of shear induced multiwall carbon nanotube agglomerates in epoxy suspensions

S.C. Schulz [a,1,*], G. Faiella [b,1], S.T. Buschhorn [c], L.A.S.A. Prado [c], M. Giordano [b], K. Schulte [c], W. Bauhofer [a]

[a] Institute of Optical and Electronic Materials, Hamburg University of Technology, Eißendorfer Str. 38, D-21073 Hamburg, Germany
[b] Institute for Composite and Biomedical Materials, National Research Council, P.le Fermi 1, 80055 Portici (NA), Italy
[c] Institute of Polymer Composites, Hamburg University of Technology, Denickestr. 15, D-21073 Hamburg, Germany

ARTICLE INFO

Article history:
Received 18 March 2011
Received in revised form 8 July 2011
Accepted 31 July 2011
Available online 12 August 2011

Keywords:
Electrical conductivity
Carbon nanotubes
Agglomeration
Rheological properties
Nanofillers
Dispersion

ABSTRACT

In this work the rheological and electrical properties of semi-dilute carbon nanotube (CNT)–epoxy suspensions have been discussed. The suspensions are produced using two types of industrially available CNTs (Nanocyl 3150 and 7000) and using two different dispersion techniques, namely 3-roll milling and sonication. In-situ optical microscopic analysis and electrical conductivity measurements have been conducted. It is shown that despite using CNTs with similar aspect ratios, the dispersability of the raw material and the time stability of the suspensions are quite different. Additionally, viscosity measurements are used to evaluate the initial dispersion quality and time stability.

1. Introduction

By filling electrically insulating polymers with small amounts of conductive particles, the electrical conductivity of the system can be increased by some orders of magnitude due to network formation of the fillers throughout the matrix [1–3]. The formation of such a conductive network can be understood by using the percolation theory which describes the relationship between the filler content and electrical conductivity [4]. In the case of carbon nanotubes (CNTs), much evidence in literature cites the strong influence of production techniques and process parameters on the final electrical properties of CNT based composites [5–9].

The key problem with CNT based composites is the dispersability of the fillers in the matrix in order to utilize the properties of the pure material. The commercially available CNTs are constituted by several bundles of hundreds of carbon nanotubes that can become entangled or clumped together by amorphous carbon.

The greater than 1 μm long ropes further entangle into networks, due to van der Waals (vdW) attraction. This precludes the dispersion of carbon-powder insolubles in aqueous and organic liquids and thus hinders the nanocomposite production process. CNTs exhibit a surface area several times greater than the surface of conventional fillers [10]. Such a high surface area contributes to the difficulty with dispersing the tubes into matrices. Much effort has been made to incorporate CNTs into polymers in order to take advantage of the exceptional properties of the individual nanotubes, but effective dispersion has proven to be extremely difficult. Hence the resulting composites do not show the expected enhanced properties, in particular with respect to the mechanical performance. Various studies

---

[*] Corresponding author. Tel.: +49 40 42878 3853; fax: +49 40 42878 2229.

E-mail address: carolin.schulz@tuhh.de (S.C. Schulz).

[1] These authors contributed equally to this work.

0014-3057/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2011.07.022

focusing on the improvement of CNT dispersion in different matrices for attaining good electrical properties are present in literature [5,11,12]. Recently, Pegel et al. [13] showed the different dispersion behavior of two commercially available CNT types in high viscous polycarbonate melts. In another study, McClory et al. [14] found a strong dependence of the electrical and rheological percolation threshold on the CNT geometry and functionality. Bauhofer and Schulz [15] showed the strong similarities between high viscous thermoplastic and low viscous epoxy systems.

Only the first part of this paper deals with the relationship between the dispersability of the CNTs in an epoxy matrix and the resulting electrical conductivity of the composite suspensions. Moreover, the dependence of the dispersion quality on the pristine tubes nature as well as on the processing technique has been shown and related to the rheological properties of the suspensions.

It is known that moderate shear can further improve the electrical properties by well-controlled shear induced agglomeration [16–19]. Depending on the applied shear rate and temperature, high and controlled conductivity values can be reached, if the initial filler dispersion is good. In fact, a coarse dispersion of CNTs in the matrix characterized by the presence of pristine, non disrupted bundles negatively influences the electrical conductivity because of the lack of free nanotubes that could contribute to the network formation [13,20–22].

As shown by Huang et al. [23], steady state shear flow measurements are able to directly characterize the dispersion state because the viscosity of the mixture is strictly related to the spatial and orientational distribution of the nanotubes in the matrix. Bad dispersion quality, due to too low forces or insufficient mixing time, results in erratic rheological values.

The work described in this paper is concerned with the simultaneous study of the rheological and electrical properties of a system where the nanotubes are suspended in a Newtonian epoxy matrix. The effect of two different mixing techniques and thus different dispersion qualities were investigated for semi-dilute epoxy suspensions containing two different types of commercially available multiwall carbon nanotubes.

The four different systems were compared regarding the rheological and electrical properties and the shear induced agglomeration tendencies. In this way, it was possible to obtain information about the dispersion abilities of the two production techniques as well as the time stability of the suspensions.

2. Materials and methods

2.1. Suspension preparation

In this study, two types of multiwall carbon nanotubes have been used. They are catalytic carbon vapor deposition (CCVD) grown CNTs purchased by Nanocyl S.A. (Belgium): NC3150 with an average diameter of 9.5 nm, an average length less than 1 μm and a purity exceeding 95 + % and NC7000 with an average diameter of 9.5 nm, an average length of 1.5 μm and a purity of 90%. The nanotubes have been used as received without any purification treatment. The matrix used for the production of the suspensions is an undiluted clear difunctional bisphenol A/epichlorohydrin (DGEBA), EPON™ Resin 828 purchased from Hexion.

The suspensions were produced using two common dispersion methods, which are sonication using a horn ultrasonicator (Misonix S3000) and milling by means of a 3-roll-mill (EXAKT® 120 E). Sonication is often used to produce small batches which makes it favorable for lab size applications [24–26]. In this work, a constant knob control setting of 1.5 has been chosen for sonication of the suspensions in order to have the same amplitude. Suspensions with several wt.% of CNTs have been produce for both types of nanotubes by using 20 g of EPON mixed with the correct amount of nanotubes. Two sonication times have been used for the suspension production, 10 and 120 min, with an average power of 20 W.

However, for larger amounts of material, sonication is not manageable due to the extreme reduction of the vibrational energy with increasing distance from the sonotrode. Here, milling is more favorable achieving good dispersion as shown before [27–29]. The dispersion of the nanotubes in the 3-roll-mill is based on high shear forces arising in the gap between the rolls. The fixed speed for the apron roll has been set at 300 rpm. In this work, the suspensions were produced by using a three cycle program with decreasing distances between the rolls for each cycle. The speed for the apron roll has been set at 300 rpm. The smallest gap size used was 5 μm. Suspensions at different nanotubes concentrations have been produced by milling from 0.02 to 0.1 wt.% CNTs for both types of nanotubes.

2.2. Rheo-optical-electrical experiments

The combined rheological and electrical measurements were carried out using a modified stress-controlled rheometer (StressTech HR, Rheologica Instruments). All measurements were performed in steady mode with an 35 mm parallel plate geometry. The lower rheometer plate is a glass plate with two evaporated rectangular gold electrodes (10 × 5 mm) with a 2 mm gap in between, which measures the conductivity parallel to the shear direction. The other rheometer plate was coated with a reflective, non-conductive coating to allow optical microscopy observations [30]. Optical, electrical and rheological in situ measurements are possible with this test setup. All conductivity and viscosity measurements were carried out with a gap size of 1 mm and varying shear rates between 0.1 and 100 s^{-1} were applied. For image capture, the gap had to be decreased to 0.5 mm to achieve better depth resolution.

All suspensions were pre-sheared with 100 s^{-1} for 60 s before measurement. The temperature for all measurements was set to 60 °C. This procedure and temperature were chosen in order to make the results comparable to previous experiments [15,17]. Additionally, temperatures above 45 °C are necessary to measure changes in the electrical conductivity [17].

Electrical conductivity was measured in AC mode using a HP 4284A LCR meter with a voltage amplitude of 1 V and a frequency of 100 Hz.

2.3. Scanning Electron Microscopy

In order to have a preliminary idea on the quality and structure of pristine nanotubes, Scanning Electron Microscopy (SEM) was performed on raw NC7000 and NC3150. A LEO 1530 FE-SEM (Carl Zeiss GmbH, Germany) microscope was used at an acceleration voltage of 5 kV.

3. Results and discussion

3.1. CNT structure

From the material datasheet provided by the manufacturer, the nanotubes used for the suspension production are similar in diameter, with NC7000 being slightly longer resulting in a higher aspect ratio. From the SEM images, at different magnifications shown in Fig. 1 one can clearly see differences in the grain size of the pristine CNTs.

NC7000 shows big smooth grains with diameters up to 500 μm (Fig. 1a). The grain appears to be constituted by densely packed nanotubes, forming a highly packed structure with smooth surfaces (Fig. 1b). At higher magnification a felt-like structure of small bundles becomes visible (Fig. 1c).

The structure of NC3150 appears to be very different, having smaller grains with a maximum size of 100 μm and more homogeneous grain size distribution (Fig. 1d). The grain structure is less dense than in NC7000, presenting disentangled structures with a ragged agglomerate surface (Fig. 1e). A higher magnification shows dreadlock-like structures with more defined edges and relatively random orientation compared to NC7000 (Fig. 1f).

3.2. Electrical properties

To evaluate the effect of shear rate on the microstructure of the composite and its electrical conductivity, the suspensions were sheared at different levels of constant shear for 5 min ("shear rate step test"). The shear rate was changed stepwise from 100 to 0.1 s^{-1} and from 0.1 to 100 s^{-1}. Four suspensions that were produced with the two nanotubes and two different dispersion techniques have been characterized by following the same procedure of the shear rate step test. As an example, the results for milled NC7000/EPON suspensions with varying filler content are shown in Fig. 2 where the conductivity is plotted as a function of the time for seven different shear rates levels.

It is evident from the plot that constant conductivity values are reached for each applied shear rate within an experimental time of 5 min. Comparable values are reached for a particular shear rate regardless whether a lower or a higher shear rate was previously applied (compare e.g. 0.05 wt.% at 1 s^{-1} in Fig. 2). So, the conductivity

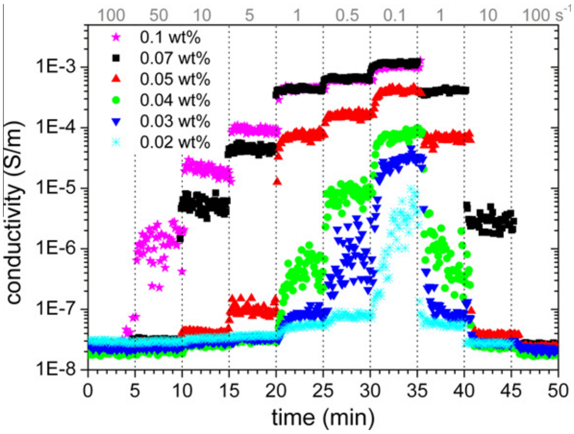

Fig. 2. Constant shear rate step test for milled NC7000/EPON suspensions with different CNT contents. Each shear rate was applied for 5 min. Dotted lines mark changes in applied shear rate.

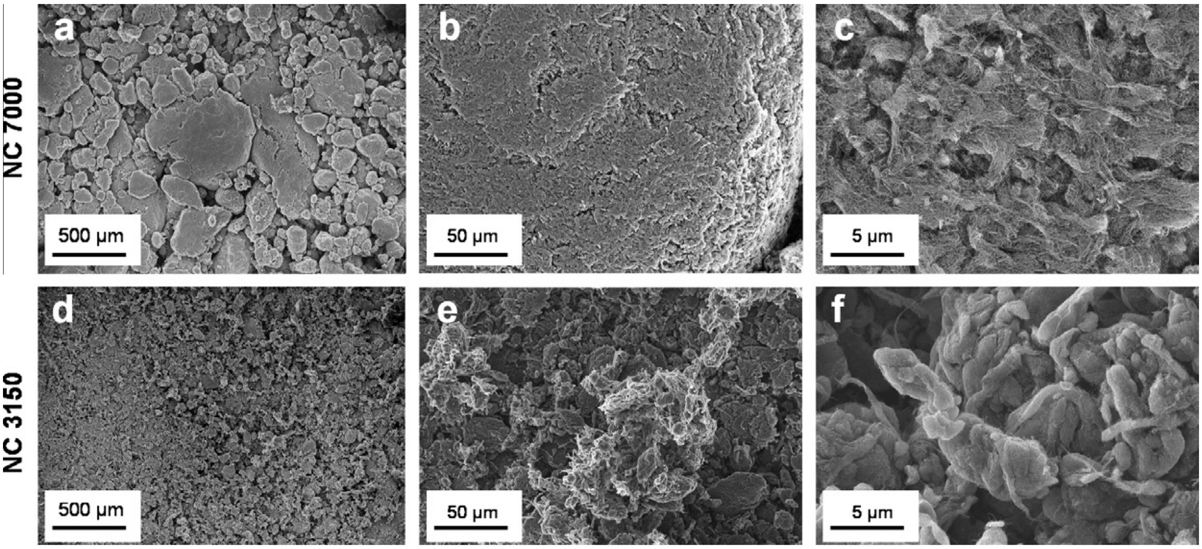

Fig. 1. SEM micrographs of the as-grown carbon nanotubes (top: NC7000 and bottom: NC3150). Magnification is 100×, 1000× and 10,000×.

level is reversible and independent of previous flow history [17]. At 0.1 s^{-1}, the conductivity is increased by five orders of magnitude compared with its initial value at 100 s^{-1} for a 0.1 wt.% CNT/epoxy suspension. Lower shear rates induce higher conductivity levels whereas higher shear rates do not substantially improve the conductivity. This shear-induced insulator-to-conductor transformation can be explained by agglomeration and network formation of the dispersed nanotubes [18,19,31]. At each shear rate the agglomerate formation is regulated by the interaction between constructive and destructive forces. These forces arise from the interaction between the nanotubes and the matrix that either helps or hinders the agglomerate construction [18,31]. Agglomerates can build up during shearing due to constructive forces present at low shear rates. With increasing shear rates, agglomeration growth is stopped when the constructive and destructive forces reach an equilibrium state, and with high shear rates the destructive forces dominate. The agglomerates are broken down. If the concentration of nanotubes is sufficient, the formation of such agglomerates leads to an increase in electrical conductivity. Driven by the shear forces, the agglomerates come in contact with each other to form a conductive path between the electrodes. On the contrary, when the shear rates are too high, the sizes of the agglomerates decrease. Thereby larger distances between the fillers are created. This disrupts the network formation and hence a drop in conductivity is observed.

The effect of applied shear rate on the agglomerate size in the NC7000/EPON system is shown in Fig. 3. The suspension contains 0.05 wt.% CNTs. The images were taken after 5 min of constant shear. After shearing with high shear rate of 100 s^{-1}, the suspension exhibits a homogeneous morphology with very small agglomerates. Decreasing shear rate allows agglomeration growth and hence an increase in agglomerate size, as shown in Fig. 3b and c for shear rates of 10 and 1 s^{-1}. As predicted before, the biggest agglomeration size is reached for the lowest applied shear rate of 0.1 s^{-1} (Fig. 3d).

The effect of increasing filler content on network formation and thus electrical conductivity was also studied. As one can see from Fig. 2, increasing filler content leads to improved electrical conductivity at all shear rates due to decreasing distances between the filler particles and therefore increasing contact. In addition, suspensions with higher filler content are less influenced by shear. Even at a shear rate of 50 s^{-1}, 0.1 wt.% CNT/epoxy suspension shows an increase in conductivity by two orders of magnitude. Suspensions with less filler content show isolating behavior at the same shear rate. Moreover, the maximum electrical conductivity is limited by the concentration of conductive fillers. Interestingly, adding more CNTs does not improve the conductivity at 0.1 s^{-1} for 0.07 and 0.1 wt.% CNT/epoxy suspensions. Here, different conductivity behavior is only observed at higher shear rates (>1s^{-1}). Once a network through the matrix is formed, the conductivity is limited by other parameters like temperature or CNT purity.

The step test also gives information about the time needed by the system to reach steady state particle size and in this way, establish a constant conductivity level. Comparing the conductivity values at 0.1 s^{-1} for all the concentrations, one can clearly see that with increasing the filler concentration a shorter time is needed to reach a constant conductivity. This can be explained by larger distances between the particles at low filler concentrations. Before coming into contact with each other, the particles have to move a longer distance. Even when agglomerates are formed, these can be too small to form an electrical path spanning through the composite for assuring an appreciable electrical conductivity.

To compare the conductivity behavior of the two different CNT types, the average electrical conductivity value at each applied shear rate was calculated for both the NC7000 and NC3150 suspensions. The results are shown in Fig. 4. Scattering of the conductivity values is shown by error bars indicating an inhomogeneous particle size distribution or the formation of a weak electrical path due to a low concentration of nanotubes. For 0.02 wt.%, a stable conductive network formation, even at 0.1 s^{-1}, does not occur despite the formation of small agglomerates. This is reflected in a pronounced scattering of the electrical conductivity. The electrical conductivity values corresponding to the NC3150 suspensions are overall higher than the NC7000 ones. Large differences are shown at intermediate concentrations of about 0.04 and 0.05 wt.% where a slight modification of external parameters (such as tube properties and shear rate) can strongly influence the electrical network morphology. For NC3150, a pronounced insulator-to-conductor transition is measured for 0.04 wt.% between 5 and 1 s^{-1}. For NC7000, a slightly higher filler concentration of 0.05 wt.% is necessary to achieve the same conductivity behavior at the same shear rates. Because of their sensitivity to process parameters, these concentrations can be considered as kinetic percolation thresholds for the NC3150 and NC7000/EPON suspensions at 60 °C [4,6].

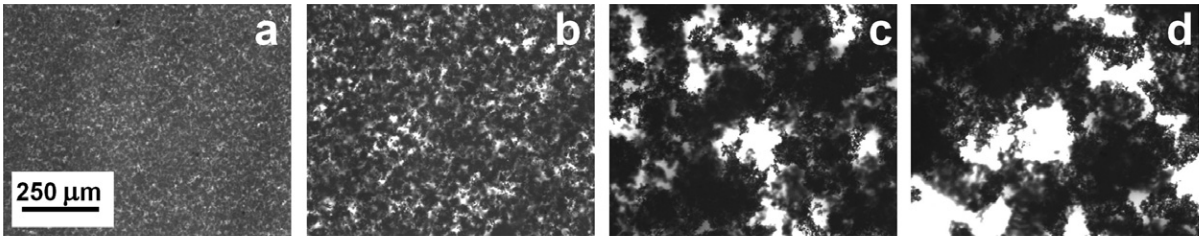

Fig. 3. Optical micrographs of 0.05 wt.% NC7000/EPON suspension after shearing with (a) 100 s^{-1}, (b) 10^{-1}, (c) 1 s^{-1} and (d) 0.01 s^{-1}. Pictures were taken after 5 min of constant shear.

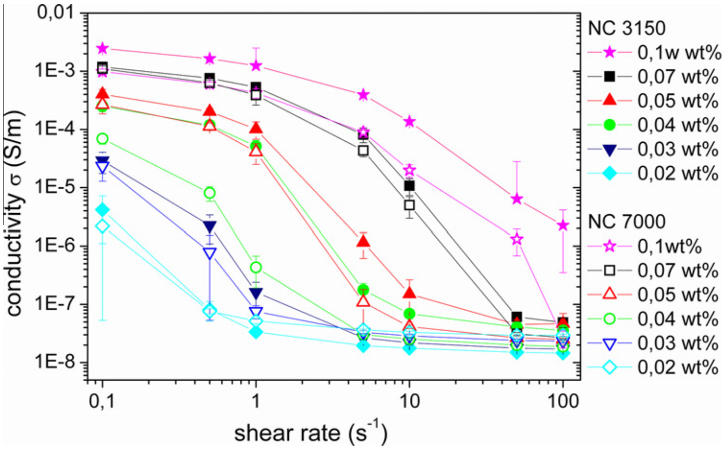

Fig. 4. Average conductivity vs. applied constant shear rate for milled NC7000/EPON and NC3150/EPON suspensions with different filler concentrations at 60 °C.

This observation is quite interesting if one considers that the aspect ratio of the NC3150 is lower than the NC7000, having a shorter length [34]. In fact, with a lower aspect ratio, NC3150 CNTs are expected to provide a higher percolation threshold compared to NC7000 [32]. However, fracturing of the NC7000 during the dispersion process might be one reason. Another possible explanation for such usual behavior might be found regarding the two pristine tube types. The properties of the raw materials affect the interaction with the matrix and hence the quality of the dispersion can be different.

3.3. Dispersion quality

3.3.1. Electrical properties depending on dispersion quality

To achieve good electrical conductivity in suspension, a defined and reproducible dispersion method is a crucial prerequisite. The dispersion method defines the size distribution, orientation and homogeneity of the fillers. The different processing parameters like mixing time or temperature thus have a strong influence on the dispersion properties [15,23]. In the final composite, additional parameters like the kind of hardener, curing time and curing temperature will further influence the electrical properties [25].

To compare different dispersion states, three different mixing procedures were used: milling, sonication for 10 min and sonication for 120 min. In this way, the influence of the mixing method (milling vs. sonication) as well as the sonication time on the electrical properties can be explored for the two different nanotubes types.

In Fig. 5, optical microscopy images of the suspensions are shown after shearing with 100 s^{-1} for 60 s. This preshear was shown to be necessary to induce a conductivity increase by several orders of magnitude in epoxy matrix systems and is related to partial demixing of fillers and matrix [17]. From these images it is possible to appreciate the different dispersion states of the nanotubes in the suspensions produced by milling and sonication. Milling is able to produce a fine and uniform dispersion (Fig. 5a and d), while short sonication times are not able to break up the initial agglomerates of pure CNTs (Fig. 5b and e). Pristine ropes with diameters $d > 100$ μm can be found within the NC7000 suspension after 10 min of sonication. Nevertheless, the miscibility seems to be improved for NC3150 because of fewer and smaller agglomerates. Longer sonication times result in a finer dispersion for both nanotubes suspensions, even if their morphologies are different. The NC3150 suspension sonicated for 120 min is more similar to the milled one, with a fine texture of well dispersed nanotubes. The NC7000 suspension shows an even smoother texture with relatively few, clearly defined agglomerates and a larger fraction of well dispersed CNTs as can be seen from the dark grey background.

Again, in order to study the shear induced agglomeration process in the sonicated suspensions, shear rate step tests were performed. As we know from Fig. 2, the highest shear-induced electrical conductivity is reached at the lowest applied shear rate. To make a clear comparison between the different production methods, average conductivities at steady shear of 0.1 s^{-1} for 0.05 wt.% suspensions are shown in Fig. 6 for both kinds of nanotubes and for the three production methods. These results are in good agreement with the micrographs in Fig. 5. Short sonication times, even with big pristine ropes, were still able to form conductive paths of agglomerates but the final conductivity is lower compared to milled suspensions. NC3150 suspensions reach conductivity values of about 10^{-4} S/m. The conductivity value of NC7000 is one order of magnitude lower. A slight improvement was measured for longer sonication time of 120 min. NC7000 suspensions reach lower values than NC3150. NC3150 achieves conductivity values equal to those obtained by milling. On the basis of these results, it is possible to affirm that in order to achieve reproducible and high conductivity values by constant shear, milling is an appropriate dispersion method for both kinds of nanotubes. Sonication is more selective, providing comparable results only for long sonication times and for NC3150.

3.3.2. Time stability

The exhibited variability of electrical properties reflects a difference in dispersion quality not only due to the

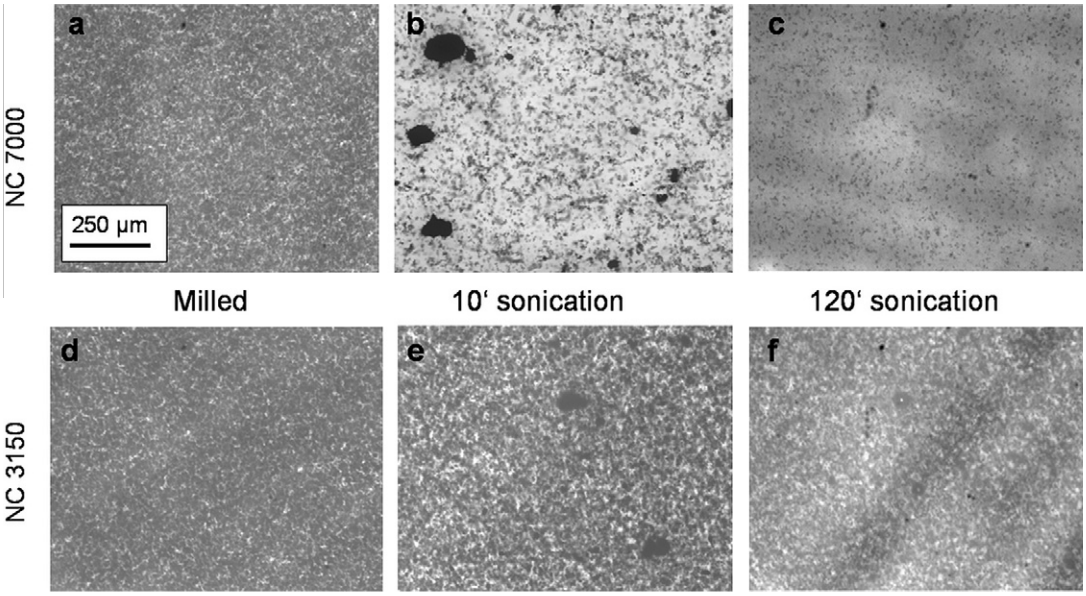

Fig. 5. Light microscopy images of 0.05 wt.% CNT/epoxy suspension after 100 s^{-1} shear at 60 °C: milled (a and d), 10 min sonication (b and e) and 120 min sonication (c and f).

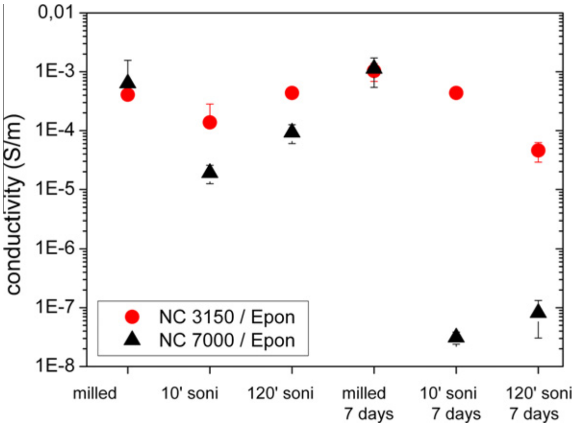

Fig. 6. Average conductivity for different dispersion methods at a constant shear rate of 0.1 s^{-1} for suspensions containing 0.05 wt.% CNTs in EPON measured at 60 °C.

different dispersion method, but also due to the different nature of the nanotubes. These differences can also affect the stability behavior of the suspensions, because it is correlated to the dispersion quality. Time stability properties of CNT suspensions is an important issue related to composites production. The possibility of storing CNT filled epoxy before the addition of the hardener can simplify the production process. It allows a mass production of suspensions (e.g. masterbatches) and a subsequent customization of the final composite through the curing process [25]. For this purpose, the produced suspensions were characterized again after 1 week of storage at room temperature. Milled suspensions showed no decrease in electric conductivity for both kinds of tubes (not shown) while interesting changes occur for sonicated samples (Fig. 6). For NC3150, the conductivity of the suspensions produced by short sonication remains almost constant with respect to the "unstored" material. The conductivity of the suspensions produced by longer sonication decreases after 1 week of storage by one order of magnitude. For NC7000, drastic decreases in conductivity by four orders of magnitude occur after 1 week of storage for both sonication times.

These results indicate that the best time stability is assured by using milling as the dispersion method for both types of nanotubes. Sonication provides very poor stability even after long sonication times for NC7000/EPON and better time stability for NC3150/EPON systems.

Because of the inhomogeneous dispersion of NC7000 suspensions confirmed by light microscopy (Fig. 5b), sedimentation is assumed to be one reason for the lack in time stability. Additionally, higher content of impurities like metal catalysts could increase the instability of the system and in this way accelerate the sedimentation process. From the material datasheet of the nanotubes the purity of NC7000 is defined to be lower compared to NC3150 [33]. In order to explain the sedimentation and lack of time stability of NC7000 suspensions, thermogravimetric analysis (TGA) was conducted on both types of nanotubes. All data is shown in Table 1. Fig. 7 contains the TGA curves of the NC7000 and NC3150. These samples have been heated up to 900 °C

Table 1
Results of TGA analysis for both types of CNTs and specific surface area (SSA) determined by BET.

CNT type	Amorphous carbon* (wt.%)	Catalyst** (wt.%)	Amount of CNT (wt.%)	SSA (m^2/g)
NC3150	6.0	0.0	94.0	280
NC7000	8.0	7.4	84.6	250

* From the TGA curve under N_2.
** From the TGA curve under air.

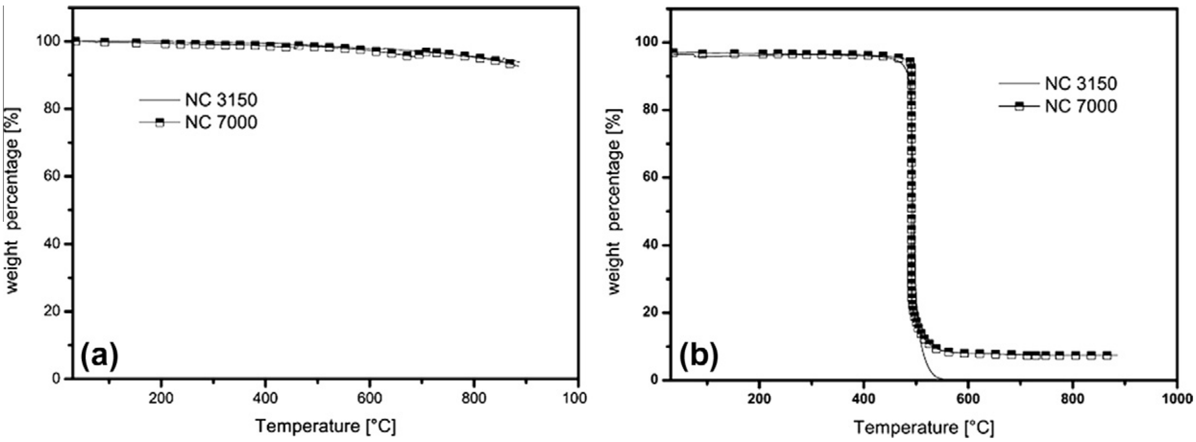

Fig. 7. TGA analysis of pristine NC3150 and NC7000 under N_2 (a) and air (b).

under N_2. The weight loss during this step can be roughly regarded as the amount of amorphous carbon impurities. The residue was then cooled down to room temperature and then the purge gas was changed to synthetic air (see Fig. 7b). Although the onset of degradation was around 490 °C, which is close to the observed value for other commercially available CNTs [34], the amount of residue at 900 °C is much higher for the NC7000 (7.4 wt.%). NC3150 contains almost no catalyst, since the char yield after heating up to 900 °C under synthetic air is nearly 0 wt.%.

Hence, it is possible that the pronounced sedimentation phenomenon in NC7000 suspensions is associated to the presence of metal impurities. Impurities are generally encapsulated in the head of the nanotubes. The heavy metals sediment quickly, taking with them a large amount of nanotubes. In this way, they reduce the effectively available amount of conductive filler within the suspension.

Another explanation might be found in a different specific surface areas (SSA) of the two nanotube types. The surface area of nanotubes induces strong attractive forces between the tubes, often leading to excessive agglomeration/entanglement behavior and thus worse dispersability [7,10]. The measured SSA values are shown in Table 1. The SSA of both kinds of tubes are quite similar, with an unexpected slightly higher value for NC3150. Thus, we assume that the main reason for the worse dispersibility of NC7000 is the difference of the raw material structure and the higher power input needed to break down the big NC7000 agglomerates.

3.4. Viscosity depending on dispersion state

Adding solid fillers to a suspension generally increases the initial viscosity of a system. For CNT/epoxy systems, various studies investigating the dependence of the suspension viscosity exist [35–38]. Regarding the pristine materials used, a common rheological behavior was observed: epoxy resins often behave like Newtonian liquids showing a constant viscosity independent of the applied shear rate. With increasing filler content a viscosity increase at low shear rate takes place. Further increase of the filler content usually results in shear thinning behavior of the suspensions. Additionally, shear-induced agglomeration at a fixed concentration is detectable if the agglomeration process is fast and thus happening during the measurement time.

To examine the influence of the different dispersion states on the rheological properties, steady shear flow measurements were performed with decreasing shear rates in the range from 100^{-1} down to 0.5 s^{-1} with 10 s measurement time. As we know from shear rate step testing, the system reacts within seconds on the applied shear rate if the concentration of the fillers is sufficiently high. Suspensions with a concentration of 0.05 wt.% CNT were tested due to their fast agglomeration times (as shown in Fig. 2).

As we can see from Fig. 8, the used resin shows a constant viscosity of 230 mPa s over the measured shear rate range. Scattering at lower shear rates is due to instrumental limitations under the given conditions.

As one can see from Fig. 8a and b, an identical rheological behavior is evaluated for milled suspensions of both nanotube types. They show a strong shear thinning behavior, starting from a viscosity of 650 mPa s. All NC3150/EPON suspensions prepared by sonication show lower viscosity values at low shear rates except the one sonicated for 10 min. Due to incomplete dispersion of the 10 min sonicated suspension, the interpretation of viscosity data is less reliable because of the initial presence of large agglomerates, which could get squeezed and lead to erratic interpretation of the rheological behavior.

By means of rheological measurements, it was also possible to evaluate the large viscosity changes that occurred after 1 week of storage in the NC7000/EPON suspensions, as shown in Fig. 6, through the evaluation of the electrical properties. The viscosities of the sonicated suspensions at low shear rates decreased by nearly 50% after 1 week of storage with respect to the fresh suspensions. Viscosity values slightly above those of the pure resin are reached. Moreover, pronounced shear thinning behavior disappears almost completely. The flattening of the viscosity curves occurs in coincidence with the strong decrease in electrical conductivity, indicating the occurrence of substantial changes in the dispersion state. A possible explanation is the migration of the undispersed large agglomerates towards the center of the rheometer plates. In a parallel-plate

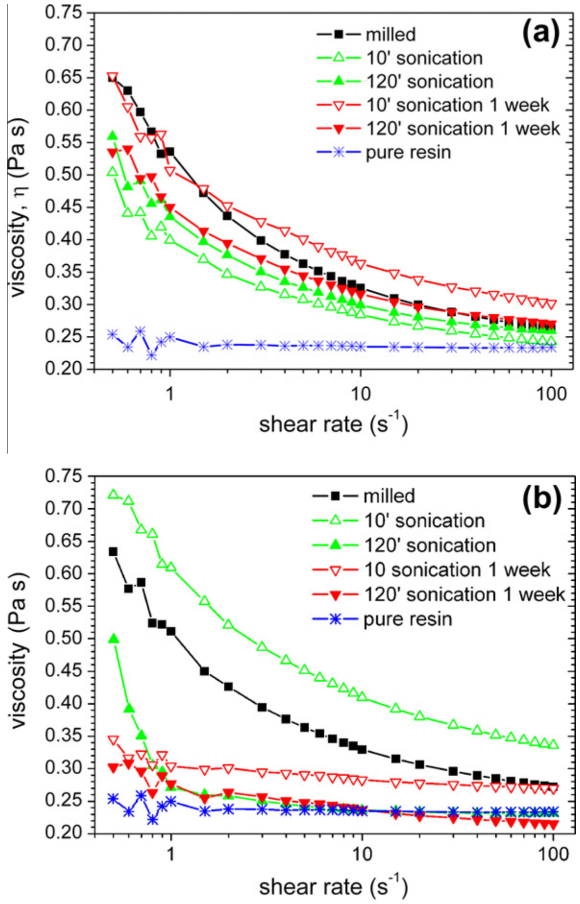

Fig. 8. Viscosity depending on applied shear rate for 0.05 wt.% CNT/epoxy suspensions: (a) NC3150 and (b) NC7000 at 60 °C. The suspensions were produced by milling and sonication with two different mixing times and partly stored for 1 week. The viscosity of the pure resin is given for comparison.

device, the shear rate varies from zero at the center of the flow ($r = 0$) to its maximum value at the edge ($r = R_{\mathrm{plate}}$). If the agglomerates, caused by the shear force gradient, gather towards the middle of the plates, they do not contribute to the flow resistance any longer. The suspension at the plate edge impoverishes which explains the strong decrease in viscosity and the nearly Newtonian liquid-like behavior for poorly dispersed suspensions.

An important achievement of this work is the correlation between the rheological, the electrical and the material properties. In fact, it is impressive how strong the correlation between the viscosity and conductivity is: the shear rate dependence of the viscosity can be related to agglomeration tendency of the suspension. This in turn determines the electrical behavior of the suspension under shear. In fact, if the viscosity shows a shear thinning behavior, it means that the dispersion of the nanotubes in the suspension is such that it is possible to form shear induced agglomerates. However, it is important to highlight that the requirement of a good initial dispersion is necessary, because insufficient initial dispersion leads to erratic viscosity values as shown in Fig. 8.

4. Conclusions

The results illustrate the importance and interdependence of several factors which are generally relevant in conductive nanocomposite related studies.

From a theoretical perspective it is clear that percolation models cannot reliably predict properties of heterogeneous media if the dispersed phase is distributed in a non-trivial manner. This work shows that, even if they would include more presumably important factors, properties would still be difficult to predict in most cases.

The results show, especially for particles with high aspect ratios, their dispersability and subsequent distribution is the result of a sequence of rather complex kinetic interactions with each other and the matrix. Even though factors such as particle geometry, agglomeration, shear rate and viscosity are shown to be important, their influence is hard to predict. They are most probably not independent but are covariant, and the parameters as well as their relationships may vary throughout the production process. Thus, macroscopic properties cannot be determined reliably even from a more comprehensive set of parameters. It becomes necessary to include the nature of the interactions throughout the whole production process. Obviously, a documentation of reported results would thus need to be extremely comprehensive to allow precise comparisons. This suggests that systematic determination of the covariance of parameters in simulations and experiments needs to be done before arriving at a more accurate empirical formula encompassing the kinetic effects in percolation.

From a practical perspective, the experiments on CNT–epoxy suspensions highlight several important parameters. Processing or storage may affect properties such as conductivity, percolation threshold, morphology, viscosity, or the time stability of properties in some cases dramatically. On the one hand, this gives the compounder flexibility to tune the composite properties to desired values. On the other hand, this complexity is generally detrimental to quality consistency.

Remedies would include a more detailed raw material characterization and choosing production methods that allow for tighter close control and higher reproducibility whenever possible. The further upstream in the processing chain these are, the more constitutive this choice is likely to be for the range of achievable properties.

The further downstream processing steps are, the more they can influence a properties' terminal value. Relatively stable values can be achieved when one phenomenon dominates the others and levels out. For example, when a steady very large shear rate reduces the agglomerate size, shortens the particles to one critical length, and lets the distribution approach a random state.

Acknowledgments

The authors would like to thank COST for financial support, Thea Schnoor (Institute of Polymer Composites/TU HH) for help with SEM and Dr. Carlos A. García-González (Institute of Thermal Separation Processes, TU HH) for help with BET.

References

[1] Sandler JKW, Kirk JE, Kinloch IA, Shaffer MSP, Windle AH. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. Polymer 2003;44(19):5893–9.

[2] Kovacs JZ, Mandjarov RE, Blisnjuk T, Prehn K, Sussiek M, Müller J, et al. On the influence of nanotube properties, processing conditions and shear forces on the electrical conductivity of carbon nanotube epoxy composites. Nanotechnology 2009:155703 (15).

[3] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. Compos Sci Technol 2009;69(10):1486–98.

[4] Kovacs JZ, Velagala BS, Schulte K, Bauhofer W. Two percolation thresholds in carbon nanotube epoxy composites. Compos Sci Technol 2007;67(5):922–8.

[5] Huang YY, Terentjev EM. Tailoring the electrical properties of carbon nanotube-polymer composites. Adv Funct Mater 2010;20(23):1–7.

[6] Zhang C, Wang P, Ma C, Wu G, Sumita M. Temperature and time dependence of conductive network formation: dynamic percolation and percolation time. Polymer 2006;47(1):466–73.

[7] Fiedler B, Gojny FH, Wichmann MHG, Nolte MCM, Schulte K. Fundamental aspects of nano-reinforced composites. Compos Sci Technol 2006;66(16):3115–25.

[8] Rosca ID, Hoa SV. Highly conductive multiwall carbon nanotube and epoxy composites produced by three-roll milling. Carbon 2009;47:1958–68.

[9] Thostenson ET, Chou TW. Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. Carbon 2006;44(14):3022–9.

[10] Peigney A, Laurent C, Flahaut E, Bacsa RR, Rousset A. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon 2001;39(4):507–14.

[11] Zhou YX, Wu PX, Cheng ZY, Ingram J, Jeelani S. Improvement in electrical, thermal and mechanical properties of epoxy by filling carbon. Express Polym Lett 2007;2(1):40–8.

[12] Antonucci V, Faiella G, Giordano M, Nicolais L, Pepe G. Electrical properties of single walled carbon nanotube reinforced polystyrene composites. Macromol Symp 2007;247:172–81.

[13] Pegel S, Pötschke P, Petzold G, Alig I, Dudkin SM, Lellinger D. Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts. Polymer 2008;49(4):974–84.

[14] McClory C, McNally T, Baxendale M, Pötschke P, Blau W, Ruether M. Electrical and rheological percolation of PMMA/MWCNT nanocomposites as a function of CNT geometry and functionality. Eur Poly J 2010;46:854–68.

[15] Bauhofer W, Schulz SC, Eken AE, Skipa T, Lellinger D, Alig I, et al. Shear-controlled electrical conductivity of carbon nanotubes networks suspended in low and high molecular weight liquids. Polymer 2010;51:5024–7.

[16] Kharchenko SB, Douglas JF, Obrzut J, Grulke EA, Migler KB. Flow-induced properties of nanotube-filled polymer materials. Nat Mater 2004;3(8):564–8.

[17] Schulz SC, Schlutter J, Bauhofer W. Influence of initial high shearing on electrical and rheological properties and formation of percolating agglomerates for multiwall carbon nanotube/epoxy suspensions. Macromol Mater Eng 2010;295(7):613–7.

[18] Skipa T, Lellinger D, Saphiannikova M, Alig I. Shear-stimulated formation of multi-wall carbon nanotube networks in polymer melts. Phys Status Solidi B 2009;246(11–12):2453–6.

[19] Skipa T, Lellinger D, Böhm W, Saphiannikova M, Alig I. Influence of shear deformation on carbon nanotube networks in polycarbonate melts: interplay between build-up and destruction of agglomerates. Polymer 2010;51(1):201–10.

[20] Du F, Scogna RC, Zhou W, Brand S, Fischer JE, Winey KI. Nanotube networks in polymer nanocomposites: rheology and electrical conductivity. Macromolecules 2004;37(24):9048–55.

[21] Ma AWK, Mackley MR, Chinesta F. The microstructure and rheology of carbon nanotube suspensions. Int J Mater Form 2008;1(2):75–81.

[22] Ma PC, Mo SY, Tang BZ, Kim JK. Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites. Carbon 2010;48(6):1824–34.

[23] Huang YY, Ahir SV, Terentjev EM. Dispersion rheology of carbon nanotubes in a polymer matrix. Phys Rev B 2006;73:125422 (12).

[24] Faiella G, Musto P, Di Florio G, Buosciolo A, D'Orazio L, Antonucci V, et al. Monitoring the dispersion process of SWNTs in aqueous solutions by UV–vis and Raman spectroscopies. J Nanosci Nanotechnol 2009;9:1–8.

[25] Faiella G, Piscitelli F, Lavorgna M, Antonucci V, Giaordano M. Tuning the insulator to conductor transition in a MWCNT/epoxy composite at substatistical percolation threshold. Appl Phys Lett 2009;95:153106.

[26] Martone A, Formicola C, Giordano M, Zarrelli M. Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites. Compos Sci Technol 2010;70(7):1154–60.

[27] Gojny FH, Wichmann MHG, Köpke U, Fiedler B, Schulte K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. Compos Sci Technol 2004;64(15):2363–71.

[28] Chapartegui M, Markaide N, Florez S, Elizetxea C, Fernandez M, Santamar A. Specific rheological and electrical features of carbon nanotube dispersions in an epoxy matrix. Compos Sci Technol 2010;70(5):879–84.

[29] Wichmann MHG, Sumfleth J, Fiedler B, Gojny FH, Schulte K. Multiwall carbon nanotube/epoxy composites produced by a masterbatch process. Mech Compos Mater 2006;42(5):395–406.

[30] Schulz SC, Bauhofer W. Shear influenced network dynamics and electrical conductivity recovery in carbon nanotube/epoxy suspensions. Polymer 2010;51:5500–5.

[31] Alig I, Skipa T, Lellinger D, Pötschke P. Destruction and formation of a carbon nanotube network in polymer melts: rheology and conductivity spectroscopy. Polymer 2008;49(16):3524–32.

[32] Balberg I, Anderson CH, Alexander S, Wagner N. Excluded volume and its relation to the onset of percolation. Phys Rev B 1984;30(7):3933–43.

[33] NC7000 and NC3150 product datasheet, www.nanocyl.com.

[34] Prado LASA, De la Vega A, Sumfleth J, Schulte K. Noncovalent functionalization of multiwalled and doublewalled carbon nanotubes: positive effect of the filler functionalization on high glass transition temperature epoxy resins. J Polym Sci B 2009;47:1860–8.

[35] Allaoui A, Bounia NE. Rheological and electrical transitions in carbon nanotube/epoxy suspensions. Nanoscience 2010;6(2):158–62.

[36] Rahatekar SS, Koziol KKK, Butler SA, Elliott JA, Shaffer MSP, Mackley MR, et al. Optical microstructure and viscosity enhancement for an epoxy resin matrix containing multiwall carbon nanotubes. J Rheol 2006;50(5):599–610.

[37] Fan ZH, Advani SG. Rheology of multiwall carbon nanotube suspensions. J Rheol 2007;51(4):585–604.

[38] Hobbie EK. Shear rheology of carbon nanotube suspensions. Rheol Acta 2010;49(4):323–34.