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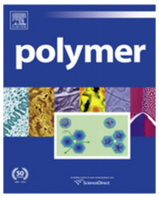

Shear influenced network dynamics and electrical conductivity recovery in carbon nanotube/epoxy suspensions

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ABSTRACT

Destruction and re-formation of conductive filler networks in a low viscous carbon nanotube (CNT)/epoxy system were investigated by online rheological, electric and optical measurements. A combined experimental setup allowed for a well-defined shear deformation of the suspension which led to a decrease in the electrical conductivity by three orders of magnitude due to network destruction and agglomerate size reduction. Subsequent to the shear induced deformation, a complete recovery of the conductivity was observed. In contrast, persistent changes in the microstructure after different shear treatments have been observed. A simple model combining classical electric percolation and time-dependent cluster aggregation was adopted to give a quantitative description of the recovery process. Recovery and aggregation process of CNT in epoxy are comparable with the behaviour in high viscous matrix systems.

1. Introduction

In recent years, the use of carbon nanotubes (CNT) in different matrixes such as polymer melt or epoxy systems has become a popular subject of research due to the excellent mechanical [1–4], electrical [5–8], and thermal [7,9] properties of the composites.

By mixing electrically insulating matrixes with small amounts of conductive particles, it is possible to increase the electrical conductivity by a few orders of magnitude due to network formation of the fillers throughout the matrix [10,11]. In comparison to other conductive fillers, the advantage of using nanotubes is the low demand for content needed to improve the conductivity [5].

The physical properties of carbon nanotube composites strongly depend on the network structure of the fillers and its formation; both are generally controlled by the thermorheological pre-history or the processing conditions [12–14]. Most commonly, fillers dispersed in a matrix are isolated from each other at low filler concentrations. The suspension shows insulating behaviour due to the absence of conductive parts. Above a certain filler content, also known as the percolation threshold, the system exhibits an insulator-to-conductor property transition. At this point, an increase in conductivity by some orders of magnitude is observed [15]. It was found that the concentration for percolation strongly depends on nanotube properties such as length, diameter, aspect ratio, purification or entanglement [16].

Flow-induced flocculation was observed and successfully modelled in a variety of fibre suspensions [17–20]. It was shown that shear forces are able to lower the onset of percolation down to one order of magnitude below the static percolation threshold in carbon nanotube (CNT)/epoxy suspensions. This effect is known as “kinetic” percolation [21]. As recently shown, this effect is only detectable after a pretreatment of the suspension with high shear rates [22]. Demixing of the fillers and the matrix was used as an explanation for this “initial shear effect” changing strongly the electrical and rheological properties. Both the rheological as well as the optical responses were studied for a number of different polymer–carbon nanotube systems [23–27]. However, no single experiment has taken advantage of a combined setup to measure the electrical, optical and rheological properties so far. Alig et al. [27–30] studied the recovery behaviour for CNT/polycarbonate systems in detail. We showed that the shear induced agglomeration behaviour is amazingly similar in different systems such as CNT/epoxy and CNT/polycarbonate [31]. In this study, we want to find similarities for the recovery process for these two systems.

The work described in this paper focuses on the simultaneous examination of the electrical conductivity and optical microstructure of a system in which the nanotubes are suspended in a low viscosity Newtonian epoxy matrix. These time-dependent properties were investigated after controlled steady shear deformation (recovery process).

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Our experiments were performed with CNT/epoxy suspensions with 0.1 wt% of CNT close to the electrical percolation concentration. The results are to contribute to the understanding of carbon nanotube agglomeration in general. The aim of this paper is to study the role of nanotube agglomeration in electric conductivity improvement and the influence of different shear treatments on the network regeneration. Additionally, we want to compare the recovery process in different systems such as CNT/epoxy and CNT/polymer melt.

2. Experimental

2.1. Suspension preparation

The suspension used in this study contains 0.1 wt% multiwalled carbon nanotubes (MWCNT) and was prepared by mixing epoxy resin and carbon nanotubes.

The polymer matrix consisted of a diglycidyl ether of bisphenol-A epoxy resin (Araldite LY 556) obtained from Huntsman Advanced Materials (Belgium). Multiwalled carbon nanotubes grown by catalytic chemical vapour deposition (CCVD) were supplied by Nanocyl S.A. (Belgium) specified with an average outer diameter of 9.5 nm and a length of up to 10 μm.

The suspensions were mechanically mixed using a dissolver disk rotating at 2000 rpm for 2 h at room temperature [21]. Similar techniques were shown to yield good dispersion results [10,21,23]. The electrical percolation of such highly-stirred samples in the cured state was determined to be $\Phi_C^{statist} = 0.15$ wt% applying static percolation theory.

The used 0.1 wt% suspension showed an electrical conductivity of approximately 4×10^{-9} S/m measured at room temperature, as outlined below. Hence, there is no conductive behaviour. Therefore, even for suspensions, the used concentration lies below the electrical percolation threshold.

2.2. Rheo–optical–electrical experiments

The combined rheological and dielectric measurements were carried out using a stress-controlled rheometer (StressTech HR, Rheologica Instruments). The rheometer was modified as schematically shown in Fig. 1 to carry out optical measurements. All measurements were performed in steady mode with a 35 mm parallel plate geometry. The lower rheometer plate consists of a glass plate with two evaporated rectangular gold electrodes (10 mm × 5 mm) with a 2 mm gap in between, in order for the conductivity to be measured parallel–parallel to the shear direction. The other rheometer plate was coated with a reflective coating to allow for optical microscopy measurements. With this special setup, optical, electrical and rheological in-situ measurements are possible. All measurements were carried out with a gap size between 0.5 and 1 mm and varying shear rates between 0.1 and 100 s^{-1}. Samples referred in the text as “pre-sheared” were sheared with 100 s^{-1} for 60 s. The temperature for all measurements was 70 °C. This temperature was chosen in order to make the results comparable to previous experiments [22,32]. Additionally, temperatures above 50 °C are necessary to measure changes in the electrical conductivity [31,32].

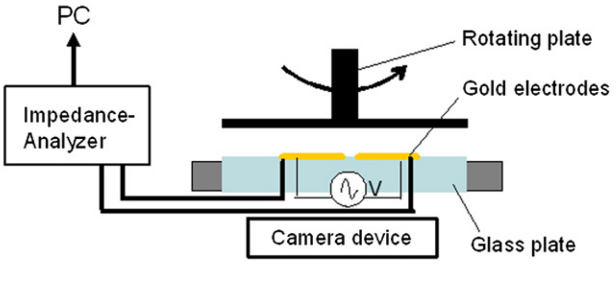

Fig. 1. Schematic representation of the combined setup for simultaneous electrical, optical and rheological measurements.

We performed the dielectrical measurements in AC mode using an HP 4284A LCR meter with a voltage amplitude of 1 V at a frequency range of 100 Hz–1 MHz. A frequency of $f = 200$ Hz was taken to be DC representative.

3. Results and discussion

3.1. Build-up of conductive network by shearing and annealing

The CNT/epoxy system was processed in two different ways to achieve an electric conductivity improvement: (a) by isothermal annealing without shear and (b) by constant shearing followed by quiescent annealing (“2-step-test”). The latter was pre-sheared for 60 s with a shear rate of 100 s^{-1} and then constant sheared with 1 s^{-1}. The realtime monitoring of the electric conductivity for the two measurements is shown in Fig. 2. It can be seen that annealing alone does not noticeably improve the conductivity. After 3 h of annealing, a conductivity of 5×10^{-8} S/m is measured. In contrast the sheared suspension shows a drastically improved electric conductivity compared to the initial value. During shearing, a constant conductivity value that is three orders of magnitude higher than the initial value is reached. This constant value is reached within less than 5 min and its magnitude depends on the applied shear rate. Lower shear rates induce higher conductivity levels whereas higher shear rates do not improve substantially the conductivity. This shear induced insulator-to-conductor transformation can be explained by agglomeration and network formation of the dispersed nanotubes [22,27,31].

The suspension contains homogeneously dispersed small agglomerates after pre-shearing as shown in Fig. 3a. Further shearing at a lower shear rate (1 s^{-1}) creates bigger agglomerates (compare Fig. 3b and c). It has been shown that pre-shear treatment at high shear rates is necessary to achieve conductivity improvement [22]. The mechanism for this necessary pre-treatment is assumed to be related to “demixing” or phase separation of fillers and matrix.

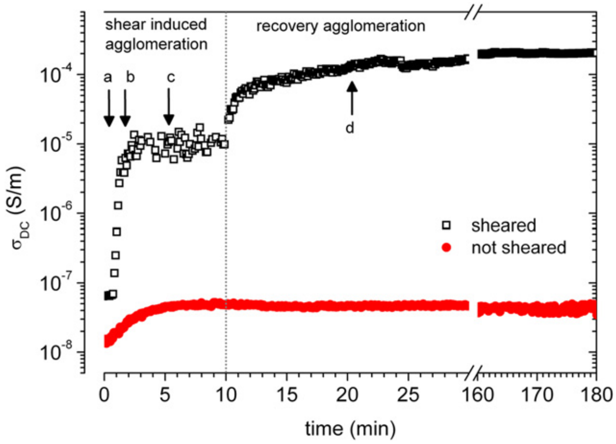

Fig. 2. DC-conductivity of a pre-sheared 0.1 wt% filled CNT/Epoxy suspension measured at 70 °C during 10 min of steady shear with 1 s^{-1} and 3 h of quiescent annealing (□) and quiescent annealing without any shear (●). Shearing induces insulator-to-conductor transition. The dotted line indicates the end of the applied shear. Arrows indicate the moment when an image was taken (see Fig. 3).

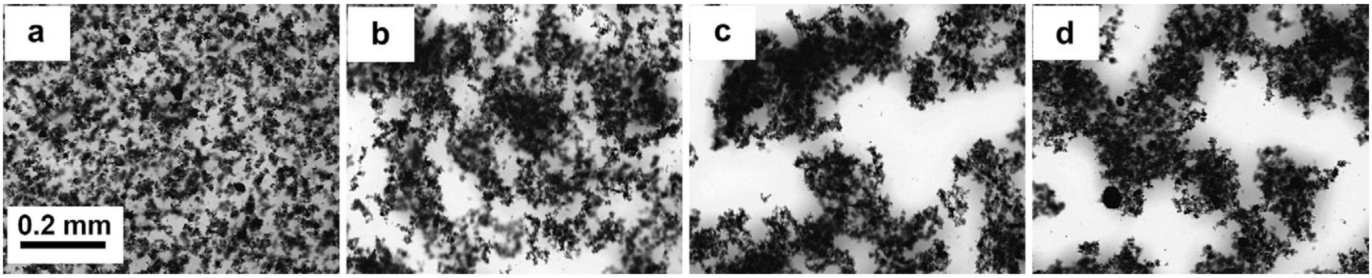

Fig. 3. Optical micrographs of the sheared sample shown in Fig. 2 at 70 °C: (a) starting point after pre-shear with 100 s^{-1}, (b) shear induced agglomeration after shearing with 1 s^{-1} for 50 s, (c) 300 s and (d) secondary agglomeration after 10 min of relaxation without shear.

In the time remaining after shearing, an additional conductivity increase by one order of magnitude is observed. This improvement is suspected to be due to further agglomeration and thus network formation, also visible in Fig. 3d. Diffusion caused by Brownian motion as well as the attractive potential between the agglomerates induces the formation of thermodynamically stable agglomerates, as discussed by Wessling [33,34] and Sumita [35].

3.2. *Shear induced destruction of conductive network and recovery*

In order to study the shear influence on the conductive network and the recovery process, some additional experiments were done. A comparable starting point of the suspensions was reached by 3-step pre-treatment: initial shearing with a shear rate of 100 s^{-1} followed by shearing with 1 s^{-1} and a final shearing with 0.1 s^{-1}. After this pre-treatment a short shear pulse of 30 s at different shear rates was applied. Fig. 4 shows the results for the measurement with shear pulses of 1, 10 and 100 s^{-1}. The time range $t > 10$ min represents isothermal annealing at 70 °C.

As mentioned above, constant conductivity values are reached that depend on the applied shear rate. Lower shear rates induce higher conductivity levels because the constructive part of network formation is higher than the destructive one resulting in the build-up of more conductive paths. The pre-treatment leads to a uniform conductivity value of about 5×10^{-5} S/m. Small variations in the conductivity occurred due to minor differences in concentration among the used suspensions.

During the shear pulse, the DC-conductivity decreases for all shear rates. For shear rates of 10 s^{-1} and 100 s^{-1}, the conductivity drops by three orders of magnitude and nearly reaches the conductivity value of the pure epoxy matrix ($\sim 2 \times 10^{-8}$ S/m). A possible explanation for this effect is the destruction of the conductive network within the system due to shearing. Applying higher shear rates to the system means that higher shear forces affect the agglomerates. The connected agglomerates are torn apart from each other and are even broken down. Thus a decrease in agglomerate size and larger distances between the particles takes place. The loss in contacts results in a lower electrical conductivity. The degree of destruction depends strongly on the applied shear rate [22,26–31].

Fig. 5 provides a more detailed version of the data from Fig. 4. In the case of low shear pulse (1 s^{-1}) the loss in conductivity is quite low. The conductivity decreases by only one order of magnitude. This means the contacts between conductive fillers were only partly destroyed by shear. Because of the fast recovery process we assume that the network was slightly torn into large agglomerates. These large agglomerates are able to quickly re-build the conductive network during annealing.

However, for higher shear pulses (10 s^{-1} and 100 s^{-1}) and thus stronger shear forces, a higher deformation of the network is expected. As previously shown [22,31], higher shear forces are able to break down agglomerates. In this experiment, we saw this deformation in the huge decrease in electric conductivity.

The recovery behaviour after shear pulse clearly differs among all shear rates. After annealing for 60 min, all curves reach final conductivity values of $\sim 10^{-4}$ S/m. This value is limited by the initial filler concentration of the system as well as by temperature and

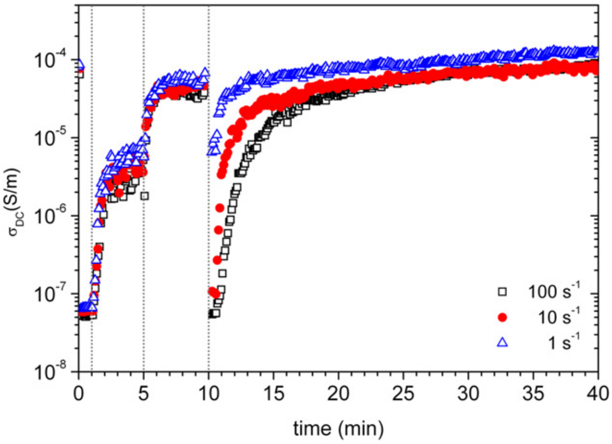

Fig. 4. DC-conductivity of a 0.1 wt% filled CNT/Epoxy suspension measured at 70 °C with 0.5 mm gap. All suspensions were sheared with 100 s^{-1} for 1 min, 1 s^{-1} for 4 min and 0.1 s^{-1} for 5 min. Transient shear deformation with different shear rates was applied for 30 s followed by isothermal conductivity recovery.

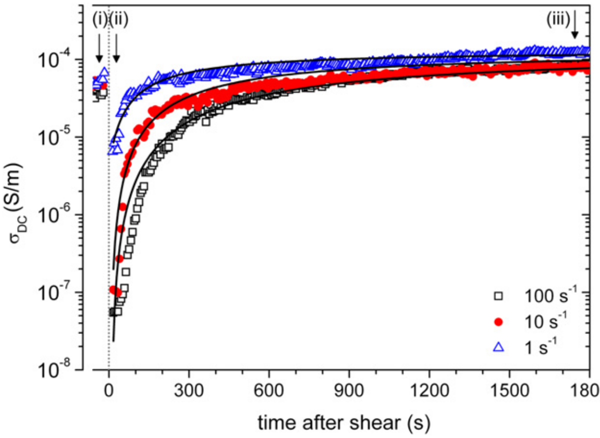

Fig. 5. Comparison of DC-conductivity after high (100 s^{-1}), medium (10 s^{-1}) and low (1 s^{-1}) shear pulse. Data were taken from Fig. 4. Solid lines represent fitting using a combined agglomeration/percolation model (parameters are given in Table 1). The arrows indicate the image capture time: (i) before shear pulse, (ii) directly after shear pulse and (iii) after 30 min relaxation.

matrix viscosity. Although the shapes of the three curves are similar, the recovery speeds differ. After applying a low shear pulse ($1\ s^{-1}$), the recovery of the conductivity is faster compared with high shear pulse ($10\ s^{-1}$ or $100\ s^{-1}$). Alig et al. [28] reported similar results for CNT/polycarbonate (CNT/PC) composites in the molten state. They suggest that the recovery process can be understood in terms of diffusion controlled re-formation of conductive network parts in a viscous surrounding. This mechanism is valid for all shear rates with differences only in the recovery speed.

During the experiment, optical light micrographs were taken. This is to measure the morphology changes due to shearing (Fig. 6). In coincidence with the high conductivity values reached by this pre-treatment, we notice network structures featuring big interconnected agglomerates (first column). Fig. 6 illustrates the morphology structures of the nanotube network at the different steps of the experiment: (i) before shear (ii) after shear, and (iii) after relaxation. Comparing the structures before and after low shear (Fig. 6a and b), no drastic changes in the morphology can be detected. The initial agglomerate size is only slightly reduced. These observations are in good agreement with the assumptions above concerning the electrical conductivity. After applying high shear rates, the conductive network is broken down into many small agglomerates as seen in Fig. 6e and h. These small agglomerates need to grow until they can form a conductive network again. Surprisingly, after recovery, the morphologies for the three samples differ even if the conductivities are identical (compare Fig. 6c and i). As shown in the last column of Fig. 6, while annealing, re-agglomeration takes place and the structure changes. A significant change in fractal structure is observed, measured by an increase in lacunarity from Fig. 6c over f to i.

Different morphologies might influence the mechanical behaviour. For CNT/PC systems, a recovery of the shear modulus G′ was measured after shearing [27]. Alig et al. showed that the maximal G′ values for samples sheared with higher shear rates stayed well below the maximal G′ values for samples with low shear rate treatment. They were unfortunately not able to make optical measurements supporting these results. Tough, Skipa et al. reported different G′ values for initially dispersed and agglomerated samples [28]. So far, no in-situ morphology recording has been performed for this system.

Due to the instrumental limitations, it was not possible to measure the G′ recovery of our CNT/epoxy system because of the very low viscosity of the system at 70 °C ($\eta \sim 0.3$ Pa s) and short recovery times which lead to insufficient collection of data. Nevertheless, recovery of the shear modulus in CNT/PC did not lead to the same ultimate value for G′ even if the electrical conductivity recovered completely. Due to the similarities between CNT/epoxy and CNT/polymer melt systems [31], it is believed that the differences in the final G′ values are due to the different morphologies after recovery that we were able to show. As a consequence, the shear history of the sample cannot be neglected when considering recovery/annealing processes even if conductivity measurements show identical values.

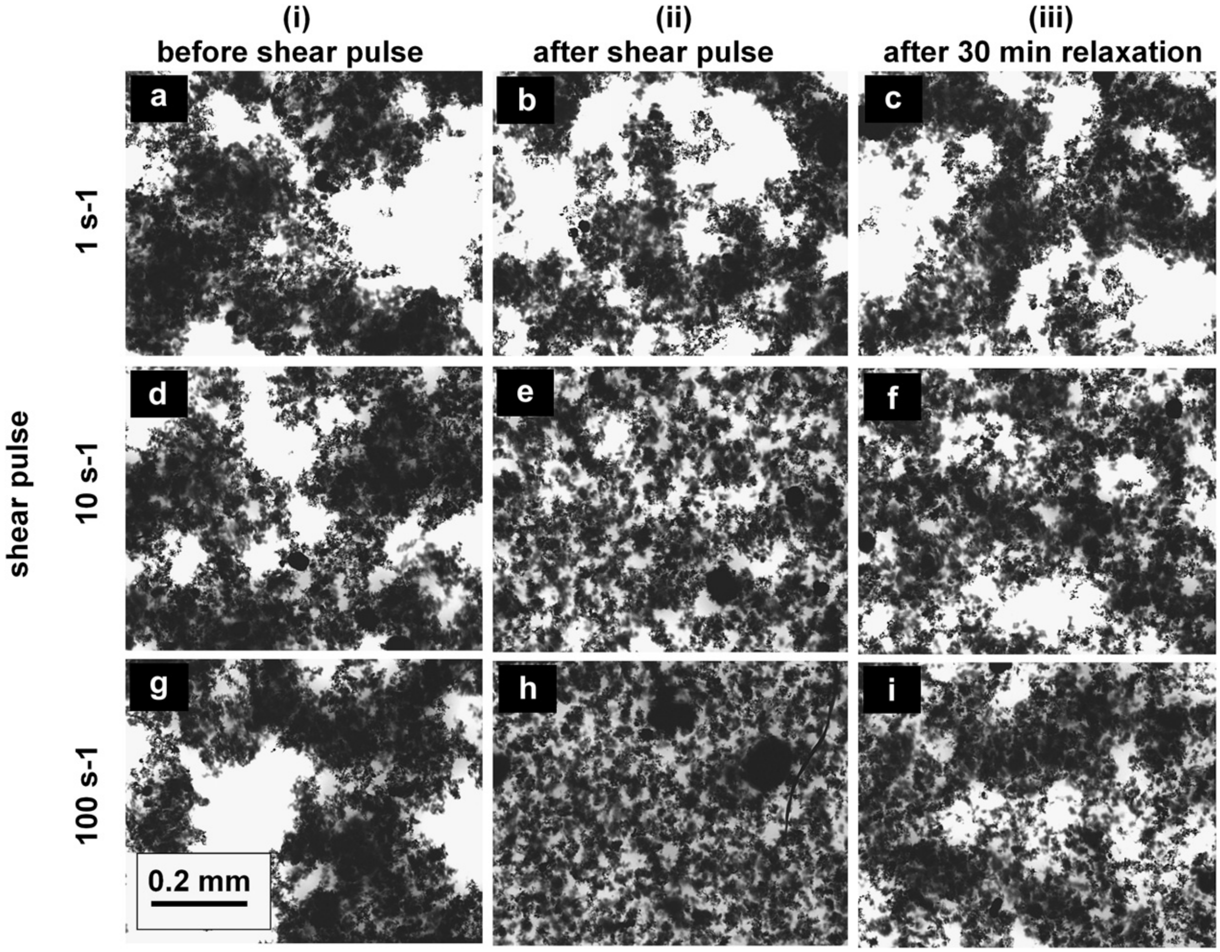

Fig. 6. Optical micrographs from 0.1 wt% filled CNT/Epoxy suspension at 70 °C: before shear pulse (first column, i); directly after shear pulse with $1\ s^{-1}$ (b), $10\ s^{-1}$ and (e) $100\ s^{-1}$ (h) and after relaxation for 30 min (last column, iii). The times at which the images were taken are shown in Fig. 5, indicated by arrows.

3.3. *Modelling of conductivity recovery*

As discussed above, the shearing of the CNT/epoxy suspension leads to the destruction of agglomerates. This was proved by optical observation as well as by conductivity measurement. The occurrence of conductive network formation can be explained by agglomeration of filler particles at a fixed filler concentration. These agglomerates occupy a larger volume within the matrix than well dispersed nanotubes. At a certain volume concentration, the agglomerates interconnect and form a pathway through the matrix and the conductivity increases by some orders of magnitude at this point. So far, the phenomenon has been described as “kinetic percolation” [21,36] and is most pronounced at filler concentrations just below the percolation threshold due to the insulator-to-conductor transition. Within the agglomerates, the distances between the nanotubes are in the range of nanometers which allows electron tunnelling [37]. The electrical conductivity is strongly dependent on distance between the particles. Shearing leads to a decrease in agglomerate size and thus larger distances between the conductive particles and loss of contacts. During annealing, the conductivity is recovered again with time. As we see in Fig. 6, re-agglomeration was also optically observed.

To understand the recovery behaviour of conductivity and particle size, a simple model combining two approaches was used [29]: (1) a model for time-dependent cluster aggregation and (2) the classical percolation theory for insulating/conductive systems. The agglomeration process was modelled using a kinetic equation of second order [29,30]. This model was introduced by Heinrich et al. [38] for the formation of networks in elastomers:

$$p_{\mathrm{A}}(t) = p_{\mathrm{A0}} + (p_{\mathrm{A}\infty} - p_{\mathrm{A0}})\left(1 - \frac{1}{1 + 4kt(p_{\mathrm{A}\infty} - p_{\mathrm{A0}})}\right) \qquad (1)$$

with p_{A0} and $p_{\mathrm{A}\infty}$ as values of starting and final $(t \to \infty)$ volume concentration of the agglomerates. k is the reaction rate. The parameter $p_{\mathrm{A}}(t)$ is the time-dependent volume concentration of conductive filler particles “A” contributing to the conductive network.

The classical theory of the electrical percolation gives the following expression for the DC-conductivity above the percolation threshold p_{c} as a function of filler concentration [3]:

$$\sigma_{\mathrm{DC}} = \sigma_0 \left(\frac{p_{\mathrm{A}}(t) - p_{\mathrm{C}}}{1 - p_{\mathrm{C}}}\right)^X \quad p > p_{\mathrm{c}} \qquad (2)$$

with $x = 3$ is usually taken for 3D systems [3], σ_0 is the conductivity of agglomerates formed by nanotubes. In this case, the value for p_{C} was fixed to 0.2 vol% and stands for statistically distributed spherical filler particles.

Fig. 5 shows the experimental DC-conductivity versus time in the recovery regime for different shear pulses together with the fitting curves. The fitting parameters are given in Table 1. The agreement between measured data and modelled curves is satisfactory even if the used model is very simple. The same model has been used and was further developed by the group of Alig [26–29] for the modelling of CNTs in PC.

Interestingly, the value of k differs for all shear rates. Different shear conditions lead to different kinetics in the network formation process. The values of k can be used as an indicator for the influence of shear impulse at different shear rates for the specific conditions used for our experiments: concentration of the CNTs as well as temperature of 70 °C. Higher shear induces stronger breakdown of agglomerates and thus longer recovery times indicated by a small reaction coefficient. Less destruction of the agglomerates leads to faster recovery and therefore higher k values. As shown before [28,31,39], the same behaviour was measured in CNT/polymer melt systems. This is really interesting since it leads to the conclusion that long polymer chains in a polymer melt obviously do not influence the filler particles’ movement that much as was earlier expected. In an epoxy matrix, no long polymer chains exist. The time dependency of the re-agglomeration process is mainly influenced by matrix viscosity and temperature, but obviously not by filler–polymer chain interactions.

Table 1
Used fit parameters for the curves in Fig. 5. Constant parameters: $t = 2$, $p_{\mathrm{c}} = 0.2$ vol%.

Shear rate γ (1/s)	σ_0 (S/m)	k (1/s)	p_{A0}(vol%)	$p_{\mathrm{A}\infty}$ (vol%)
100	1	0.04	0.18	1.4
10	1	0.075	0.18	1.4
1	1	0.17	0.40	1.4

4. Conclusion

In this paper in-situ monitoring of optical and electrical properties was done for shear-stimulated networks in a modified rheometer setup. Annealing after shear led to an additional increase in conductivity due to the recovery processes. The time-dependent changes of the conductive network after shear indicate that the CNT/epoxy system was not in thermodynamic equilibrium. In-situ electrical measurements showed the recovery of the conductivity. Light microscopy images taken during the experiment show re-agglomeration and thus indicate re-formation of the network. We observed different morphologies of the conductive network after recovery although the electric behaviour was identical for all treatment methods at sufficiently long annealing times. Thus, the previous history of the samples cannot be neglected.

A simple model combining classic percolation theory and time-dependent particle agglomeration was used to fit the experimental results. Using this kinetic model, the reaction rate k can be used as a measure to characterize the grade of network destruction. Lower k values indicate higher destruction and deformation of the network.

We observed the same mechanism for particle agglomeration and recovery after shear in low viscous CNT/epoxy systems as was published for highly viscous CNT/polymer melt systems. Thus, we dare to say that the mechanism for network formation is a fundamental feature/property of the filler particles.

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