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Shear-controlled electrical conductivity of carbon nanotubes networks suspended in low and high molecular weight liquids

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ABSTRACT

Controlling the electrical conductivity is a critical issue when processing material systems consisting of an insulating matrix filled with conductive particles. We provide experimental evidence that given shear rates result in specific conductivity levels in such different systems as high-viscosity carbon nanotube/polymer melt or low-viscosity carbon nanotube/epoxy fiber suspensions. The steady-state conductivities are independent of the initial state of the dispersion. The observed behavior is modeled phenomenologically by the competition between build-up and destruction of conductive filler network. A particle-level simulation of flowing fiber suspension also reflects the observed behavior. Our results show that properties of particulate suspensions can be controlled by steady shear. They should be considered to obtain reproducible properties in shear-based processing technologies as injection molding or resin transfer molding.

1. Introduction

Agglomeration can lead to the formation of connected particles, i.e. filler networks, in particle suspensions. The physical properties of such systems strongly depend on the structural morphology of network and its formation which are generally controlled by the thermorheological prehistory and/or the processing conditions. Flow-induced flocculation has been observed and successfully modeled in a variety of fiber suspensions [1–4]. In this way, network structures of the suspended fibers can be formed well below the statistical percolation threshold [5]. Percolation is here defined as the formation of a system-spanning cluster of connected fibers. A composite consisting of an insulating matrix filled with conducting particles exhibits an insulator to conductor transition at the percolation threshold. Thereby, the network formation can be characterized by specifying the electrical conductivity of the composite. For fibers with high aspect ratio r_a the statistical percolation threshold Φ_C^{stat} is well approximated by $\Phi_C^{stat} \approx 1/r_a$ [6]. In a series of papers [7,8] it has been shown that shear forces are able to lower the onset of percolation down to one order of magnitude below Φ_C^{stat} in low-viscosity carbon nanotube (CNT)/epoxy suspensions. This lowering seemed to decrease with increasing shear rate. A clear relation between shear rate and conductivity could not be derived mainly due to a lack of suitable experimental conditions. For CNTs suspended in low-viscous polydimethylsiloxane Moreira et al. [9] determined a critical shear deformation which separates increasing conductivity for low deformation from decreasing conductivity at high deformation. In highly viscous polymer composites the effect of shear was generally accepted to be destructive [10–15]. Recently, a shear-induced insulator to conductor transition was observed for well-dispersed high-viscosity CNT/polycarbonate melts [16,17]. These investigations were performed by simultaneous time-resolved measurements of electrical conductivity and rheological properties under steady shear. Flow induced orientation of MWNT in PC nanocomposites with subsequent conductivity measurements have been reported [18].

In this paper we show that for CNTs dispersed in low and high molecular weight liquids a given shear rate leads to a specific electrical conductivity whose value depends on CNT concentration and temperature but is independent of the initial state of dispersion. Since this observation is made for such different systems as high-viscosity polymer melt/carbon nanotube or low-viscosity epoxy/carbon nanotube suspensions, we conclude that the CNT networks can be unambiguously characterized by their electrical conductivity.

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2. Experimental

The CNT/polycarbonate (PC) samples used in this study are injection molded plates supplied by Bayer Technology Service (Germany) filled with high purity multi-walled carbon nanotubes (MWCNT) (Baytubes, Bayer) having an outer diameter of 5–20 nm, a length of 1–10 μm. At 230 °C the viscosity of the CNT/PC melt is in the range of 5–10 kPa s. Thermal annealing of the as-produced CNT/PC composites results in a shift of the percolation threshold from above 5 wt% to about 0.75 wt% (17). CNT/PC samples with 1 wt% MWNT were used throughout this paper.

The experiments with CNT/epoxy were performed with MWCNTs with an average inner and outer diameter of 4 and 15 nm, respectively, and average lengths of 15 μm. The polymer matrix consisted of bisphenol-A-based epoxy resin (Araldite LY 556). The suspensions were prepared using a dissolver disk rotating at 2000 rpm for 2 h at room temperature. The electrical percolation of such highly-stirred samples, which was determined to be $\Phi_{\mathrm{C}}^{\mathrm{statist}} = 0.15$ wt% in this case, has been identified with the statistical percolation threshold $\Phi_{\mathrm{C}}^{\mathrm{statist}}$ [5]. CNT/epoxy samples with 0.1 wt% CNT were used throughout this paper. At 70 °C the viscosity of a CNT/epoxy suspension is 0.5 Pa s.

Rheology experiments for CNT/PC samples were carried out at 230 °C using 25 mm diameter parallel plates and 1 mm gap (Ares, Rheometric Scientific) equipped with a ring electrode for conductivity measurements. CNT/epoxy measurements were performed in with 35 mm diameter parallel plates and 1 mm gap (StressTech HR, Rheologica Instruments) at 70 °C.

3. Results and discussion

Our experimental findings required measurement equipment which allowed for a simultaneous determination of rheological and electrical quantities. The experimental setup used for CNT/PC melts has been described elsewhere [13,16] in detail. CNT/epoxy samples were measured with the lower plate made of quartz glass so that sheared samples can be observed with an optical microscope while the upper plate is rotating. Comparable results have been obtained for conductivity measurements parallel or perpendicular to the shear flow.

The central result of this paper is illustrated in Figs. 1 and 2. Under steady shear, samples with different initial states approach identical conductivity values. Fig. 1 shows results for CNT/PC with 1 wt% CNT at 230 °C. Depending on their initial conductivities we characterize the CNT distributions as agglomerated, intermediate or dispersed (see schematic drawings which visualize corresponding TEM images [15]). For the ‘dispersed’ nanotubes the injection molded sample was taken. For preparation of the ‘agglomerated’ nanotubes we applied the following procedure: 1 h of steady shear for initiation and acceleration of agglomeration followed by 1 h of network improvement in the quiescent melt [16,17]. The intermediate CNT distributions were prepared by shorter times of quiescent annealing. After different transient periods all four curves coalesce into a unique conductivity value which depends only on the applied shear rate. Interestingly, the transient period for the agglomerated state is significantly shorter than for the dispersed state.

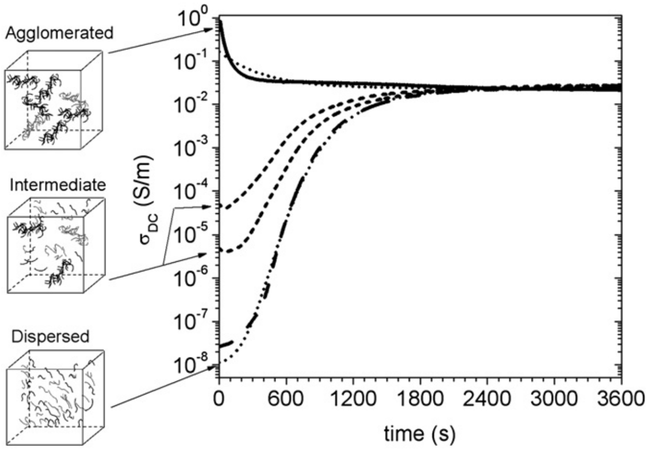

Fig. 1. Time dependent conductivity of CNT/polycarbonate suspensions containing 1 wt% MWNT at 230 °C for samples with different CNT initial states ranging from initially dispersed (– – –), intermediate (···) to agglomerated (—). The drawings illustrate the CNT network morphologies. All four curves converge into a common conductivity value under steady shear of 0.02 s^{-1}. The dotted lines for upper and lower curve represent fits using the kinetic equation.

The same type of behavior was found for CNT/epoxy with 0.1 wt% CNT at 70 °C. Here we compare samples containing agglomerated CNTs with samples containing well-dispersed CNTs. In the latter case, an initiation step of 5 min shearing with 100 s^{-1} was necessary to obtain samples that exhibit subsequent conductivity increase at low shear rates. The agglomerated state for CNT/epoxy suspensions was reached by 10 min of steady shear with 0.1 s^{-1} followed by 10 min recovery without shear. Optical micrographs in Fig. 2 visualize the initial and final CNT configurations. Agglomerated and dispersed states can be clearly distinguished at the beginning while the final states appear similar. Again, the two curves approach an identical conductivity value under steady shear with a slower transient for the dispersed state. The length scale of the agglomerates in the epoxy systems are in the order hundreds of micrometers, whereas the agglomerates in high viscous thermoplastic melts are usually in the order of 100 nm [14–16,19]. However, in [19] agglomeration in the micrometer scale initiated by an oscillating shear field was also found for CNTs in PC. Therefore, we assume self-similar structures with characteristic length scales depending on viscosity and rheological case history.

The four orders of magnitude difference in maximum electrical conductivities shown in Figs. 1 and 2 are mainly accounted for by the different CNT concentrations. Our CNT/epoxy with 1 wt% MWNT approaches 1 S/m [5] as does the analogous CNT/PC system. This agreement indicates that the tunneling contacts between connected CNTs are not significantly affected by the host material.

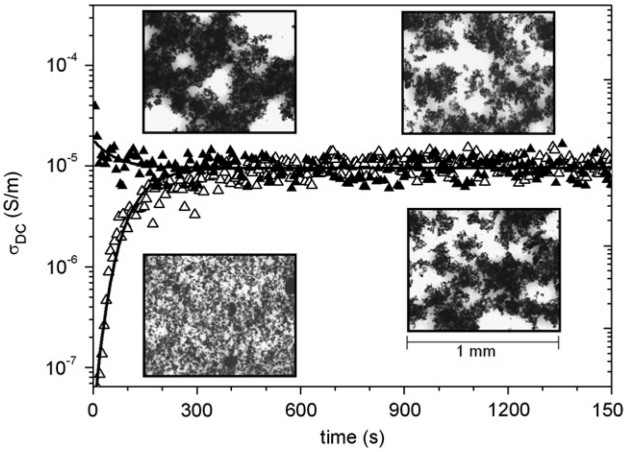

Fig. 2. Time dependent conductivity of CNT/epoxy suspensions containing 0.1 wt% MWCNT at 70 °C for samples with different CNT initial states ranging from initially dispersed (△) to agglomerated (▲). Optical micrographs (1 mm width) show that the initially differently agglomerated states approach comparable final states with identical conductivities at a steady shear rate of 0.5 s^{-1}. The solid lines represent fits using the kinetic equation.

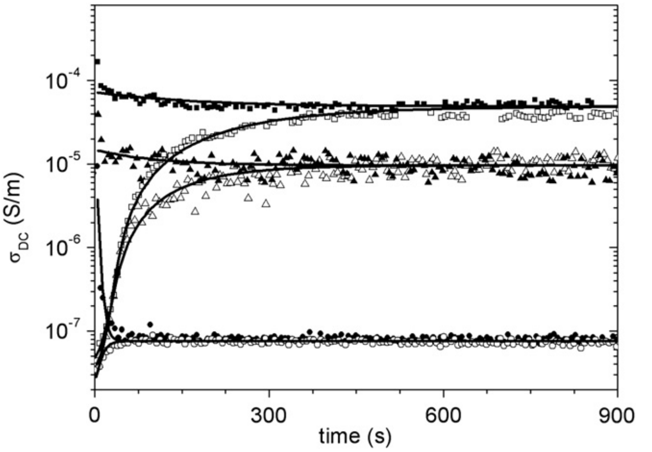

Fig. 3. Electrical conductivity of initially dispersed (open symbols) and agglomerated (filled symbols) CNT/epoxy suspensions exposed to different steady shear rates as a function of time at 70 °C. Shear rates of 0.1 s^{-1}(□,■), 0.5 s^{-1}(△,▲) and 5 s^{-1}(○, ●). Lower shear rates lead to higher conductivity values and to transient periods for the agglomerated state which are significantly shorter than for dispersed state. The solid lines represent fits using the kinetic equation.

Thus, the conductivity is predominantly determined by the CNT network. No difference has been detected between conductivity measurements performed with moving plates using brush type electrical contacts between the CNT network and electrodes, and measurements with static electrodes. In addition it should be mentioned that the level of conductivity in CNT/PC is nearly preserved after cooling below the glass transition temperature [15] just as the level of conductivity in CNT/epoxy is preserved when the experiments are conducted with the hardener added and subsequent curing.

The steady-state conductivity value decreases for both systems with increasing shear rate. This behavior is illustrated in Fig. 3 for the case of CNT/epoxy. Analogous results have been obtained for the CNT/PC system [16]. When starting with a more agglomerated state the effect of shear on the existing CNT network is predominantly destructive and proceeds faster than formation of a network when starting with a more dispersed state. Fig. 4 shows the dependence of the steady-state conductivity on the shear rate for different temperatures for the CNT/epoxy system. The lower limit of the conductivity at high shear rates is determined by the conductivity of the neat epoxy. At temperatures exceeding 50 °C we observe saturation of the conductivity at low shear rates. At lower temperatures we expect the same behavior for shear rates below our experimental window. The same is the case for CNT in high viscous systems [10,11,16].

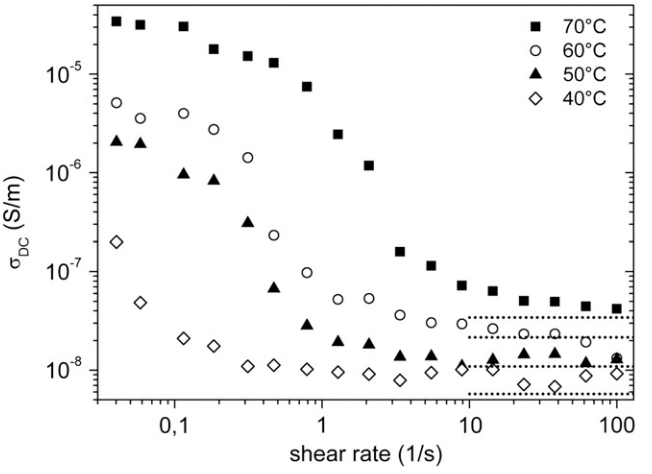

Fig. 4. Steady-state conductivities for CNT/epoxy suspensions as a function of shear rate for different temperatures. The dotted lines illustrate the conductivities of the pure epoxy for different temperatures.

Skipa et al. [16] have shown that the mechanical properties of CNT/PC suspensions, viscosity η and complex shear modulus (G', G''), also converge to identical values under steady shear independent of the initial state of agglomeration. For the CNT/epoxy system with 0.1 wt% MWCNT the variation of η is limited between 0.18 Pa s and 0.55 Pa s for shear rates between 100 s^{-1} and 0.1 s^{-1}. Again, steady shear leads to identical values independent of the initial state of dispersion.

The idea of competing destructive and build-up effects of steady shear has been expressed in terms of a kinetic equation $\mathrm{d}p_A/\mathrm{d}t = k_1(\dot{\gamma})(p_{A\infty} - p_A) - k_2(\dot{\gamma})p_A$ where p_A is the volume concentration of conductive agglomerates, $p_{A\infty}$ is the agglomerate concentration at $t \rightarrow \infty$, $k_1(\dot{\gamma})$ is the kinetic coefficient for shear-stimulated agglomeration and $k_2(\dot{\gamma})$ for shear-stimulated destruction process [17]. The conductivity is then calculated using an effective medium approximation for a non-conductive system with conductive inclusions. As can be seen from Fig. 1, upper and lower curve, Figs. 2 and 3, the time evolution of electrical conductivity under steady shear can be satisfactorily fitted with this approach. In order to describe the local minima observed in the conductivities of CNT/PC with initially intermediate dispersion (Fig. 1, small dashed curves) the above model has to be extended to a hierarchy of length scales of the agglomerates [17]. Although all curves of Figs. 1–3 can be fitted with a physically meaningful set of parameters we want to point out that such a fit is by no means unique. However, we consider this phenomenological description as a first valuable attempt to describe the observed effects.

In order to account for the microscopic mechanisms of network formation and destruction we performed computer simulations based on particle-level simulations of flexible fiber suspension which were described in Refs. [1–3,20]. With these simulations, we can model the effects of different parameters such as fiber shape, aspect ratio, shear pre-history and interparticle interactions on the conductive network formation. Each fiber is modeled as a series of rigid cylinders with hemispherical end caps each connected by ball and socket joints. Hydrodynamic forces and torques, contact forces (repulsive, attractive and friction forces), constraint forces (which maintain inextensibility), restoring torques (which resist fiber deformation) are the forces and torques on the fibers that are used during simulations. Brownian motion, particle inertia and hydrodynamic interactions between fibers are neglected.

Fiber flexibility, shear rate and suspending fluid viscosity appear in a single dimensionless parameter called the dimensionless effective stiffness $S_{\mathrm{eff}} = \frac{E_y I}{\eta_0 \dot{\gamma} L^4}$ where E_y is the Young's modulus of fiber, I is the moment of inertia, η_0 is the suspending fluid viscosity, $\dot{\gamma}$ is the shear rate and L is the fiber length. Increasing shear rate or increasing suspending fluid viscosity will decrease effective stiffness of the fibers which results in more flexible fibers. As predicted by Schmid and Klingenberg decreasing fiber flexibility hinders agglomeration [1]. Finally, generated microstructures were used to compute effective conductivities by using a resistor-network algorithm which considers tunneling length and resistance at the contacts. Despite employing various simplifications, the simulation method predicts several phenomena that have been experimentally observed in sheared nanotube-polymer systems. These include increased nanotube alignment at increased shear rates and electrical percolation at concentrations below than predicted by excluded-volume theories [20].

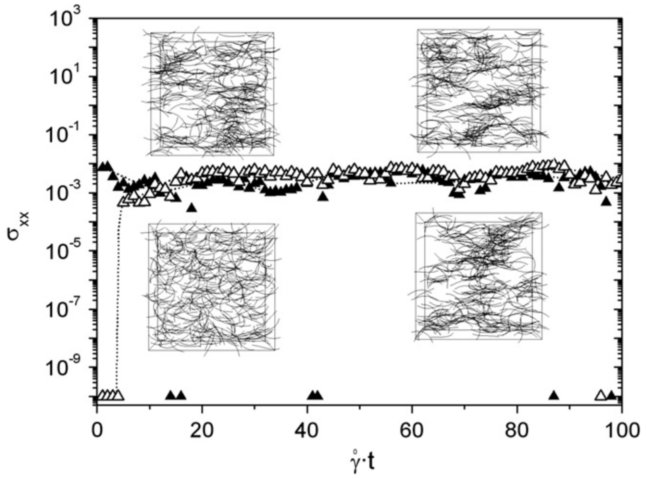

Fig. 5. Simulations of fiber suspensions under steady shear. The electrical conductivities σ_{xx} parallel to flow direction converge into identical values independent of the initial state. The insets visualize the configurations of initial and final states as obtained from the simulations. Due to finite-size effects the CNT-network conductivities are restricted to a range of two orders of magnitude and casually drop to zero. The dotted lines serve as guides to the eye.

Fig. 5 illustrates that the simulations also reflect the main experimental finding of this paper: Under steady shear, the system conductivities approach identical values independent of the initial configuration (well-dispersed or agglomerated). While predictions of a quantitative nature would require detailed data on nanotube interactions in specific liquids or polymer melts, the qualitative agreement between the experiments and simulation lends support to the claim that there is a single-valued relationship between shear rate and steady-state electrical conductivity in these systems.

4. Conclusions

The reported experiments show that the electrical conductivities of suspensions of CNTs in high and low molecular weight liquids both converge into identical values under steady shear independent of the initial state. Particle-level simulations reveal a comparable behavior. Consequently, a given shear rate is unambiguously connected with a specific state of network formation. Depending on the initial configuration the final state is obtained through competing destructive and build-up processes of the filler network. We believe that our findings may have important implications for processing of polymer composites and epoxy resins filled with nanoparticles as well as for fundamental considerations. On one hand, we have shown how the properties of particulate suspensions can be controlled by steady shear. On the other hand, we believe that our results might be representative for polymer nanocomposites with fillers of different shape as well as for particulate suspensions in general.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2010.09.013.

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