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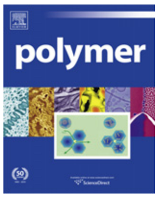

Influence of shear deformation on carbon nanotube networks in polycarbonate melts: Interplay between build-up and destruction of agglomerates

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ABSTRACT

Shear-induced destruction and formation of conductive and mechanical filler networks formed by multi-wall carbon nanotubes in polycarbonate melts were investigated by simultaneous time-resolved measurements of electrical conductivity and rheological properties under steady shear and in the quiescent melt. The steady shear experiments were performed at shear rates between 0.02 and 1 rad/s and for nanotube concentrations ranging from 0.5 to 1.5 wt%. The influence of thermo-mechanical history on the state of nanotube dispersion and agglomeration was studied in detail.

For melts with well-dispersed nanotubes a *shear-induced insulator–conductor* transition was observed, which is explained by the agglomeration of nanotubes under steady shear and the formation of an electrical conductive network of interconnected agglomerates. Simultaneously, a drastic decrease of the shear modulus ($G^* = G' + iG''$) during steady shear was observed, which can be related to a reduction of mechanical reinforcement due to agglomeration of dispersed nanotubes. These findings indicate a substantial difference in the nature of “electrical” and “mechanical” network and contradict earlier assumptions that steady (or transient) shear is always destructive for the conductive filler network in highly viscous polymer composites.

It was also shown that after a certain time of steady shear the filler network asymptotically reaches its steady state characterized by the constant electrical conductivity and shear modulus of the composite melt. Such asymptotic behaviour of composite properties was experimentally shown to be related to the interplay of the destructive and build-up effects of steady shear. For modelling of the electrical conductivity in presence of steady shear a kinetic equation was proposed for filler agglomeration with shear-dependent destruction and build-up terms. This equation was coupled to the generalized effective medium (GEM) approximation for insulator–conductor transition.

1. Introduction

Polymers filled with carbon nanotubes (CNT) are in focus of industrial interest due to a plenty of possible applications as materials having unique combinations of physical properties [1]. Small amount of CNT additive turns an electrically insulating polymer to a highly conductive composite and can simultaneously lead to the reinforcement of its mechanical properties, which is usually not possible with conventional fillers ([2] and refs. therein). Apart from the traditional field of utilization of conductive and reinforced plastics, new specific applications of nanotube-filled polymers were proposed during last years for gas-sensing [3], liquid crystal displays [4], optical transparent films [5], smart materials or actuators [6,7].

The electrical conductivity and reinforcement mechanism in such composite materials can be addressed to the formation of the percolation network of interconnected filler particles which may transfer electrical current and mechanical stress [8]. The high aspect ratio (length to diameter ratio) of up to 1000 is considered to be one of the main advantages of carbon nanotubes with respect to other fillers what theoretically enables nanotube networking at extremely low critical volume fractions ~ 1/(aspect ratio) [9]. In reality the CNT are rather worm-like objects, which tend to form agglomerates, so that the experimental percolation concentrations usually exceed the theoretical expected values for fully elongated objects. However, the nanotube amounts for the conductor–insulator transition in thermoplastic polymers are still low, so that – in contrast to classical conductive fillers – the desired properties of the polymer matrix (for example its elongation to break) are almost unchanged.

Although different types of multi-wall carbon nanotubes (MWNT) meanwhile are commercially available, a wide industrial

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acceptance of the nanotube-polymer composites is still restricted due to the broad variation of their physical properties depending on the processing conditions. During compounding, extrusion and mould injection of the composite, polymer melts undergo strong (to moderate) mechanical deformations influencing the state of filler network. It was shown previously [10–15], that the state of the nanotube network which is induced by processing of the polymer melt and in the short period prior to vitrification or crystallization mainly defines the physical properties of the final plastic part. In this context, the processing conditions and what is called "processing history" seem to be crucial for the electrical and mechanical characteristics of a composite. A deeper understanding of the underlying physical mechanisms of the nanotube network evolution in shear flows could be obtained by "rheo-electrical" experiments combining measurements of DC or AC conductivity and rheological properties of composite melts under well-defined shear conditions [16–19].

Following the results of both, processing-related studies [10–15] as well as laboratory experiments [16–19] the influence of shear (either steady or transient) on the nanotube network in highly viscous polymer composites is generally accepted to be destructive. The first indication of the simultaneous destruction of electrical and mechanical networks under *steady shear* flow was demonstrated by Kharchenko et al. [16] in laboratory experiments for polypropylene (PP) composites filled with multi-wall nanotubes (PP/MWNT). The break down of the conductive nanotube network under steady shear for a wide variation of shear rates and MWNT concentrations was later observed by Obrzut et al. for PP/MWNT [17]. A dramatic decrease of electrical conductivity during *transient shear* was monitored in similar laboratory experiments on polycarbonate/MWNT composite melts [18,19]. In the latter case a time-dependent recovery of the conductivity after transient shear was attributed to the reformation of the conductive network in the quiescent state of melt. In polymer processing-related studies, the destructive mechanism of shear due to nanotube de-agglomeration and orientation was observed for the first time in in-line AC/DC conductivity experiments during extrusion of polypropylene [10], polycarbonate (PC) and polyamide 6 (PA6) [11] containing different amounts of MWNT. Pegel et al. [12] demonstrated the role of shear in the nanotube dispersion and agglomeration in PC/MWNT composites prepared by melt mixing. Villmow et al. [13,14] illustrated the destructive effect of mechanical deformation for the electrical conductivity on the example of mould injected plastic parts. In [13] a broad conductivity variation (up to 5 orders of magnitude) within the same mould injected PC/MWNT plastic part was related to different flow conditions and correlated with TEM study of the nanotube network morphology in the layer cuts of the sample. Similar results were obtained by in-line conductivity measurements during mould injection and off-line conductivity measurements on plastic parts of PC/MWNT, polyamide/MWNT and an acrylonitrile-butadiene-styrene/polycarbonate blend (Bayblend™) with MWNT for a wide variation of the processing parameters [15]. The results were explained by the competition of deformation-induced (shear and elongation) formation and destruction of a conductive CNT network, which is followed in this study.

In addition to highly viscous nanotube-filled thermoplastic polymers, there are series of works on *low viscous* colloidal suspensions [20–22] and epoxy resins filled with MWNT [23–26]. In those systems shear can induce agglomeration of nanotubes similar to flow-induced flocculation of particles in colloidal suspensions [27–29] or shear-induced phase separation in polymer blends (see e.g. [30,31]). The network structures which appear under shear can lead to a notable change in the composite viscosity and conductivity [20–29]. Agglomeration of CB in low viscous matrices (e.g. colloidal suspensions or epoxy resins) under shear was investigated elsewhere [32–34].

For epoxy systems containing carbon black (CB) a shear-induced agglomeration and a strong dependence of electrical percolation on the 'processing history' was first reported by Schueler et al. [32,33]. The authors attributed the increase of electric conductivity to the agglomeration of CB induced by external shear forces. The agglomeration of particles in sheared carbon black-filled epoxies was explained analogically to colloidal dispersions by the interplay between attractive London-van der Waals forces and repulsive Coulomb forces causing a potential energy barrier between filler particles. Since it is difficult to overcome such barrier by thermal energy alone, shear deformation can accelerate the agglomeration process. Furthermore, it was theoretically shown [29] that rigid elongated objects like carbon nanotubes in the presence of shear will always aggregate due to friction forces (even without attraction between them).

Although there is already plenty of work on low viscous nanotube-polymer composites and suspensions under shear flow, up to now there are no systematic reports on the *shear-induced* nanotube network formation in *highly viscous* (thermoplastic) polymer melts and on the related electrical conductivity *and* rheological properties. In order to understand the interplay between formation and destruction of the filler network in presence of shear deformation, we focus therefore in this paper on simultaneous measurements of DC conductivity and the complex dynamic shear modulus ($G^* = G' + iG''$) in *highly viscous* thermoplastic composite melts under well-defined steady shear conditions. The rheo-electrical experiments have been carried out for PC/MWNT composites using a recently modified rheo-electrical setup, which allows simultaneous monitoring of the time evolution of the 'electrical conductive' and 'mechanical' (viscoelastic) network under quasi-steady flow. In extension to steady shear experiments reported by Kharchenko et al. [16] and Obrzut et al. [17], we are able to monitor the *time evolution* of electrical conductivity and shear modulus of composite melts *under* quasi-*steady shear*. This allows us to study all stages of the formation of a network in the shear flow, which approach a dynamic equilibrium, characterised by constant macroscopic properties. The experiments were performed for different initial states of the CNT-filler network (related to different thermo-mechanical history) ranging from almost dispersed MWNT to agglomerated fillers.

2. Experimental

2.1. Samples

The samples used in this study are mould injected plates [35] (supplier: Bayer Technology Services) which were prepared from polycarbonate (PC, Makrolon 2600, Bayer Material Science AG) filled with high purity multi walled carbon nanotubes (MWNT, Baytubes® [36]). The as-prepared nanotubes have an outer diameter of 5–20 nm, a length of 1–10 μm and an electrical conductivity $>10^4$ S/cm. The technological parameters for the mould injection were the following: injection velocity of 10 mm/s, the diameter of the shank of 25 mm, and the melt and mould temperatures of 340 °C and 120 °C, respectively. For the simultaneous conductivity and rheological measurements round samples of 25 mm diameter were cut from mould injected plates of 2 mm thickness.

Transmission electron microscopy (TEM) investigations showed that samples produced with the same mould injection parameters contain dispersed MWNT with only a small amount of agglomerates [35] (see e.g. the TEM image for PC/MWNT with 5 wt% MWNT in Fig. 1a). It was also shown by X-ray experiments that these composites do not contain significant amounts of oriented MWNT

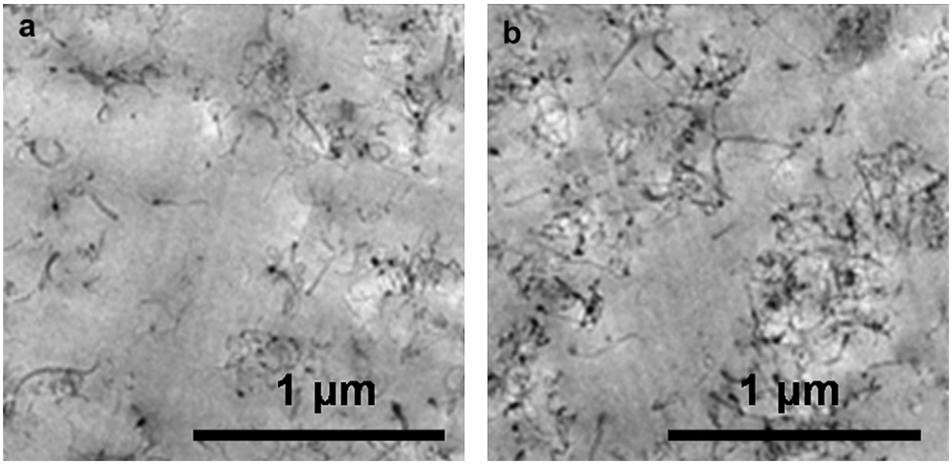

Fig. 1. TEM images of the as-produced PC/MWNT with 5 wt% MWNT (a) and after 1 h of annealing at 300 °C (b) [35].

[37]. The electrical conductivity of the mould injected plates at room temperature was estimated to be quite low, having percolation threshold well above 5 wt% MWNT [35].

After annealing for 1 h at 300 °C the electrical conductivity (measured at 1 kHz) of the composite shown in Fig. 1a increased from 10^{-13} S/cm to 0.1 S/cm. In Fig. 1b one can see the TEM image of the annealed composite with a larger amount of MWNT agglomerates. The tremendous increase of conductivity of the PC/MWNT melts during isothermal quiescent annealing in the absence of shear was earlier attributed [11,18,19,35] to the agglomeration of nanotubes and formation of a conductive network of interconnected agglomerates.

It was discussed for PC/MWNT that the dispersed state of nanotubes leads to low composite conductivity probably due to the insulating polymer chains wrapped around MWNT [18,19,38] The process of nanotube agglomeration ensures denser packing of nanotubes inside the agglomerates what results in smaller distances between MWNT. As discussed in literature [34,39–41] very small inter-particle distances (~few nm, almost physical contacts) are needed for low contact resistance and efficient electron transport through the conductive filler network. For the electron transport between CB tunnelling of electrons was proposed [34], which can be extended to CNT. These small MWNT distances are expected to be achieved only by formation of densely packed filler agglomerates.

In this study different thermo-mechanical pre-treatments of composite melts (like quiescent annealing of various duration and well-defined shear deformations) were used in order to prepare samples with well-defined history (degree of dispersion/agglomeration of MWNT). For the rheo-electrical experiments the following ‘filler histories’ we investigated: composites with (i) ‘dispersed MWNT‘ resulting in very low conductivity (as-produced sample in Fig. 1a), (ii) ‘partially agglomerated MWNT’ representing an intermediate state of the conductive network, and (iii) ‘agglomerated MWNT’ forming an almost complete conductive network. The details of the thermo-mechanical treatment for preparation of the different initial network structures are given in the respective chapters.

2.2. *Rheo-electrical experiments*

The time-dependent dielectric measurements were performed using a Novocontrol impedance analyser coupled with a laboratory rheometer (Ares, Rheometric Scientific) in which the rheometer tools act as electrodes [18,19,35,42,43]. Originally the tool geometry was a plate-plate-geometry of 25 mm diameter. For the present study the plates were equipped with ring electrodes (inner diameter 19 mm, outer diameter 25 mm). By utilizing such ring electrodes, it is possible to ensure a relatively narrow distribution of the shear rates in the relevant region of electrical field during steady rotation. A tangential shear is applied to the melt by rotating the lower rheometer plate. The electrical conductivity is measured perpendicular to the direction of applied shear, which allows monitoring of the electrical conductivity in the volume between the two ring electrodes. The rheometer is equipped with an oven which maintains stable temperature of the composite melt. The setup allows covering a broad range of AC-frequencies for the dielectric measurements (from 10^{-3}–10^{7} Hz) [19]. Since the recording of a conductivity (or permittivity) spectrum over a wide range of frequencies needs at least several minutes, the system characteristics can change during the measurement. Thus, for the monitoring of kinetics of fast processes, we performed the conductivity measurements only at a single frequency of $f = 1$ kHz, which was taken as representative for the DC conductivity as discussed in [19].

For the simultaneous electrical and rheological measurements during steady shear, the rheometer was connected to a data acquisition system (NI PXI-10042) with analogue output for the motor control [42,43]. By the analogue inputs it is possible to measure strain, torque and conductivity with high acquisition rate and perfectly synchronized with the motor control signal. With this unique setup it became possible to create a combined program for overlaying steady and oscillatory motions of the rheometer motor. The motor thus can simultaneously produce steady rotation $\dot{\gamma}_{\mathrm{steady}}$ (shear flow) and short oscillations $\dot{\gamma}(t) = \dot{\gamma}_0 \sin 2\pi f t$. From the torque data of the oscillations the complex shear modulus of the composite melt can be deduced. The oscillation frequency was taken to be $f = 1$ Hz, the strain rate amplitude $\dot{\gamma}_0 = 0.0628$ rad/s (corresponding to $\gamma_0 = 1\%$ of sample strain). For calculation of the transient shear viscosity $\eta^{+} = \langle \tau(t) \rangle / \dot{\gamma}_{\mathrm{steady}}$ the torque $\langle \tau(t) \rangle$ data (averaged over one period of the overlaid oscillation) were related to the averaged shear rate $\dot{\gamma}_{\mathrm{steady}}$. The setup was used for time-resolved monitoring of shear-induced evolution of electrical DC conductivity (σ_{DC}), components of the complex shear modulus (G' and G'') and transient viscosity (η^{+}).

In order to measure G' and G'' in quiescent melts, small oscillatory shear of 1% strain was applied. As proved before, the influence of such small oscillations on the electrical conductivity can almost be neglected (“quasi-quiescent” experiment).

All the measurements on PC/MWNT composites were performed in the melt state at a constant temperature of 230 °C. The details of the measurement procedure are described for each experiment together with the results in Section 3.

3. Results and discussion

3.1. Shear-induced build-up and destruction of conductive network

To achieve a more general understanding of the influence of shear on the electrical conductivity and the related filler networks, we performed a series of 'basic' experiments, where a well-defined "shear pulse" of 600 s duration (shear rate $\dot{\gamma}_{\text{steady}} = 0.02$ rad/s) was applied to PC/MWNT samples representing different thermo-mechanical history.

Fig. 2 shows the time-dependent DC conductivities of two as-prepared samples with 1 wt% MWNT during quiescent annealing of different durations, a short steady 'shear pulse' ($\dot{\gamma}_{\text{steady}} = 0.02$ rad/s, duration: 600 s) and quiescent recovery after shear.

The first sample was annealed for only 10 min (dotted line in Fig. 2) at 230 °C and the second sample was annealed for 2 h (solid line). As one can see from Fig. 2, isothermal annealing of the composites leads to a slight conductivity increase, which can be explained by a slow formation of conductive agglomerates from initially dispersed MWNT. Different durations of the quiescent annealing thus result in different conductivity levels corresponding to different stages of MWNT agglomeration: 'dispersed' MWNT (dashed line) and 'partially agglomerated' MWNT (solid line). During the 600 s of shear 'pulse' (denoted in Fig. 2 by vertical arrows) both samples show a fast increase of their conductivities, indicating an acceleration of the network formation under shear. This is more clearly seen in Fig. 3, where the time interval of the 'shear pulse' for the 'partially agglomerated' sample (solid line) is shifted along the time axis to the onset of shear for the 'agglomerated sample at 600 s. For the sample annealed for only 10 min – and so containing almost dispersed MWNT – the conductivity during the 'shear pulse' increases *monotonically* by about 3 orders of magnitude. The sample annealed for 2 h, and therefore representing a 'partially agglomerated state', shows first a *local minimum* in the conductivity after about 100 s, which is followed by a conductivity increase.

The occurrence of the minimum as well as the shear-induced increase of conductivity can be explained by the interplay of destruction and build-up effects of shear on the agglomerate network. A simple kinetic model for this behaviour is given in Section 3.2 together with the fit for these conductivity data (see Fig. 11 below). The appearance of a local minimum in the conductivity can be qualitatively explained as follows: first, the already existing CNT network – which was formed under quiescent conditions – will be deformed by the shear until it breaks into smaller fragments. Thus, the conductivity decreases. These fragments can now start to built-up a new conductive network. This new "dynamic" network – generated under shear flow – differs from the initial quiescent one. Its formation can be explained for instance by a 'picking-up' mechanism. In the shear flow the broken agglomerates and/or individual nanotubes can *pick up* other particles on their way and stick to each other (shear-induced agglomeration). As we will show in Section 3.3 for long duration of shear, build-up and destruction effects will equilibrate and lead to a constant (stationary) conductivity.

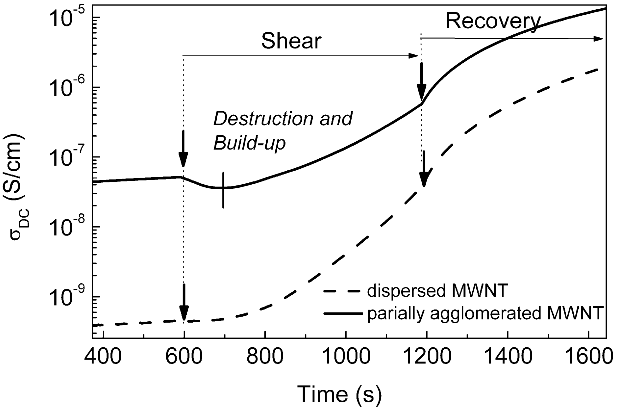

Fig. 3. Comparison of electrical conductivity of a sample with 'dispersed' MWNT (solid line) and 'partially agglomerated' MWNT (dashed line) in the time interval of the applied shear pulse. The curve for the sample sheared after 2 h of annealing from Fig. 2 (dotted line) is shifted to the onset of shear of sample annealed for 600 s (solid line). The prehistory and notations are described in Fig. 2.

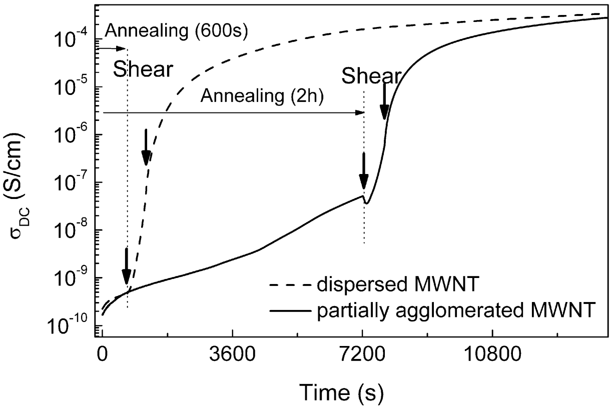

Fig. 2. Shear-induced insulator–conductor transition for two PC/MWNT samples (1 wt% MWNT) with different thermal history: (i) the first sample (dashed line) was sheared after 10 min of annealing at 230 °C and (ii) the second sample (solid line) was sheared after 2 h of annealing. The duration of the steady 'shear pulses' were 600 s and the shear rate was 0.02 rad/s. The arrows indicate the interval of applied steady shear for both samples.

It is obvious in Figs. 2 and 3 for both samples, that conductivity increase after the short steady 'shear pulse' is much faster than for the quiescent melt before shear, which indicates a shear-induced activation of the nanotube agglomeration [43]. Surprisingly, even a short duration of shear is sufficient to initiate the growth of nanotube agglomerates.

The same effects were observed for PC with different MWNT concentrations (0.5, 0.75, 1 and 1.5 wt%) in Fig. 4 for similar

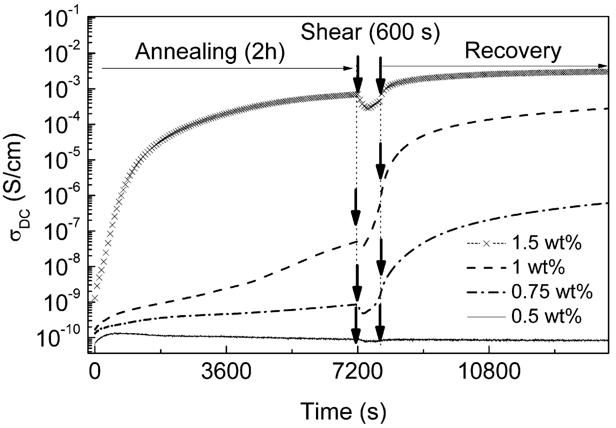

Fig. 4. DC conductivity of the PC/MWNT melts at 230 °C (MWNT concentrations of 0.5, 0.75, 1.0 and 1.5 wt%) in a three-step experiment: 2 h of annealing ('partially agglomerated' state); 600 s of steady shear (shear rate of 0.02 rad/s); ~2 h of quiescent recovery. Vertical arrows show the onset and the end of steady shear.

experiments. Fig. 4 shows the time dependence of the DC conductivities of the composites during isothermal *annealing* for 2 h, short *steady shear* ($\dot{\gamma}_{\mathrm{steady}} = 0.02$ rad/s for 600 s) and isothermal *recovery* ($\sim$2 h) at 230 °C.

By the isothermal *annealing* (2 h, 230 °C) a ‘partially agglomerated’ state was ‘prepared’ for all samples, before applying the ‘shear pulse’. During annealing the DC conductivities show the expected increase for all concentrations, except for the sample with 0.5 wt% MWNT, where one can observe a slight conductivity decrease. A possible explanation of this decrease is the formation of separated agglomerates, which do not come into contact due to the low MWNT content of 0.5 wt%. For the three larger concentrations one can observe the local minimum in conductivity followed by the shear-induced insulator–conductor transition (as discussed above).

In contrast to the findings presented above, all previous works on thermoplastic melts with MWNT [10–19,35] report on a decrease of the conductivity by the applied shear. Such domination of the *destruction* of the conductive network under steady shear (0.02 rad/s, 600 s) is demonstrated in Fig. 5 for three samples with 0.75 wt%, 1 wt% and 1.5 wt% MWNT with initially ‘well-agglomerated’ MWNT corresponding to high electrical conductivities. The agglomerated network states were prepared for all three samples by identical thermo-mechanical pre-treatment: First, a shear deformation of 0.02 rad/s was applied to the composite melts (as-produced sample) at 230 °C for 1 h in order to initiate and accelerate MWNT agglomeration. In a second step, the conductive network was improved additionally by isothermal annealing (*recovery*) in the absence of a shear field. The steady shear (0.02 rad/s, 600 s) was applied to the thus prepared samples.

For all three concentrations a gradual conductivity decrease during steady shear deformation is clearly seen in Fig. 5. This finding is in agreement with the dominance of shear-induced conductivity decrease reported earlier [10–19,35]. For the samples with ‘well-agglomerated’ nanotubes a further network ‘perfection’ by shear-induced agglomeration is not expected and the *destructive effect* of shear is therefore dominant. Interestingly, the conductivities of all samples tend to approach stationary values already after about 600 s of shear. These stationary values are a further indication for the above proposed competition between build-up and destruction effects under steady shear.

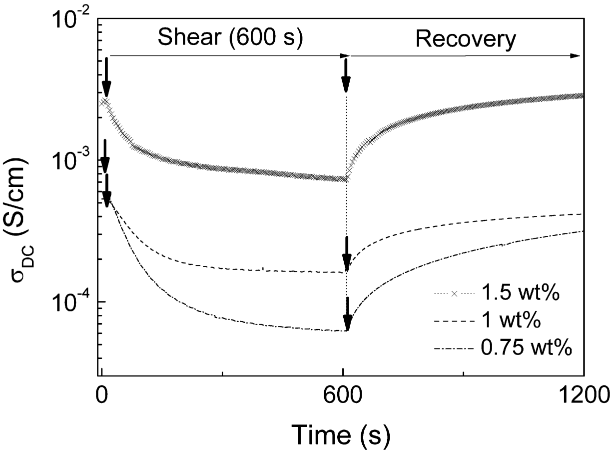

Fig. 5. DC conductivity of PC/MWNT melts at 230 °C (MWNT concentrations of 0.75, 1.0 and 1.5 wt%) during 600 s of steady shear (shear rate of 0.02 rad/s) and quiescent recovery. The vertical arrows indicate the onset and the end of steady shear. Prior the experiment all samples were thermo-mechanically pre-treated (shear for 1 h, steady shear rate of 0.002 rad/s and annealing) in order to achieve maximum agglomeration at $t = 0$.

In the quiescent melt (after 600 s of shear) the expected recovery of the electrical conductivity due to reformation of the agglomerate network is observed for all three MWNT concentrations.

3.2. Electrical and mechanical filler network under steady shear: asymptotic behaviour

From the results discussed above the question arises, how the destructive and build-up effect of shear will compete for longer times ($t \to \infty$). Another interesting question is, whether the rheological properties (mechanical reinforcement by the filler network) and electrical properties show the same tendencies under shear or not. In order to study these questions, the evolution of the electrical conductivity and shear modulus (G' and G'' at $f = 1$ Hz) was measured simultaneously under quasi-steady shear ($\dot{\gamma}_{\mathrm{steady}} = 0.02$ rad/s). The steady shear deformation was applied for 1 h to composite melts at 230 °C. After one hour of shear the quasi-quiescent recovery of σ_{DC}, G' and G'' was monitored also.

The measurements were performed on PC/MWNT melts with 1 wt% MWNT. Two samples, which are representative for ‘dispersed’ and ‘agglomerated’ nanotubes were compared. For the ‘dispersed’ nanotubes the as-prepared sample was taken. For preparation of the ‘agglomerated’ nanotubes the procedure described in Section 3.1 for the samples in Fig. 5 was used: 1 h of steady shear for initiation and acceleration of agglomeration followed by 1 h of network improvement in the quiescent melt.

Fig. 6 presents the simultaneously measured DC conductivity and the real (G') and imaginary (G'') part of the shear modulus for the sample with ‘dispersed’ MWNT during ‘*shear*’ and ‘*recovery*’.

In Fig. 6a a monotonic increase of the DC conductivity from a non-conductive state (*insulator–conductor transition)* by about 6 orders of magnitude can be seen, which is typical for shear-induced agglomeration [43]. Obviously the conductivity approaches a constant value after about 50 min, which is equivalent to $\sim$60 rad of total shear. This value is representative for the “dynamic” filler network formed by the interplay between the destructive and build-up effect of shear for longer times. It should be noted here, that for the quiescent agglomeration of MWNT, the conductivity vs. time (log–log scale) does not approach its limiting value even for long measuring times >10 h [44]. The conductivity increase in the quiescent melt seems to follow a power law, similar to physical quantities at intermediate or late stage of phase separation in binary mixtures or polymer blends [46].

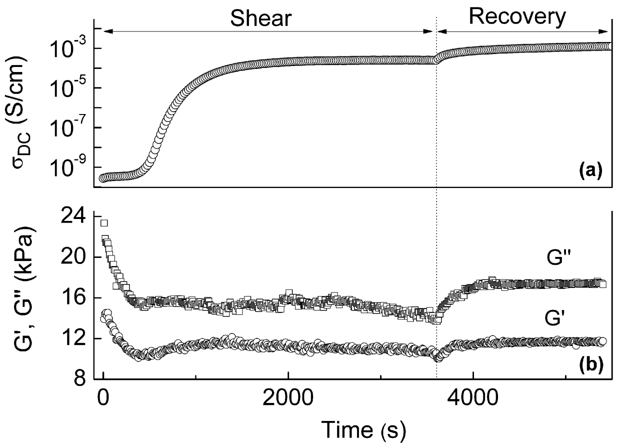

Fig. 6. Shear-induced insulator–conductor transition (a) during 1 h of steady shear (shear rate: 0.02 rad/s) and the quiescent recovery after shear and (b) simultaneously measured storage G' and loss modulus G'' during 1 h of shear and the quiescent recovery after shear (1 wt% MWNT).

Fig. 6b shows G' and G'' values measured simultaneously with the conductivity. In contrast to the increase of the conductivity in Fig. 6a, G' and G'' decrease under steady shear. For longer shear durations both quantities tend to approach asymptotically constant values. Despite the different tendencies (*formation of an electrical conductive network* vs. *reduction of mechanical reinforcement*) the relative changes in electrical properties are much more pronounced (logarithmic scale) than the changes of the rheological properties (linear scale). These findings provide a clear evidence for the different nature of the 'conducting electrical' and 'mechanical' filler network. This is not surprising since the mechanisms of the charge transport and reinforcement in composite materials are expected to be different [45]. In order to obtain a conducting pathway in the matrix, a percolation network of electrically interconnected filler particles is necessary. Moreover, very small inter-particle distances [34,39–41] are needed for low contact resistance and efficient electron tunnelling through the network. Since the nanotubes in thermoplastic composites are considered to be surrounded by insulating polymer chains [38], very small distances between CNT can be achieved only for densely packed nanotubes inside the agglomerates. In contrast, for an efficient mechanical reinforcement strong interfacial interaction of nanotubes with the matrix and a homogeneous filler distribution is needed. The optimal 'mechanical network' is thus a hybrid structure of well-dispersed MWNT strongly interacting with the polymer chains [38,45]. During (shear-induced) agglomeration nanotubes are withdrawn from the reinforced areas creating a new type of the reinforcement: micro-fillers with low aspect ratio (sphere-like agglomerates) instead of nano-fillers with high aspect ratio (individual MWNT). Therefore, the percolated agglomerate network (conductive 'micro-filler') appears to be less effective for reinforcement, but highly effective for charge carrier transport [43].

In Fig. 7 the data from Fig. 6 are shown together with the same experiment on a sample with 'agglomerated nanotubes' (1 wt% MWNT), prepared by the thermo-mechanical pre-treatment as described for the samples in Fig. 5. For the 'agglomerated' sample, the DC conductivity as well as G' and G'' decrease during shear deformation. That means that both, electrical conductivity and mechanical reinforcement undergo partial destruction and finally approach constant values corresponding to a stationary state of the dynamic filler network in the shear flow.

Interestingly, both samples regardless of the initial state of the filler network (either 'dispersed' or 'agglomerated' MWNT) asymptotically approach nearly identical values of the conductivity as well as G' and G'' for sufficient duration of steady shear. It is further noteworthy, that the asymptotic values for the rheological properties are approached faster than for the electrical conductivity. Although the mechanisms for the charge transport and reinforcement in the filler networks are expected to be quite different, the similar tendency for both electrical conductivity and G' and G'' to approach constant values supports our hypothesis that a stationary filler network is formed in steady shear flows.

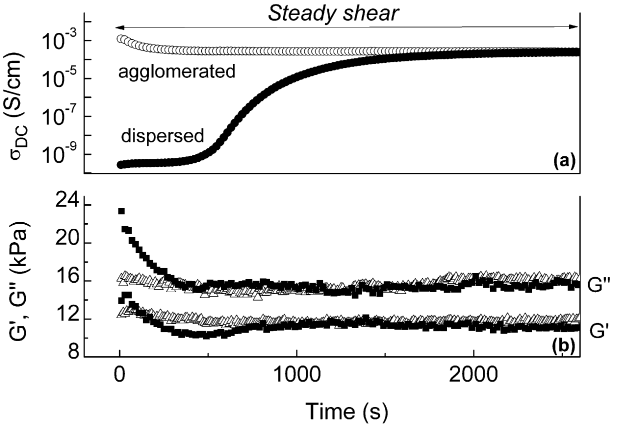

Fig. 7. Time dependence of the DC conductivity (a) during 1 h of steady shear (shear rate: 0.02 rad/s) and the simultaneously measured components of the complex shear modulus G' and G'' (b) for two samples (1 wt% MWNT) with initially 'dispersed' (solid symbols) and 'agglomerated' nanotubes (open symbols).

3.3. Shear rate dependence

In order to investigate the shear rate dependence of the destruction and build-up effects six similar samples (PC/MWNT, 1 wt% MWNT) were cut out of one mould injected plate and thermo-mechanically pre-treated by the procedure (not shown) used for the samples in Figs. 5 and 6 in order to obtain samples with 'well-agglomerated' MWNT and a high (nearly identical) level of electrical conductivity. Different shear rates varying from 0.02 rad/s to 0.5 rad/s were applied to thus prepared samples. In Fig. 8 the electrical conductivity (a), the storage modulus G' (b) and the transient shear viscosity $\eta^{+} = \langle\tau(t)\rangle/\dot{\gamma}_{\text{steady}}$ (c), where $\langle\tau(t)\rangle$ is the torque averaged over one period of the superimposed small oscillation and $\dot{\gamma}_{\text{steady}}$ is the averaged (steady) shear rate, are shown as a function of time t after the shear deformation started. The values of $\eta^{+}(t)$ from Fig. 8c are replotted in Fig. 8d as a function of the total shear $\gamma = \dot{\gamma}_{\text{steady}} \cdot t$.

The transient viscosity shown in Fig. 8c shows a small shear overshoot, which shifts towards smaller times with increase of the shear rate. It is seen in Fig. 8d, that for shear rates below 0.1 rad/s the overshoot appears at $\gamma_{\max} = \dot{\gamma}_0 t_{\max} \approx 2$ and gradually shifts to $\gamma_{\max} \approx 4$ at higher shear rates. It is important to note, that the pure polycarbonate matrix does not show shear-thinning for the shear rates and temperatures used in our experiment and does not exhibit a shear overshoot. Furthermore, no indication for (re)-orientation of MWNTs has been found for this system as it was proven by X-ray measurements [37]. Hence, the appearance of maxima in the transient viscosity curves can be definitely ascribed to the shear-induced destruction of the MWNT network. Such an overshoot is a typical feature of polymer melts filled with attractively interacting filler particles, see for example [37,48].

After 600 s of shear all three quantities reach almost constant values corresponding to a stationary state of the dynamic filler network for every shear rate. Therefore, the values of σ_{DC}, G' (G'') and η^{+} at $t = 600$ s can be taken for the stationary (subscript: stat) values ($t \to \infty$). In Fig. 9a, b $\sigma_{\text{stat}} = \sigma_{\text{DC}}$ ($t \to \infty$) and the shear viscosities $\eta_{\text{stat}} = \eta^{+}$ ($t \to \infty$) are plotted versus shear rate.

The decrease of σ_{stat} and η_{stat} with increase of the shear rate corresponds to the destruction of the 'conducting' and 'viscoelastic' networks, respectively. Similar data sets (σ_{stat} and η_{stat} vs. shear rate) were obtained for different MWNT concentrations and various melt temperatures [47]. These results will be discussed in a forthcoming paper in more detail.

The shear rate dependence of the electrical conductivity and viscosity in a steady shear flow was first reported by Kharchenko et al. [16] and Obrzut et al. [17]. In [16] the authors described the shear-thinning of a PP/MWNT composite (2.5 wt% MWNT) by the empirical Carreau equation [49], $\eta(\dot{\gamma}) = \eta_0[1 + (\dot{\gamma}\tau_\eta)^2]^{-n} \propto \dot{\gamma}^{-m_\eta}$, where τ_η and $\dot{\gamma}\tau_\eta$ are the characteristic time and the reduced shear rate, respectively. The value of the asymptotic shear-thinning exponent m_η was found in [16] to be 0.76, which is close to the values typical for highly entangled polymer solutions (see references in [16]). The τ_η value at 200 °C was about 20 s. The decrease of the electrical conductivity was described with an analogous function $\sigma(\dot{\gamma}) = \sigma_0[1 + (\dot{\gamma}\tau_\sigma)^2]^{-n'} \propto \dot{\gamma}^{-m_\sigma}$, where $\tau_\sigma \approx 0.24 \cdot \tau_\eta$ and $m_\sigma = 0.66$. The decrease of both transport quantities with $\dot{\gamma}$ was

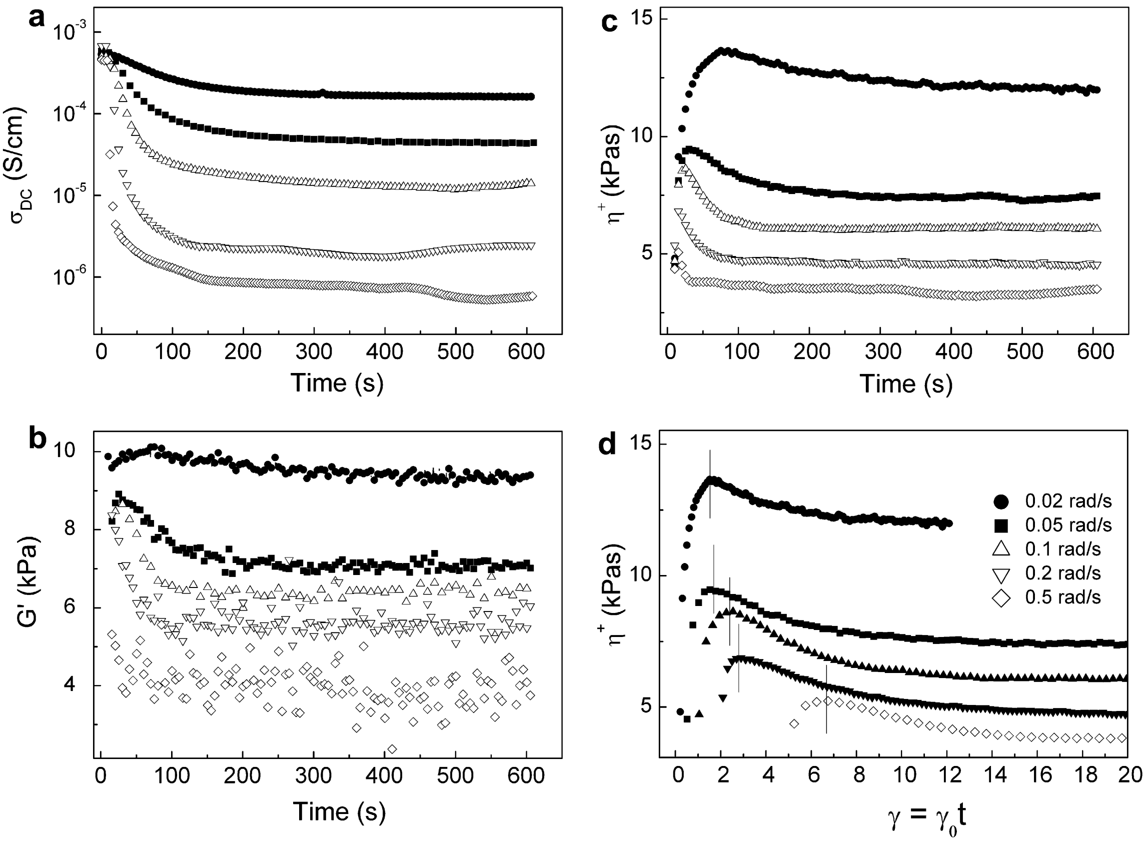

Fig. 8. Time evolution of the electrical conductivity (a), the real part of the storage modulus G' (b) and the transient shear viscosity $\eta^+ = \tau(t)/\dot{\gamma}$ (c) of a PC/MWNT melt (230 °C, 1 wt% MWNT) with initially well-agglomerated nanotubes during 1 h of steady shear for different shear rates. The transient shear viscosity $\eta^+(t)$ from (c) is replotted in (d) as a function of total shear $\gamma = \dot{\gamma}_{\text{steady}} \cdot t$.

explained by changes in the structure of the filler network, e.g. by reduction of the number of nanotube contacts by orientation or by disrupture in the flow. Our data yield a lower value of the asymptotic shear-thinning viscosity exponent, $m_\eta = 0.41$; the difference presumably arises from to the lower MWNT concentration (1 wt%) of our samples compared to that (2.5 wt%) used by Kharchenko et al. [16]. For similar PC/MWNT samples filled with 5 wt% MWNT the exponent m_η was found to be 0.75 [50].

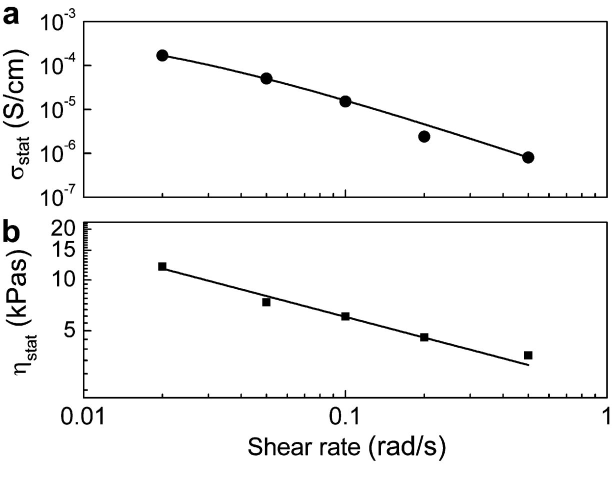

Fig. 9. Steady state values for the DC conductivity (a) and viscosity (b) after 600 s of steady shear vs. shear rate (data extracted from Fig. 8). The lines indicate fits with a semi-empirical function (see text) (a) and a power law (b).

In order to fit the steady state conductivity data, we propose the simple semi-empirical equation:

$$\sigma_{\text{stat}} = \frac{\sigma_0}{(1 + t_1\dot{\gamma})^x}. \tag{1}$$

This equation is derived from the classical percolation equation above the percolation threshold (see for example [8]):

$$\sigma_{\text{DC}} = \sigma_0\left(\frac{p_A - p_C}{1 - p_C}\right)^x \approx \sigma_0(p_A - p_C)^x, \tag{2}$$

by assuming that the volume content of the agglomerates composing the conductive percolation network $p_A - p_c$ is inversely proportional to the shear rate $\dot{\gamma}$:

$$(p_A - p_C) \propto \frac{1}{(1 + t_1\dot{\gamma})}. \tag{3}$$

This simple assumption implies that the shear-induced destruction of the conductive agglomerates increases stronger with $\dot{\gamma}$ than the build-up effect. Therefore, steady conductivity values drop down with $\dot{\gamma}$. In terms of the kinetic equation (5), discussed in the next section, such assumption corresponds to $k(\dot{\gamma}) = a\dot{\gamma}^{m-1}$ and $k_2(\dot{\gamma}) = b\dot{\gamma}^m$ with $t_1 = \text{b/a}$. In Fig. 9a the DC conductivity values vs. shear rate are fitted to Eq. (1). The fit parameters are: $t_1 = 64.5$ s and $\sigma_0 = 8.9 \times 10^{-4}$ S/cm. The exponent x was taken to be 2, corresponding to the exponent for the so-called 'critical zone' just above the percolation threshold [51,52]. It can be seen that Eq. (1) with $x = 2$ provides a very good fit of the conductivity data up to the shear rate of 0.5 rad/s. For higher shear rates, however, we found that the shear-thinning exponent 2 is not sufficient to describe a dramatic drop of electrical conductivity which is especially pronounced for lower nanotube concentrations. At high shear rates, $\dot{\gamma} \geq 1$ rad/s, both viscosity and conductivity approach the limiting values of the matrix polymer. These results will be discussed in a forthcoming paper in more detail.

3.4. *Combined model for conductivity of shear-induced network*

It was proposed by us earlier [11,18,19,43], to describe the time evolution of the electrical conductivity in polymer melts with MWNT by percolation of conductive sphere-like nanotube agglomerates. In absence of steady shear the agglomerates can appear due to attractive interactions of the nanotubes. This process named 'quiescent agglomeration' can be described by the solution of a first or higher order kinetic equation [11,18,19,43,53]: $\mathrm{d}p_\mathrm{A}/\mathrm{d}t = k_0(p_{\mathrm{A}\infty} - p_\mathrm{A})^n$, where n is the order of reaction, p_A is the volume concentration of conductive agglomerates, $p_{\mathrm{A}0}$ and $p_{\mathrm{A}\infty}$ are the agglomerate concentrations at $t = 0$ and $t \to \infty$ and k_0 is the kinetic coefficient for quiescent agglomeration. Since our data analysis [11,18,19] did not show significant differences between first and second order kinetics, for simplicity in the following considerations a first order kinetics ($n = 1$) was taken. In the presence of steady shear flow, the kinetic equation has to be extended by two additional shear-dependent terms [43] for shear-induced breakdown and build-up of agglomerates:

$$\frac{\mathrm{d}p_\mathrm{A}}{\mathrm{d}t} = k_0(p_{\mathrm{A}\infty} - p_\mathrm{A}) + k_1(\dot{\gamma})(p_{\mathrm{A}\infty} - p_\mathrm{A}) - k_2(\dot{\gamma})p_\mathrm{A}, \tag{4}$$

where $k_1(\dot{\gamma})$ is the kinetic coefficient for shear-stimulated agglomeration and $k_2(\dot{\gamma})$ for shear-stimulated destruction process. A similar kinetic equation was proposed earlier for flow-induced agglomerate breakdown and build-up for inelastic suspensions [54]. Eq. (4) can be rewritten as:

$$\frac{\mathrm{d}p_\mathrm{A}}{\mathrm{d}t} = k(\dot{\gamma})(p_{\mathrm{A}\infty} - p_\mathrm{A}) - k_2(\dot{\gamma})p_\mathrm{A}, \tag{5}$$

where $k = (k_0 + k_1)$. The solution of Eq. (5) can than be set into any equation for the insulator–conductor transition, for example into the classical percolation theory [11,18,19] or the Generalized Effective Medium (GEM) approximation [43,55] for dielectric properties of the non-conductive systems with conductive inclusions:

$$(1 - p_\mathrm{A}(t))\frac{\sigma_\mathrm{M}^{1/s} - \sigma_\mathrm{DC}(t)^{1/s}}{\sigma_\mathrm{M}^{1/s} + Z\sigma_\mathrm{DC}(t)^{1/s}} + p_\mathrm{A}(t)\frac{\sigma_\mathrm{A}^{1/t} - \sigma_\mathrm{DC}(t)^{1/t}}{\sigma_\mathrm{A}^{1/t} + Z\sigma_\mathrm{DC}(t)^{1/t}} = 0, \tag{6}$$

where $p_\mathrm{A}(t)$ is given by Eq. (5), $Z = (1 - p_\mathrm{C})/p_\mathrm{C}$, $\sigma_\mathrm{DC}(t)$ is the actual value of the measured DC conductivity, p_C is the percolation threshold, and σ_M and σ_A are the conductivity values of the polymer matrix and agglomerates, respectively. The critical exponents t and s were taken to be 2 and 0.73, respectively, which are typical values for 3D systems (see references in [56]).

The assumption of an additional shear-dependent *build-up term* can be helpful for understanding the physical processes in composite melts during processing. It can explain the relatively high conductivity values in the presence of strong shear fields, which was experimentally proven by in-line monitoring of conductivity during mould injection process [15].

3.4.1. *Modified three-component kinetic equation for shear-induced effects*

The solution $p_\mathrm{A}(t)$ of the differential equation (5) for the fixed coefficients $k(\dot{\gamma})$ and $k_2(\dot{\gamma})$ (at a certain $\dot{\gamma}$) can either be an exponential decay or an exponential growth function. The latter is not able to describe a local minimum in conductivity as shown in the experimental curves in Figs. 2–4.

In order to describe the shape of those curves, two ways are possible: (i) using the second order differential equation $\mathrm{d}^2p_\mathrm{A}/\mathrm{d}t^2 = f(p_\mathrm{A}, \dot{\gamma}, p_{\mathrm{A}\infty})$ for the agglomeration kinetics, what seems to be inappropriate, or (ii) to use multiple first order differential equations (Eq. (5)) assuming different species participating in the agglomeration process. The latter case is considered in the following.

As the simplest approximation a three-component system taking part in the agglomeration and network formation is assumed: (i) large agglomerates *A*, (ii) small agglomerates *S*, and additionally, (iii) separated nanotubes *T*. The large and the small agglomerates percolate (form a network) and are considered to be 'conductive'. Furthermore, one has to assume that individual nanotubes are not contributing to the conductivity. It should be noted that our three-component model is only the simplest possible approach to fit the non-monotonic conductivity curves. As it was mentioned earlier [19], a hierarchic system of equations for the species of all possible sizes could be a better approximation for a composite with a size distribution of the conductive agglomerates. In case of the three-component system Eq. (5) can be rewritten as a system of two differential equations. Here, weight fractions w_i are used instead of the volume content $p_\mathrm{A}(t)$ by the reason of convenience:

$$\frac{\mathrm{d}w_\mathrm{A}}{\mathrm{d}t} = -aw_\mathrm{A} + bw_\mathrm{S} + cw_\mathrm{T}, \tag{7}$$

$$\frac{\mathrm{d}w_\mathrm{S}}{\mathrm{d}t} = -dw_\mathrm{S} + fw_\mathrm{T} + gw_\mathrm{A}, \tag{8}$$

with the normalization condition:

$$w_\mathrm{A}(t) + w_\mathrm{S}(t) + w_\mathrm{T}(t) = w_\mathrm{CNT}, \tag{9}$$

where w_A, w_S, and w_T are the total weight fractions of MWNT inside the large and small agglomerates and of the individual nanotubes, respectively. w_CNT is the total weight fraction of nanotubes in the composite (1 wt% = 0.01). In this consideration, the large agglomerates A disappear due to shear-induced destruction (term: $-aw_\mathrm{A}$), and appear due to the shear-induced agglomeration of the small agglomerates S (term: bw_S) and by agglomeration of the nanotubes T (term cw_T). Analogically, the small agglomerates S disappear due to shear destruction (term: $-dw_\mathrm{S}$) and appear from the shear-

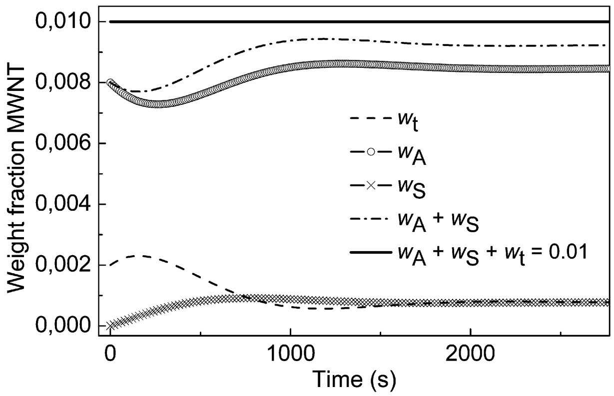

Fig. 10. Time evolution of the weight fractions of nanotubes $w_\mathrm{T}(t)$, large agglomerates $w_\mathrm{A}(t)$ and small agglomerates $w_\mathrm{S}(t)$ (numerical solutions of the system of Eqs. (7)–(9)) for the arbitrary parameters $a = 0.001\ \mathrm{s}^{-1}$, $b = 0.01\ \mathrm{s}^{-1}$, $c = 0.001\ \mathrm{s}^{-1}$, $d = 0.001\ \mathrm{s}^{-1}$, $f = 0.001\ \mathrm{s}^{-1}$, $g = 10^{-8}\ \mathrm{s}^{-1}$ (see text for detail).

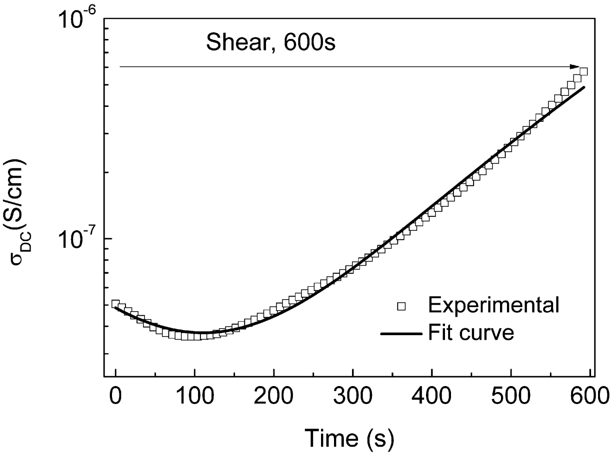

Fig. 11. Experimental DC conductivity (squares) of PC/MWNT (1 wt% MWNT) during steady shear fitted with Eq. (3) and the numerical solutions of Eqs. (6)–(9) (solid line). Fit parameters: $w_{A0} = 0.00535$ (0.535 wt%), $w_{S0} = 8.41 \times 10^{-12}$, $a = 1.7 \times 10^{-4}\ s^{-1}$, $b = 1.96 \times 10^{4}\ s^{-1}$, $c = 2.35 \times 10^{-7}\ s^{-1}$, $d = 6.13 \times 10^{-9}\ s^{-1}$, $f = 1.12 \times 10^{-14}\ s^{-1}$, $g = 6.7 \times 10^{-11}\ s^{-1}$, $\alpha = 40$, $p_C = 0.2$, $\sigma_m = 10^{-12}$ S/cm, $\sigma_A = 1.58 \times 10^{-4}$ S/cm.

induced agglomeration of tubes T (fw_T), and from the decay product of large agglomerates A (gw_A). The coefficients a, b, c, d, f and g describe both shear-induced and quiescent agglomeration/destruction and are thus shear rate dependent. Fig. 10 illustrates the evolution of the weight fractions $w_A(t)$, $w_S(t)$, $w_T(t)$, and $(w_A(t) + w_S(t))$ (numerical solutions of Eqs. (7–9)) for the fixed arbitrary coefficients: $a = 0.001\ s^{-1}$, $b = 0.01\ s^{-1}$, $c = 0.001\ s^{-1}$, $d = 0.001\ s^{-1}$, $f = 0.001\ s^{-1}$, $g = 10^{-8}\ s^{-1}$ and following starting values $w_{A0} = 0.008$, $w_{S0} = 0$ and $w_{T0} = 0.002$.

Within this three-component agglomeration model the values $w_A(t)$ as well as $(w_A(t) + w_S(t))$ can have a minimum. The applied shear destroys the large agglomerates *A* but, at the same time, produces smaller agglomerates *S* and disperses nanotubes *T* which will re-build the agglomerates *A* and *S* (see the evolution of curves in Fig. 10). Therefore, the conductivity $\sigma_{DC}(t)$ described by (Eq.(6)) which was assumed to be dependent on the volume fraction $p_A(t) = \alpha w_A(t)$ of large agglomerates A can also have a local minimum. Here, α is a re-scaling factor (fit parameter) for the weight fraction of nanotubes w to the volume fraction p of the agglomerates. The sum of large and small agglomerates can be equally taken for the conductivity evaluation since it also can show a minimum (Fig. 10). In order to test the proposed model, the evolution of the experimental DC conductivity of a PC/MWNT melt (1 wt% MWNT) measured for the steady shear flow of $\dot{\gamma}_{steady} = 0.02$ rad/s (solid line in Figs. 2 and 3) was fitted. The result is shown in Fig. 11, together with the fit parameters.

It should be noted that the model contains at least 6 fit parameters (a, b, c, d, f, g) and different parameter combinations can fit the experimental data with similar accuracy. Therefore, we do not attribute much physical meaning to these values. We also expect that the real network formation in shear flows is a much more complicated process. In general, the coefficients a, b, c, d, f, g must depend on the shear rate, composite history, temperature, polymer viscosity, etc. Therefore, the experimental estimation of those values can be difficult or even impossible. However, this model is a first approach to account additionally for different network structures.

4. Conclusion

In the present paper we report on the shear-induced network destruction and build-up in polycarbonate/MWNT melts which was monitored by simultaneous time-resolved DC conductivity and shear modulus (G' and G'') measurements during quasi-steady shear. A recently developed setup allowed such simultaneous conductivity (dielectric) and rheological measurements under steady shear and in the quasi-quiescent melt. The experiments were performed for different shear rates, nanotube concentrations and degree of nanotube dispersion (thermo-mechanical 'history').

In our work we concentrated on the *time evolution* as well as on the *very early stages* of the network formation where one can see the 'double-sided' effect of shear-induced destruction and build-up. Our experiments gave us a clue to understand the processes of formation of a network of attractively interacting filler particles in highly viscous polymer melts under steady shear conditions.

Depending on the initial state of the nanotube dispersion (or agglomeration) we observed under steady shear: (i) a shear-induced insulator–conductor transition for melts with well-dispersed MWNT, (ii) a non-monotonic behaviour of electrical conductivity for melts with 'partially agglomerated nanotubes', which is attributed to the competition of the destruction and build-up effects of shear, and (iii) a shear-induced conductor–insulator transition for composite melts with 'well-agglomerated' nanotubes. To our actual understanding, the interplay of the destructive and the build-up effects has a fundamental origin and acts on the different types of attractively interacting filler particles in polymer matrices subjected to shear flows.

We also demonstrated that after certain duration of shear, the nanotube network, as well as the related electrical and rheological properties of the composite will asymptotically approach their steady state values. For the understanding of time evolution of the composite properties under shear flows a concept of a network in dynamic equilibrium was proposed.

From the comparison of the simultaneously measured electrical conductivities and the shear modulus (G' and G'') it became evident, that a network of MWNT agglomerates formed under shear leads to an increase of the electrical conductivity, whereas the agglomeration reduces the mechanical reinforcement. This can be explained by the different mechanisms of the charge transport via electron tunnelling at CNT contacts in the densely packed agglomerates and mechanical reinforcement by the nanofiller networks.

For the modelling of the network formation in presence of steady shear a kinetic equation for the nanotube agglomeration was supplemented with shear-dependent destruction and shear-dependent build-up terms. The formation of a 'dynamic' network under shear was considered in a first approximation as agglomeration/dis-agglomeration of small agglomerates (including individual nanotubes) and into larger agglomerates and visa versa. This is the simplest hierarchical process of shear-induced agglomeration and destruction, which can describe the non-monotonic behaviour of the DC conductivity under steady shear. For more detailed hierarchical models, experimental data on the structure of the filler network are necessary. The experimental DC conductivity was fitted to the kinetic equation for the evolution of conductive nanotube agglomerates under shear coupled with the GEM approximation for the insulator-to-conductor transition. The destruction and build-up kinetic constants were deduced as fit parameters for fixed shear conditions. Regardless of its simplicity the proposed model gives a good qualitative description of the effects in nano-composite melts subjected to steady shear flows. The interplay between the destruction and build-up effects of the nanotube network seems to have a fundamental origin in the flowing polymer matrices filled with attractively interacting filler particles.

Apart from the scientific interest, the reported results point to a technological way for the production of highly conductive polymer composites with low filler contents by applying a well-defined flow during processing of composite melts.

Acknowledgments

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