

Destruction and formation of a conductive carbon nanotube network in polymer melts: In-line experiments

Ingo Alig^{a,*}, Dirk Lellinger^a, Martin Engel^a, Tetyana Skipa^a, Petra Pötschke^b

^a *Deutsches Kunststoff-Institut (DKI), Schlossgartenstrasse 6, D-64289 Darmstadt, Germany*

^b *Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Hohe Strasse 6, D-01069 Dresden, Germany*

Received 7 December 2007; received in revised form 31 January 2008; accepted 31 January 2008

Available online 19 February 2008

Abstract

Investigations on electric conductivity and dielectric permittivity have been performed during melt processing of polycarbonate (PC) and polyamide 6 (PA6) containing different amounts of multi-walled carbon nanotubes (MWNT). For the experiments a measurement slit die containing two electrodes in capacitor geometry was flanged to the outlet of a twin-screw extruder. AC conductivity and the related complex permittivity were measured in the frequency range from 21.5 to 10⁶ Hz for different processing conditions (melt temperature and throughput) and after stopping the extruder. It was found that the conductivity dropped down to values typical for the matrix polymer when the extrusion started. After the extruder was stopped the conductivity shows an increase of up to eight orders of magnitude with time. This conductivity recovery in the rest time after mechanical deformation was found to be faster for increasing melt temperature or samples with higher CNT concentration. The increase of the conductivity in the quiescent melt is explained by reorganization of the conductive network-like filler structure, which was – at least partially – destroyed under mechanical deformation. The reformation kinetics of the conductive network after mechanical deformation is considered to be an agglomeration process, which can be approximated by a combination of cluster aggregation and percolation theory.
© 2008 Elsevier Ltd. All rights reserved.

Keywords: Polymer/carbon nanotube composite; Extrusion; Electric conductivity

1. Introduction

Due to the high aspect ratio and the extraordinary electrical and mechanical properties of carbon nanotubes (CNTs), the addition of low levels of them into polymers can enhance material properties considerably [1–8]. This is especially the case for electric conductivity and mechanical strength. Today, first CNT–polymer composites are commercially available on the market. However, a major restraint in a broad market acceptance of this new class of polymer composites is the wide variation in electric conductivity and other material properties of the finished plastic products as function of the processing conditions and the matrix polymer. Moreover, broad

property variations can occur within the very same plastic part itself.

Some years ago, we reported on dielectric investigations of pressed polycarbonate plates containing multi-walled carbon nanotubes (MWNT) done at room temperature [8]. The samples were prepared by melt mixing with different contents of MWNT and by varying the screw speed and mixing time. This study demonstrated the sensitivity of dielectric or conductivity spectroscopy for investigation of polymer composites containing CNT. The composition dependence of the electric conductivity could be described by a percolation threshold. Furthermore, a strong indication was found that the nanotubes are separated at their contacts by polymer chains. These local contact regions can create a considerable contact resistance and contact capacity. In addition, a first indication of the influence of the extrusion conditions on the electric conductivity has been reported. The dielectric “off-line” measurements revealed the influence of screw speed

* Corresponding author. Tel.: +49 6151 16 2404; fax: +49 6151 29 2855.
E-mail address: ialig@dki.tu-darmstadt.de (I. Alig).

and mixing times on dispersion of the CNT. More recently, we could show by time-resolved conductivity measurements during isothermal annealing of pressed plates (polypropylene with 2 wt% MWNT) that the thermal treatment above the melting temperature leads to an increase of the conductivity by about eight orders of magnitude in about 5 h [9]. This was a clear indication for the built-up of a conductive network structure.

In order to study the influence of shear and thermal history on electrical properties in more detail model experiments have been performed on polycarbonate (PC) melt containing 0.6 vol% MWNT by combined rheological and AC conductivity measurements [10]. The conductivity spectra were recorded during isothermal annealing at 260 °C after a short shear deformation ($t_s = 10$ s, $d\gamma/dt = 1$ rad/s) applied to the composite melt. The recovery of the conductivity after shear was attributed to the reformation of the conductive CNT network destroyed – at least partially – by the shear deformation. Based on cluster aggregation and percolation theory a simple model for the conductivity recovery of the conductive filler network in polymer melts has been proposed and was used to fit the data [10]. In the following the term “cluster aggregation” is used synonymically for the agglomeration of nanotubes.

A similar conductivity recovery was found for polypropylene containing 2 wt% MWNT, measured in a slit die which was flanged to the outlet of an extruder, after the extruder was stopped [11]. It was also shown that the time needed for the reformation of the filler network (and related to this, recovery of conductivity) from about 10 min to several hours considerably exceeds the usual processing times for injection moulding (below 60 s) or extrusion (below 10 min). This has of course consequences for polymer processing.

Since the kinetics of destruction and reformation of the conductive CNT network in the polymer melt is extremely important for the understanding (and simulation) of extrusion and injection moulding processes and prediction of the final properties of the plastic parts, we present here a systematic study of the influence of processing parameters (melt temperature and throughput) on the conductivity of the melt. Furthermore, we extended the in-line experiments to a twin-screw extruder with an advanced sensor design having a higher resolution. Finally, we used our combined model for cluster aggregation and percolation [10] to describe the in-line measured conductivity recovery curves.

2. Experimental

2.1. Materials and composite preparation

2.1.1. Polycarbonate (PC)

The nanotubes used in this study were multi-walled carbon nanotubes (MWNT) supplied as a PC masterbatch containing 15 wt% MWNT from Hyperion Catalysis International Inc. (Cambridge, USA). The MWNT were produced by chemical vapour deposition (CVD) and have diameters of approximately 10 nm. According to the supplier, the length of the MWNT after production with CVD is above 10 μ m, therefore

the aspect ratio is about 1000. Using a Haake PTW16/25 twin-screw laboratory extruder (Thermo Electron Corporation, Waltham, USA) with $d = 16$ mm and $L/D = 25$ the masterbatch was melt mixed into PC of the same type. Mixing was performed at rotational speeds between 100 and 325 rpm and throughputs between 0.3 and 2.7 kg/h starting from granular pre-mixtures. The frequency dependent measurements of conductivity and dielectric permittivity have been performed on polycarbonate (PC) melts with 0.5, 0.875 and 2 wt% MWNT. The processing temperatures were 260, 250, 240 and 230 °C.

2.1.2. Polyamide 6 (PA6)

The PA6 masterbatch containing 20 wt% of MWNT was also provided by Hyperion Catalysis International Inc. The MWNT were identical to those used in the PC masterbatch. The masterbatch was melt mixed into PA6 of the same type by using the Haake PTW16/25 twin-screw laboratory extruder. Mixing was performed at a rotational speed of 175 rpm and a throughput of 1.3 kg/h starting from granular pre-mixtures. The measurements of conductivity and dielectric permittivity have been performed using PA6 melts containing 0.7, 1.3 and 2.7 wt% MWNT. The processing temperatures were 270, 260 and 250 °C.

2.2. In-line experiments

For the in-line experiments the CNT–polymer composites were extruded into the measurement slit die which was flanged to the outlet of a Haake PTW16/25 twin-screw extruder. The die is equipped with dielectric sensors (arranged in plate–plate geometry, see below), pressure and temperature sensors. In order to investigate the time dependent changes of AC conductivity under quiescent melt conditions, the extruder was stopped for some time. The melt temperature was controlled by electric heating of the measurement die. This allowed us to guarantee isothermal conditions within ± 3 K. Two pressure transducers allow the determination of the mean and difference pressure so that the die can be used as in-line rheometer as well.

2.3. Dielectric measurements

The measurement slit die equipped with dielectric sensors shown in Fig. 1a and b was recently developed to monitor the extrusion of conductive polymer composites. The sensors were redesigned compared to the sensors described in Refs. [12,13] in order to improve the capacitance and thus the resolution of conductivity and permittivity measurements.

The new sensors (plate–plate geometry: 16 \times 95 mm) were mounted face to face in the melt channel with a distance of 4 mm, equal to the thickness of the channel (Fig. 1a). The air capacity was calculated by a finite element simulation of the electric field for the actual sensor geometry, resulting in a value of 3.2 pF. An LCR bridge (HP4284A, Agilent) was used to measure parallel capacitance C_p and $\tan \delta$ in the frequency range from 21.5 to 1 MHz with three points per decade

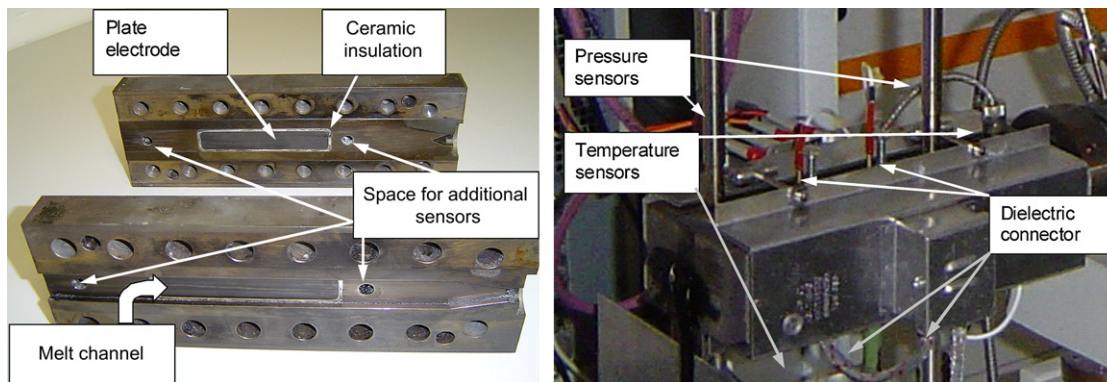


Fig. 1. Measurement slit die equipped with two dielectric sensors (four wire measurement), two pressure transducers and two temperature sensors. The left figure shows the open slit die and the right figure shows the slit die with sensors and electric heating.

(equidistant in logarithmic scale). The measuring voltage was 1 V. All frequency spectra were recorded continuously starting from low to high frequencies. The total measuring time for a full frequency sweep was about 30 s.

The real parts of the complex conductivity σ' and permittivity ϵ' spectra are obtained from the air capacitance and the measured values of C_p and $\tan \delta$, respectively. The lower conductivity measurement limit of the LCR bridge with the setup described is about 4×10^{-14} S/(m Hz), resulting in 8×10^{-11} S/cm at the lowest measurement frequency of 20 Hz. Therefore, for neat PC no reliable conductivity values could be obtained by this setup.

3. Results and discussion

3.1. Carbon nanotubes in polycarbonate

3.1.1. Influence of melt temperature

In order to investigate the influence of temperature on the AC conductivity of the sheared and quiescent melt, extrusion–stop–annealing experiments were performed on a melt of polycarbonate containing 0.875 wt% of MWNT at different temperatures. During the extrusion the turning speed and throughput were kept constant at 175 rpm and 1.4 kg/h, respectively. After at least 20 min of extrusion at a certain temperature, the extruder was stopped in order to investigate the melt under quiescent conditions. Fig. 2 shows an example for such extrusion–stop–annealing cycles with melt temperatures of 250, 240 and 230 °C.

The real part of the specific conductivity (at 21 Hz) is plotted versus the processing time. During the extrusion, the conductivity is very small and close to the measurement limit of the setup. However, the measured values are in the order of magnitude of the conductivity of the pure polymer melt. After the extruder was stopped, the shear rate in the melt becomes zero and the conductivity increases by about eight orders of magnitude. Once the extruder is switched on again, the conductivity drops down in a very short time interval, which is explained by a fast destruction of the conductive network by the shear and/or elongational flow. It can be seen from Fig. 2 that the speed of the recovery process is temperature dependent.

This is visualized for representative temperatures in Fig. 3, where the conductivity is plotted versus the recovery time, i.e. the time after stopping the extruder. Conductivity values below 10^{-10} S/cm are not shown, because those values are below the experimental limit of our setup. The recovery process is considerably faster for the higher temperatures. This can be attributed to the decreasing melt viscosity as the temperature of the melt increases. Interestingly, a two-step recovery process was observed for all temperatures. Although the mechanism of the conductivity recovery in polymer–CNT composites is still in discussion we address the first (fast) process to contact formation by de-orientation or translational diffusion of well dispersed nanotubes, whereas the second (slow) process is related to a cluster aggregation mechanism. For a model description see Section 4.

Conductivity spectra acquired during the recovery process for the PC/MWNT composite (0.875 wt% CNT) extruded at $T = 260$ °C are shown in Fig. 4. The small arrows indicate the crossover frequency f_c , which is defined as the transition between two frequency ranges: in the low frequency range

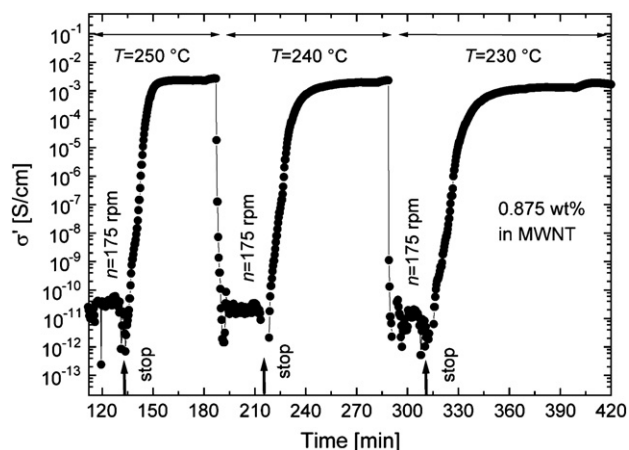


Fig. 2. Time dependence of the conductivity ($f = 21.54$ Hz) of polycarbonate with 0.875 wt% MWNT measured during extrusion and after the extruder was stopped. The three extrusion–stop–annealing sequences (from left to right) represent experiments at 250, 240 and 230 °C, respectively. The screw speed and the throughput for all three temperatures were $n = 175$ min and 1.4 kg/h, respectively.

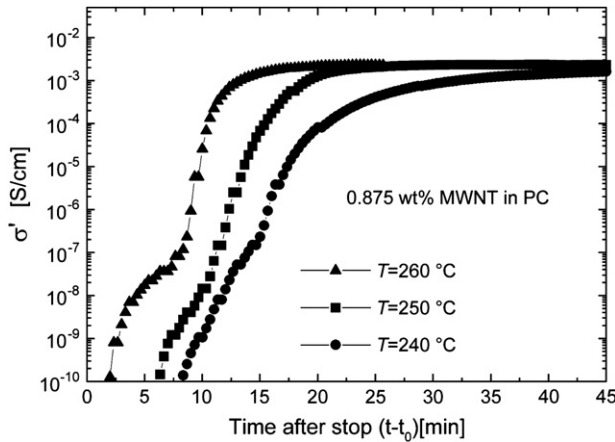


Fig. 3. Influence of temperature on the conductivity recovery ($f = 21.54$ Hz) in polycarbonate containing 0.875 wt% MWNT after the extruder was stopped at t_0 .

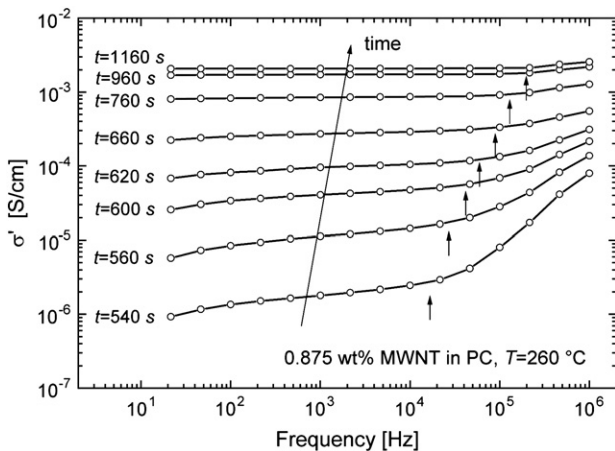


Fig. 4. Time dependence of the conductivity spectra of PC with 0.875 wt% MWNT during reformation of the conductive network at 260 °C after the extruder has been stopped at t_0 .

($f < f_c$), which is determined by the resistivity of the matrix and the CNT network, the conductivity is nearly frequency independent. The high frequency range ($f > f_c$) is mainly determined by the internal capacitances, thus the conductivity increases with increasing frequency. Assuming charge carrier diffusion in a self-similar conductive network or a random network of complex impedances this frequency region is characterized by a power law $\sigma' \propto \omega^n$ with the exponent n . For details see references in Ref. [8].

As it can be seen in Fig. 4, the crossover frequency rises up during the recovery process. In the framework of percolation theory (references in Ref. [8]), the crossover frequency is predicted to increase with increasing filler content, if the system is above the percolation threshold. Therefore we can conclude for recovery times above 540 s that the system is already percolated.

3.1.2. Influence of CNT concentration

Similar start–stop experiments were performed with polycarbonate melts for various contents of MWNT. After

extrusion for at least 20 min at 260 °C, 175 rpm, and a throughput of 1.4 kg/h the extruder was stopped. The recovery of the conductivity (21 Hz) after stopping the extruder is shown in Fig. 5. Again, conductivity values below the experimental limit are not shown. For all concentrations the conductivity during extrusion is below this limit. Obviously, the recovery process is as faster the higher the concentration of CNT in the melt is. This can be explained by the higher probability for nanotubes or cluster contacts. In contrast to Fig. 3, the final values of the conductivities are different, which can be understood considering the different CNT contents. Even for as low CNT content as 0.5 wt%, a fairly high conductivity level can be reached after 50 min of recovery. Again a two-step process could be observed for 0.5 and 0.875 wt% CNT content.

3.1.3. Influence of throughput

Experiments to investigate the influence of the mass throughput were performed using PC with 0.875 wt% MWNT. During the extrusion the temperature and screw speed were kept constant at 260 °C and 175 rpm, respectively. Three extrusion–stop–recovery experiments were performed with throughputs of 0.7, 1.4 and 2.7 kg/h. In order to replace old material in the die by freshly extruded material for all throughputs in a similar way (i.e. to guarantee the same amount of extruded material), the extrusion times before stopping were chosen to be 40, 20 and 10 min. The recovery of conductivity for these experiments is shown in Fig. 6. The speed of the recovery process increases with increasing throughput.

In order to understand this result, we have to differentiate between the influence of throughput inside the extruder barrel (shear and elongation) and in the measurement slit die (only shear). Whereas the shear rate in the slit die increases with increasing throughput, the total amount of shear inside the extruder depends on torque, screw speed and throughput. As mentioned above, in our experiments the screw speed was kept constant. The specific mechanical energy (SME) $\omega_m = (2\pi\omega\tau)/\dot{m}$, where ω is the screw speed (rev/s), τ is the torque (Nm) and \dot{m} is the throughput, is considered to be the relevant quantity characterizing the degree of network destruction

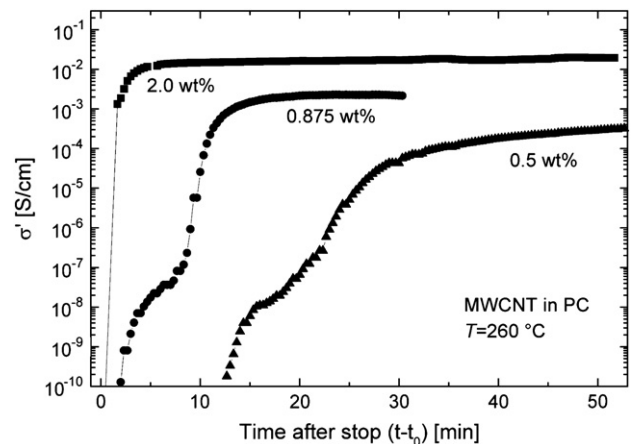


Fig. 5. Conductivity recovery ($f = 21.54$ Hz, $T = 260$ °C) in polycarbonate containing different amounts of MWNT after the extruder was stopped at t_0 . The data for 0.875 wt% MWNT correspond to Fig. 3.

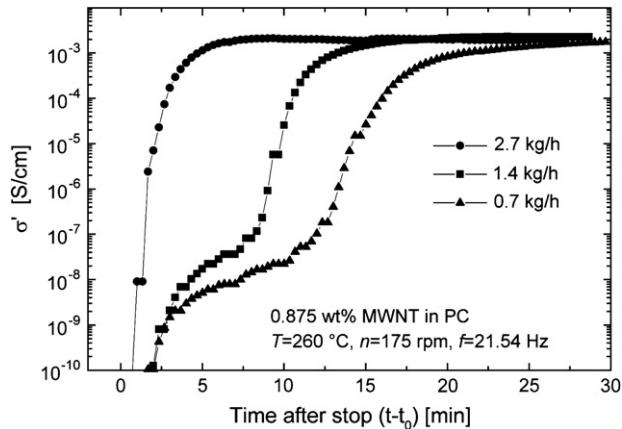


Fig. 6. Conductivity recovery ($f = 21.54$ Hz, $T = 260$ °C) in a polycarbonate–carbon nanotube composite containing 0.875 wt% MWNT for different throughputs after the extruder was stopped at t_0 .

inside of the barrel. Since the torque increases only slightly with increasing throughput, the SME decreases with increasing throughput. This leads to a lower level of destruction of the conductive network and consequently to faster conductivity recovery. Although, a similar trend is expected for the shear induced destruction in the slit die, this contribution is considered to be of second order (see Section 4).

3.2. Carbon nanotubes in polyamide 6

3.2.1. Influence of temperature

The results obtained for PA6/MWNT composites in the extrusion–stop–recovery experiments are similar to those for the PC/MWNT composite. As an example, Fig. 7 shows the recovery of the electric conductivity in the rest time after the extruder was stopped for a PA6/MWNT composite with 2.7 wt% MWNT (screw speed 175 rpm and throughput 1.3 kg/h) for three different melt temperatures. As for the PC/MWNT composites, the recovery kinetics becomes faster with increasing temperature.

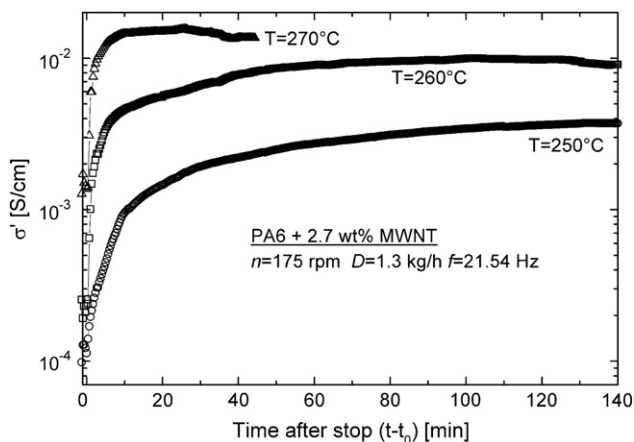


Fig. 7. Temperature dependence of the conductivity recovery ($f = 21.54$ Hz, $T = 270$ °C) in PA6 containing 2.7 wt% MWNT after the extruder was stopped at t_0 .

In contrast to the PC/MWNT composites, the starting value of electric conductivity $\sigma'(t_0)$, corresponding to the electric conductivity measured during the extrusion, is in the order of 10^{-4} S/cm, which is much higher than the values observed for PC/MWNT composites and only one process can be seen. Based on conductivity measurements on pure PA6, the high conductivity of the composite can be attributed to the higher intrinsic conductivity of the matrix polymer. This possibly masks the first recovery process, which was found for the PC at short times.

3.2.2. Influence of CNT concentration

In Fig. 8 the conductivity recovery is shown for different contents of MWNT in PA6 after extrusion at 270 °C, 175 rpm and 1.3 kg/h. As for the PC/MWNT composite, the recovery is significantly faster for higher concentrations. This can be again explained by the increasing probability for CNT or cluster contacts. As it already has been seen, the starting value of conductivity is relatively high due to the intrinsic conductivity of the matrix polymer.

4. Modeling of conductivity recovery

When considering shear dependent destruction and recovery of the conductive network in the extrusion die, one should take into account that there is no constant shear rate over the channel's cross-section of the measurement slit die. This is different to model experiments performed by us, using a rheometer with ring-shaped electrodes to study the recovery process under well-defined conditions [10,14].

In fact, the shear rate in the measurement slit die reaches its maximum value at the channel walls, whereas the shear rate in the centre of the channel is zero. Therefore, one can expect higher conductivities in the centre of the channel. Our sensor configuration consists of two capacitor plates, measuring an average value over the cross-section of the channel. In order to describe such an experiment quantitatively, the channel can be modeled by multiple layers with different conductivities. Because of the lack of data on the shear rate profile this

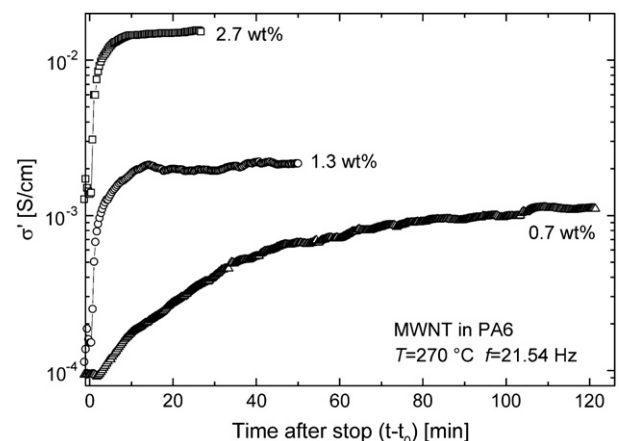


Fig. 8. Conductivity recovery ($f = 21.54$ Hz, $T = 270$ °C) in PA6 for different contents of MWNT after the extruder was stopped at t_0 .

was not possible here. Since the conductivity of a serial connection of impedances is mainly determined by the element with the lowest conductivity, we assume for the following discussion that the measured conductivity is mainly determined by the outer layers. These layers experience the highest shear rates by flowing through the slit die. However, it is noteworthy here that the shear deformation in the slit die is small compared to the deformation of the conductive network by shear and elongation inside of the extruder. Since the resulting destruction of the CNT network is a superposition of both (i) destruction in the extruder barrel and (ii) in the slit die, we assume the deformation by the extruder screw to be the dominant effect. This is supported by the result in Section 3.1.3.

As stated above, two conductivity recovery processes are evident for PC/MWNT composites: (i) a fast process with low step height and (ii) a slower process with high step height. Since the origin of the first one is not yet understood, we will concentrate in the following on the slow recovery process. Because the content of conductive filler material does not change with time, it seems to be impossible to describe the conductivity recovery in the framework of classical percolation theory. Nevertheless, the system undergoes a change from a non-percolated state with very low conductivity (dominated by the matrix conductivity) to a well-percolated state with high conductivity. Because of the time dependence, this phenomenon is sometimes called “dynamic percolation”.

In order to model the electrical recovery, we take into account the following experimental findings:

- It seems that systems with well separated CNT exhibit only a very low conductivity [10,14,15].
- During the recovery process the electric conductivity always increases [9,10,14].
- Electron micrographs show the appearance of agglomerates during the recovery process [10,14,15].
- Samples containing many agglomerates are found to be more conductive than those samples that are well dispersed [10,14,15].

These experimental findings for CNT are in agreement with earlier findings by Schueler et al. [16,17] and Sandler et al. [18] for carbon black and CNT dispersed in epoxy resins and time-resolved experiments by Zhang et al. [19] on polymer blends containing carbon black and carbon fibers. Therefore it seems that the formation of agglomerates during the recovery process is crucial for the increase of conductivity. Clusters are considered to form larger agglomerates by a cluster aggregation process. We assume here that well dispersed individual nanotubes do not contribute considerably to the electric conductivity of the composite, whereas the agglomerates do so. For the latter we assume a more intimate contact between the CNT. The mechanism for that is not yet understood.

For the formation of an infinite filler network in elastomers as well as in polypropylene Heinrich et al. [20] proposed a second order kinetics. This idea is transferred here to the agglomeration process in polymer–CNT composites:

$$\frac{dN_A}{dt} = kN_T^2, \quad (1)$$

where k is the reaction rate, N_T is the number density of particles that agglomerate, and N_A is the number density of agglomerates per unit volume. The particles which agglomerate are considered to be agglomerates of smaller size (clusters) or individual CNT. We should note that the second order kinetics is an oversimplified assumption, since the cluster aggregation is rather a hierarchical process on several length scales where clusters and agglomerates of different size interact. Therefore, the reaction rate and all other parameters are apparent quantities representing an average over different length and time scales. Heinrich et al. (see Ref. [20]) proposed thermodynamic driven nonlinearities related to “regulation in complex systems” to be an alternative description.

Solving Eq. (1) using the boundary condition $N_T(t) = N_{T0} - 2(N_A(t) - N_{A0})$, where N_{T0} and N_{A0} are the starting concentrations of agglomerating particles and agglomerates, respectively, we get the number density of agglomerates as function of time:

$$N_A(t) = N_{A0} + \frac{N_{T0}}{2} \left(1 - \frac{1}{1 + 2ktN_{T0}} \right) \quad (2)$$

The result is a time dependent number concentration of conducting agglomerates. In order to calculate the electric conductivity of the composite, we can now use the percolation theory, describing the dependence of conductivity on the agglomerate content. Thus we effectively “map” the dynamic agglomeration process due to CNT–CNT and CNT–polymer interactions to the static picture of percolating spherical agglomerates. This allows us to keep the percolation equation, which assumes a random distribution of conducting species and exclude interactions between them. The following expressions were used:

$$\sigma_{DC} = \sigma_M \left(\frac{p_C - p_A}{p_C} \right)^{-s}, \quad p_A < p_C \quad (3)$$

$$\sigma_{DC} = \sigma_A \left(\frac{p_A - p_C}{1 - p_C} \right)^\mu, \quad p_A > p_C \quad (4)$$

Here, p_A is the effective volume concentration of the agglomerates, p_C is the volume concentration of agglomerates at the percolation threshold, μ and s are critical exponents, and σ_M and σ_A are the conductivities of the matrix and of the agglomerates, respectively. Assuming a spherical shape of the agglomerates the percolation threshold for them is expected to be in the range between 10 and 30 vol%.

In order to relate the volume concentration in Eqs. (3) and (4) to the number density used in Eqs. (1) and (2), one has to multiply the number densities by the volumes V_T of the agglomerating particle and V_A of the agglomerate, respectively. Replacing $p_T(t) = N_T(t)V_T$ and $p_A(t) = N_A(t)V_A$ in Eq. (2) one finally gets

$$p_A(t) = p_{A0} + (p_{A\infty} - p_{A0}) \left(1 - \frac{1}{1 + 2k'tp_{T0}} \right), \quad (5)$$

with the modified reaction rate constant $k' = k/V_T$ and the final value ($t \rightarrow \infty$) for the volume concentration of the agglomerates, $p_{A\infty}$. Assuming that finally all nanotubes are agglomerated, the parameter $p_{A\infty}$ depends on the ratio of the total volume concentration of nanotubes in the sample, p_{NT} , and the volume concentration of nanotubes inside an agglomerate, $p_{NT,Aggr}$:

$$p_{A\infty} = \frac{p_{NT}}{p_{NT,Aggr}} \quad (6)$$

The fitting of our conductivity data based on this concept is illustrated in Fig. 9. The measurement values (open squares), representing the conductivity recovery of PC/0.875 wt% MWNT, are identical to those of Fig. 3 for $T = 260$ °C. As already discussed in Section 3.1.1, two processes can be clearly differentiated. We address the cluster aggregation to the process at longer times. The fitting parameters are given for both processes at the end of this section.

In the first 5 min, a strong and fast increase in the electric conductivity (fast process) is observed, which then flattens off. Although no final explanation for this first process can be given, one can interpret this as a reorientation of individual nanotubes aligned (oriented) by the shear flow. The orientation in the slit die would cause a lower electric conductivity perpendicular to the shear direction. After the extruder is stopped, this orientation may relax back. Alternatively, the first process is the formation of a weak conductive network of homogeneous dispersed nanotubes, which phase separate afterwards (second process) in a CNT-rich (agglomerates) and CNT-

poor phase. In order to fit the data of the first process we used an empirical relaxation function (dash-dot-dot line):

$$\sigma = (\sigma_{1,inf} - \sigma_{1,0}) \left[1 - \exp\left(-\frac{t}{\tau_1}\right)^\beta \right] + \sigma_{1,0}, \quad (7)$$

where $\sigma_{1,inf}$, $\sigma_{1,0}$, τ_1 and β are empirical parameters. The values for the fit in Fig. 9 are $\sigma_{1,inf} = 1.5 \times 10^{-7}$ S/cm, $\sigma_{1,0} = 10^{-11}$ S/cm, $\tau_1 = 600$ s and $\beta = 1.5$.

Simultaneously, the agglomeration (second process) starts. The dotted line in Fig. 9 represents the volume concentration of agglomerates, calculated from Eq. (5) using $p_{A0} = 0$ vol%, $p_{T0} = 0.49$ vol%, $p_{A\infty} = 24.6$ vol%, and $k' = 0.0096$ s⁻¹. At a recovery time of 8 min, the volume concentration of the agglomerates reaches the percolation concentration of 20 vol%. For shorter times, the conductivity was calculated using Eq. (3) with $\sigma_M = 10^{-11}$ S/cm and $s = 0.73$ (dashed line). Above the percolation threshold, the conductivity was calculated using Eq. (4) with $\sigma_A = 3$ S/cm and $\mu = 2$ (solid line). An agglomerate concentration of about 20 vol% at the percolation threshold would correspond to percolation of spherical species. However, since some of the fitting parameters are covariant and the conductivity in the slit die is taken as an average value, the good agreement between the fitting curve and the data is rather a qualitative support for our agglomeration picture than a quantitative parameter determination.

5. Summary and conclusions

In this paper, we presented frequency dependent conductivity measurements on MWNT/polycarbonate and MWNT/polyamide 6 composites in the molten state during extrusion and after the extruder was stopped. The measurements were obtained using a measurement slit die flanged to the outlet of a laboratory twin-screw extruder, equipped with dielectric, pressure and temperature sensors. Both composites have shown distinctive recovery behavior of the electric conductivity, after the extruder was stopped and the melt comes to rest.

The main results can be summarized as follows:

- (1) Due to mechanical deformation (shear forces and elongational flow) the conductivity of the investigated melts is at a very low level during the extrusion. We attribute this to the disruption of the nanotube contacts in the shear field and (partially) to the orientation of the nanotubes. On larger length scales this leads to a destruction of conductive clusters, and finally of the conductive network.
- (2) The conductivity was found to increase with annealing (rest time after the extruder was stopped) of the melt. This behavior is addressed to reformation of local nanotube–nanotube contacts by translational diffusion and/or reorientation of the nanotubes. Simultaneously, the nanotubes start to form agglomerates, which further increase the electric conductivity. This can be considered to be a phase separation in a CNT-rich and a CNT-poor phase.
- (3) The speed of the recovery process increases with increasing temperature due to the lowered viscosity of the melt

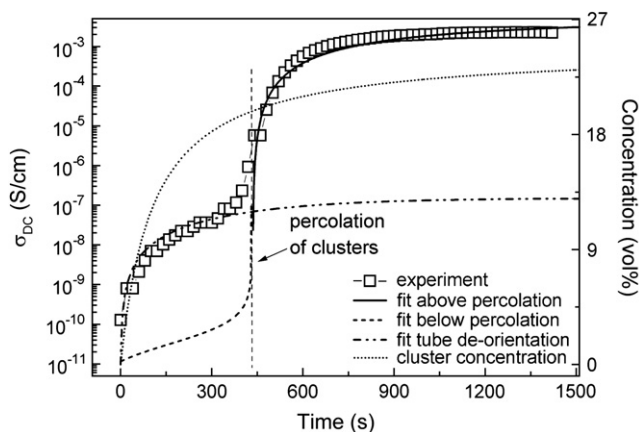


Fig. 9. Modeling of the conductivity recovery after stopping the extruder by combination of an agglomeration model with percolation theory and a simple relaxation equation at early times. Squares are experimental values of PC with 0.875 wt% at $T = 260$ °C. The calculated volume concentration of conductive agglomerates is indicated by dotted line. Percolation theory is used to calculate the conductivity below p_c (dashed line) and above p_c (solid line) from the time dependent agglomerate concentration. The first increase of conductivity is fitted by a simple relaxation equation (dash-dot-dot line). Details of the models and the parameters are given in the text.

(and thus increased mobility of the nanotubes). Furthermore, the recovery process is faster for increasing CNT content, presumably because of the decrease of average particle-to-particle distance of agglomerating species.

- (4) The reformation kinetics can be described by a simple model using a second order kinetic equation for a cluster aggregation process combined with the percolation theory that is applied here to the conductive agglomerates. The percolation theory relates the time dependent volume concentration of the agglomerates to the time dependent conductivity of the quiescent melt. Alternatively the time dependence of the conductivity can be described by a spinodal decomposition into a CNT-rich and a CNT-poor phase, where the CNT-rich phase is equivalent to the agglomerates.

The results presented here clearly show that dielectric conductivity spectroscopy is a viable tool for the characterization of the interplay between processing conditions and dielectric properties of melt processed CNT–polymer composites. From the results of this study one can conclude that there is no simple relation between the processing conditions and the conductivity of the final parts. Too many processing steps, influencing the conductivity, are lying in-between. In each of those steps, the kinetics of destruction and reformation of the conductive network structure has to be known.

Experiments on CNT–polymer composites using a combination of a commercial rheometer with ring-shaped plates with dielectric (conductivity) spectroscopy are in progress [14]. From these experiments it is expected to get a more quantitative understanding of the coupling between shear induced network rearrangements and dielectric properties. Despite the understanding of conductivity recovery it is necessary to consider the network destruction in more detail.

Acknowledgements

This project is funded by the Bundesministerium für Wirtschaft und Arbeit via the Arbeitsgemeinschaft industrieller

Forschungsgesellschaften (AiF Project Nos. 122Z and 14454N). We thank Hyperion Catalysis International, Cambridge, USA for providing the masterbatches and pure polymers. I.A. thanks Gert Heinrich (Leibniz-Institut für Polymerforschung Dresden e.V.) for the helpful discussions on cluster aggregation kinetics.

References

- [1] Thostenson ET, Li C, Chou TW. *Compos Sci Technol* 2005;65:491–516.
- [2] Breuer O, Sundararaj U. *Polym Compos* 2004;25(6):630–45.
- [3] Coleman JN, Khan U, Gun'ko YK. *Adv Mater* 2006;18(6):689–706.
- [4] Sandler JKW, Kirk JE, Kinloch IA, Shaffer MSP, Windle AH. *Polymer* 2003;44(19):5893–9.
- [5] Jiang X, Bin Y, Matsuo M. *Polymer* 2005;46:7418–24.
- [6] Andrews R, Jacques D, Minot M, Rantell T. *Macromol Mater Eng* 2002;287:395–403.
- [7] Coleman JN, Cadek M, Blake R, Nicolosi V, Ryan KP, Belton C, et al. *Adv Funct Mater* 2004;14:791–8.
- [8] Pötschke P, Dudkin SM, Alig I. *Polymer* 2003;44:5023–30.
- [9] Alig I, Lellinger D, Dudkin SM, Pötschke P. *GAK Gummi Fasern Kunstst* 2007;5:280–3.
- [10] Alig I, Skipa T, Lellinger D, Engel M, Pötschke P. *Phys Status Solidi B* 2007;244(11):4223–6.
- [11] Alig I, Lellinger D, Dudkin S, Pötschke P. *Polymer* 2007;48:1020–9.
- [12] Alig I, Fischer D, Lellinger D. *Macromol Symp* 2006;230:51–8.
- [13] Steinhoff B, Lellinger D, Alig I, Pötschke P. *PPS-21 conference proceedings*, ISBN 3-86010-784-4; 19–23 June 2005. SL 15–19.
- [14] Alig I, Skipa T, Lellinger D, Pötschke P. *Polymer*, submitted for publication.
- [15] Pegel S, Pötschke P, Petzold G, Dudkin SM, Lellinger D, Alig I. *Polymer* 2008;49:974–84.
- [16] Schueler R, Petermann J, Schulte K, Wentzel HP. *Macromol Symp* 1996;104:261–8.
- [17] Schueler R, Petermann J, Schulte K, Wentzel HP. *J Appl Polym Sci* 1997;63(13):1741–6.
- [18] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. *Polymer* 1999;40:5967–71.
- [19] Zhang C, Wang P, Ma CA, Wu G, Sumita M. *Polymer* 2006;47(1):466–73.
- [20] Heinrich G, Costa FR, Abdel-Goad M, Wagenknecht U, Lauke B, Härtel V, et al. *Kautsch Gummi Kunstst* 2005;58(4):163–7.