



Influence of shear deformation on the electrical and rheological properties of combined filler networks in polymer melts: Carbon nanotubes and carbon black in polycarbonate



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ABSTRACT

The influence of shear on combined filler systems containing multi-walled carbon nanotubes (MWNT) and carbon black (CB) in polycarbonate (PC) melts was investigated by time-resolved combined rheological and electrical measurements. Samples with different MWNT/CB ratios and total carbon filler contents (0.25–10 wt%) were studied. The morphology of the filler network was analyzed by TEM and SEM in charge contrast mode whereby a combined MWNT/CB filler network is indicated.

Rheo-electric measurements in the quiescent melt after a defined shear deformation show an increase in electrical conductivity with recovery time for all combined filler systems. Similarly to earlier findings for composites containing only MWNT or CB, the time-dependent conductivity data for the combined filler systems can be described by an agglomeration model with one kinetic constant. This supports the assumption of a combined filler network. In steady shear experiments (1 rad/s) equilibrium values for conductivity and viscosity are reached. At a constant carbon filler content, the electrical conductivity increases on a logarithmic scale with the MWNT ratio, whereas the transient shear viscosity increases linearly. The conductivity of an MWNT/CB 50/50 composite is six orders of magnitude higher than the conductivity of a composite containing only CB. In comparison, the viscosity increases only by a factor of two. These experiments were carried out at a constant carbon filler content of 3 wt%. Equilibrium values of conductivity and viscosity are described by mixing laws based on effective medium approximations.

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1. Introduction

Triggered by the interest in electrically conductive polymer composites, polymer materials containing carbon allotropes received an increasing attention. In the last years carbon nanotubes (CNT) were studied intensively in basic research (see e.g. Refs. [1–7] and references therein) and for industrial applications [8,9]. The latter is especially due to their wide range of possible applications of CNT based composites like electrostatic painting, electrical shielding [10], flammability reduction [11] or sensor applications [12]. An often used approach to achieve a conductive polymer composite is the incorporation of conductive fillers into an insulating polymer matrix by generating a suitable filler arrangement. The insulator–conductor transition at a certain filler amount is related to the buildup of a continuous filler network in the polymer matrix [13,14]. The critical amount that results in a pronounced

increase of the electrical conductivity is the so called “percolation threshold”. For randomly distributed non-interacting filler particles this threshold is described by the classical percolation theory [15–17]. In the case of fillers with particle–particle interactions the classical percolation theory is not valid and effects like filler agglomeration or segregation have to be considered. These effects are of special importance when regarding nanoparticles, since the kinetic energy of the particles’ Brownian motions is of the same order of magnitude as their interactions.

Carbon black (CB) has been used for many decades to improve conductivity and mechanical performance of polymeric materials [18–21]. Furthermore, many attempts have been made over the last years to use multi-walled carbon nanotubes (MWNT) as alternative filler materials, due to their high mechanical modulus and their high intrinsic conductivity [22,23]. In addition to that, the much higher aspect ratio of carbon nanotubes leads to a lower nanotube concentration for the insulator–conductor transition (“lower percolation concentration”) compared to CB [3,22,24]. One disadvantage of CB composites is the high filler amount needed to achieve a sufficient conductivity, which simultaneously reduces other

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desired properties of the polymer matrix like elasticity, strain to rupture or impact resistance. On the other hand, nanotubes increase the melt viscosity more considerably, which makes processing difficult. Another important aspect is the higher price of MWNT compared to CB. In order to overcome the disadvantages of both filler types, combined filler systems with MWNT and CB are under discussion. Based on theoretical considerations of combined filler systems containing rods and spheres, a co-supporting network structure is expected [25,26] and mixing laws for the “percolation threshold” are proposed. Experimental studies by Sumfleth et al. [27,28] have reported that the combination of MWNT and CB fillers forms such co-supporting network structures in an epoxy matrix. For MWNT/CB systems in polyamide 12 the addition of CB increases the dispersion of the MWNTs in the polymer matrix and therefore the conductivity of the composite is increased [29].

When nanoparticles with attractive interactions are incorporated into a highly viscous polymer matrix the resulting composite materials are usually out of equilibrium. Typical effects are agglomeration or segregation. Therefore, the resulting material properties are time dependent and strongly influenced by the thermo-mechanical history. The electrical and rheological properties of CB and MWNT based nanocomposites depend on the actual structure of the filler network. In the quiescent polymer melt well-dispersed nanofillers tend to form agglomerates due to the attractive forces between them. These agglomerates are disrupted again when shear stresses are applied. The resulting electrical and rheological properties in a shear flow are thus determined by the interplay between reformation and disruption of filler agglomerates [6,7,30–33].

For a systematic investigation of the structural evolution of combined filler networks it is important to start with a well-defined structure of the filler network. Because of the interplay between agglomeration and disruption it is rather difficult to achieve such an initial state. This well-defined state would be a random distribution of the filler particles, which can be approximated by proper melt mixing and vitrification of the dispersed particles in the polymer matrix. As shown before this is rather difficult [30]. Another “equilibrium state” can be achieved for MWNT composites [5,32] in a polymer melt at steady shear conditions with defined shear rates. At steady shear the buildup of agglomerates and their disruption are in steady balance and constant electrical and rheological properties of the melt are achieved after sufficient time. An additional defined state is achieved through a well-defined thermo-rheological history, e.g. after a defined shear deformation and a following recovery of the filler network in quiescent melt. For long recovery times equilibrium values for the conductivity are reached.

In order to characterize the dynamic percolation behavior of combined filler networks time-resolved rheo-electrical experiments under well-defined steady shear conditions and after a well-specified thermal and shear history in the quiescent melt were performed. Based on this defined states it is possible to compare the electrical and rheological properties for samples with different MWNT/CB ratios and total carbon filler contents (including the single filler systems). Through the sustainable data received from these experiments we were able to analyze agglomeration kinetics and to test effective medium models for conductivity and viscosity of combined filler networks.

2. Experimental

2.1. Samples and characterization

In this study a combined filler system of MWNT and CB is incorporated in polycarbonate (PC) Makrolon® 2600 (Bayer Material Science AG). These samples are compared to identically prepared composites containing only CB or MWNT. The carbon black used was

Printex XE2 (Orion Engineered Carbons, Germany). The primary particle size, as given by the supplier, is 30–35 nm and the BET value is 400 m²/g [34]. The multi-walled carbon nanotubes were MWNT Nanocyl™ NC7000 (Nanocyl S.A., Sambreville, Belgium) with a diameter of 10 nm and an average length of 1.5 μm [35]. As described in Ref. [36] the length distribution of the MWNT is lowered by melt processing. The composites were prepared by melt mixing using a conical small-scale DSM Xplore 15 ccm microcompounder (Geleen, Netherlands). The MWNT/CB ratios (per weight) were 0/100, 25/75, 50/50, 75/25 and 100/0 and the total filler concentration varied from 0.25 to 10 wt%. For the compounding, the PC was vacuum dried for 4 h at 120 °C before the composites were melt-mixed at 280 °C at 250 rpm for 5 min. The fillers were fed alternately with the polymer granules into the hopper of the running compounder. After mixing, the strands were taken out from the 2 mm diameter die without additional cooling at the set rotation speed. If needed, the strands were pressed (250 °C, 50 kN, 6 mm/min) to plates with a thickness of 1 mm. Before the measurement in the rheometer, the samples were again dried in vacuum for 90 min at 120 °C. As given by the suppliers the filler densities of MWNT and CB are 1.8 g/ccm for both.

2.2. Electron microscopy

The pressed plates were analyzed using a transmission electron microscope (TEM) Libra 200 (Carl-Zeiss AG, Germany) operated at an acceleration voltage of 200 kV. For this, thin sections with a thickness of 80 nm were prepared using an ultrasonic diamond knife from Diatome (Switzerland) mounted on an ultramicrotome Reichert Ultracut S (Leica, Germany). The cuts were performed at room temperature in sample thickness direction in the middle of the pressed plates. Exemplarily, Fig. 1 shows TEM micrographs of samples with 3 wt% filler content and different filler ratios of MWNT/CB.

For all systems a good distribution and dispersion is achieved by the melt mixing procedure described above. In the combined MWNT/CB filler system no separate MWNT or CB particles can be found, indicating a combined filler network buildup by both fillers.

Scanning electron microscopy (SEM) was performed using an Ultra Plus-REM (Carl-Zeiss AG, Deutschland) in charge contrast imaging (CCI) mode, to get information about the initial filler dispersion and distribution of the composites. This was done on cut surfaces as obtained as counterpart from TEM cutting. Fig. 2 shows the image of a sample with an MWNT/CB ratio of 25/75 and a total filler content of 3 wt%. Assuming that the highlighted regions represent conductive pathways, the image indicates the existence of a co-supporting conductive filler network. However, the interpretation of charge contrast images is still in discussion [37,38].

2.3. Dielectric spectroscopy

The AC conductivity of pressed plates was measured at room temperature by dielectric spectroscopy (Novocontrol, Germany) in the range from 10⁻²–10⁶ Hz. As an example Fig. 3a shows the frequency dependent conductivity $\sigma'_{AC}(\omega)$ for different filler contents of an MWNT/CB system with a wt% ratio of 50/50. The DC conductivity is extrapolated from the frequency dependent conductivity at low frequencies $\sigma_{DC} = \sigma'_{AC}(\omega \rightarrow 0)$ [2]. The results for the different filler concentrations are shown in Fig. 3b.

Since the samples were prepared under identical conditions, it is possible to estimate a percolation threshold for each filler type. To obtain the values for the electrical percolation concentration ϕ_c the curves in Fig. 3b were fitted using the power law of the classical percolation theory:

$$\sigma \sim (\phi - \phi_c)^t \quad (1)$$

where t is a critical exponent. The results are discussed in Section 5.

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