



Conductivity of carbon black-based polymer composites under creep in the molten state



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ABSTRACT

The mechanical deformation of conductive polymer composites during melt processing affects their final electrical properties considerably. To get an insight in this relationship, simultaneous electrical-rheological measurements can be used to follow the changes in composite phase structure induced by defined deformation. In this work, the evolution of electrical conductivity was investigated during and after shear deformation at constant stress. From the experiments performed it can be concluded, that the flow-induced build-up mechanism leads to the formation of conductive pathways with enhanced stability compared to the structures build-up under quiescent conditions. This finding can be explained by the orientation of particle structures in the shear direction. Therefore, materials with different deformation history but the same electrical conductivity can display markedly different electrical behaviour under deformation.

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1. Introduction

In the last two decades a gradually increasing interest in conductive polymer composites (CPC) can be observed. These materials are used for antistatic packaging or as materials for shielding of electromagnetic interference [1]. Albeit not yet commercialized, their usage in sensor applications, e.g. gas sensors, is a progressive direction of current research [2,3]. The electrical properties of polymer composites containing conductive fillers are determined by their morphology, as percolating particle structures, which interpenetrate the material, are required to reach desirable level of electrical conductivity. Therefore, the value of electrical conductivity of a CPC is affected not only by the filler concentration and particle–polymer interactions, but also to large extent by the conditions of processing, usually in the molten state [4]. On one hand, the lowest possible filler concentration is desired to diminish the changes of flow behaviour induced by incorporation of solid particles. On the other hand, at low filler concentration the percolating particle structures are weak and they can be destroyed easily by hydrodynamic stress applied in mixing devices, which can result in a non-conductive material [5]. Therefore, the knowledge and the understanding of particle structures behaviour under

mechanical deformation in the molten state are crucial in production of CPC with balanced electrical and processing properties. For this purpose simultaneous electrical-rheological measurements are a suitable experimental tool which monitors sensitively the changes in composite phase structure induced by a defined mechanical deformation [6–12].

The evolution of electrical conductivity during the deformation is a result of a competition between flow-induced destruction and build-up of conductive pathways formed by filler particles. Moreover, in the case of nanocomposites thermal motion of nanoparticles leads often to aggregation due to high interfacial area and pronounced interfacial tension between particles and matrix and, thus, to the formation of conductive pathways [13–15]. This effect called dynamic percolation is responsible for an increase in conductivity under quiescent conditions but it affects the conductivity evolution under deformation as well. The conditions of deformation inserted on a specimen determine whether the flow-induced destruction exceeds the build-up processes and the conductivity decreases. Generally, using common shear rheometers the deformation can be applied in oscillatory or steady mode. It was observed that under oscillation at sufficiently low frequencies the electrical signal oscillates at a frequency, which is exactly the double of the frequency of deformation [10,12,16]. In the initial stage of the oscillatory shear the flow-induced destruction of the conductive pathways is the dominant process. The amplitude of these oscillations decreases over time and at long times it becomes constant, which corresponds to the

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dynamic equilibrium between destruction and build-up of conductive paths [12]. Concerning steady shear, the experiments reported in the literature were performed at constant strain rate [6–10,17]. From the experiments performed on polycarbonate/MWCNT composites [9,10] and epoxy/CNT suspensions [18] it follows, that for a given shear rate applied there is a steady-state value of electrical conductivity, which is independent on the initial degree of the carbon nanotubes dispersion. If the CNT's are well dispersed in the matrix prior to deformation, they agglomerate and the conductivity increases during the shear. On the other hand, if the CNT's are agglomerated at the beginning, the agglomerates are destroyed by the shear and the conductivity decreases. At long shear times the conductivity attains a constant value identical for both cases mentioned above.

Recently, an increased attention has been paid to shear experiments at constant stress, i.e. creep experiments [19]. Besides their advantages regarding the investigations of molecular structure of linear and branched polymers, they were used as a method enabling the study of polymer–particle interactions or the characterisation of the quality of dispersion in polymer composites [20–22]. It was shown that stress is a decisive parameter which determines whether the polymer molecules stay adsorbed or they are detached from the particle surface. In analogy to that, we believe that also in the case of particle–particle interactions in conductive structures, the shear stress applied is a crucial parameter. At low stresses the conductive pathway stays rigid or only spatial rearrangement of particles occurs and the pathway can transfer the electric charge. At high stresses, attractive forces between particles are overruled by hydrodynamic forces, the contact between particles is interrupted and the conductive pathway is destroyed. Therefore, performing creep experiments is a convenient method to study the behaviour of conductive particle structures under deformation.

In this work the simultaneous electrical-rheological experiments were performed in the creep mode on polymethylmethacrylate/carbon black composites. The effect of filler concentration, shear stress and creep time was investigated systematically. Besides that, the recovery of the electrical conductivity after the shear was evaluated as well.

2. Experimental

2.1. Materials and sample preparation

The polymethylmethacrylate (PMMA) used in this study was Plexiglas 7N (Evonik Röhm GmbH, Germany) with the weight-average molar mass M_w of 86 kg mol⁻¹ and the polydispersity index M_w/M_n of 1.19. A special conductive grade of carbon black (CB) Printex XE2 with the specific surface area of 900 m² g⁻¹ measured by the BET-method was provided by Evonik Röhm GmbH (Germany).

Prior to the composite preparation the materials were always dried under vacuum at 80 °C for at least 24 h. The PMMA and CB were mixed in an internal kneader PolyDrive (Haake, type 557–8310) at a temperature of 200 °C and a rotation speed of 60 min⁻¹. The mixing time was 8 min in all cases. In this way PMMA/CB composites with 1–5 vol.-% of carbon black were prepared.

2.2. Electron microscopy

The morphology of the PMMA/CB composites was visualised by transmission electron microscopy (TEM) using an electron microscope CM30 T/STEM from Philips at an acceleration voltage of 300 kV. The ultrathin sections with a thickness of 70 nm were

prepared at room temperature using an ultramicrotome EM UC7 from Leica.

2.3. Simultaneous rheological and electrical measurements

To perform simultaneous rheological and electrical measurements, a stress controlled shear rheometer GEMINI from Malvern Instruments (UK) with a plate–plate geometry was modified. The rotor was insulated from the driving unit of the rheometer by inserting a peg made of polyetheretherketone. The insulated rotor and the bottom plate of the rheometer were connected to a Picoammeter 6487 from Keithley (USA) which serves as a source of a constant voltage of 1 V and as a unit, measuring the current flowing through the specimen between the plates. The detailed description of the experimental setup was published by Krüchel et al. [11].

Simultaneous electrical-rheological measurements were performed according to the following protocol. After inserting the specimen between the plates of the rheometer and reaching the measuring temperature of 200 °C the sample was kept for ten minutes under quiescent conditions prior to shear. Then a constant shear stress in the range between 1 and 20 kPa was applied for a given period of time. After the creep the conductivity was recorded further on to observe the electrical behaviour of composite after the shear. Every simultaneous measurement was performed at least three times on three individual specimens. The experimental curves presented are representative examples of the data obtained. Characteristic parameters extracted from the raw data are mean values from all measurements performed.

3. Results and discussion

The morphology of the composites was characterised by transmission electron microscopy. As an example the structure of the composite containing 2 vol.-% of carbon black is shown in Fig. 1 (the micrographs of the composites with 1 and 5 vol.-% can be found in Ref. [11]). It can be seen that the carbon black is homogeneously distributed in the matrix. The carbon black particles consisting of primary aggregates have irregular shape and they are of typical size around 100 nm. Large CB agglomerates were not observed in the material.

Fig. 2 shows electrical conductivities of composites with different carbon black concentration during the simultaneous electrical-rheological measurements including a shear step at a constant stress τ_c of 5 kPa. The creep time t_c was set to 100 s. Concerning the initial conductivity values one can determine the region of the percolation threshold. The neat PMMA and the composite with 1 vol.-% of carbon black are nonconductive materials. Increasing the CB content to 2 vol.-%, a tremendous increase in conductivity of about six orders of magnitude can be observed. Further increase in the filler amount leads to higher conductivity values; the increase is not so pronounced anymore, however. It suggests, that in the composites with the CB amount of 2 vol.-% and higher, conductive particle structures are developed thorough the whole specimen. This finding is in a good agreement with our previous study [11], where the percolation threshold was estimated to 1.8 vol.-% using a general effective media theory as proposed by Mc Lachlan and Sauti [23]. This relatively low percolation threshold is given by the fact that CB is dispersed in the matrix in the form of highly structured anisotropic aggregates (cf. Fig. 1), which decreases the CB concentration needed to reach percolation threshold [24]. Moreover, a direct contact between the particles is not necessary to build a conductive pathway as in polymer composites quantum mechanical tunnelling is considered as a dominant conduction mechanism [1,24,25]. During the annealing period prior to

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