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Oscillations of the electrical resistance induced by shear deformation in molten carbon black composites

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ABSTRACT

The time-dependent electrical resistance of polymethylmethacrylate containing carbon black was monitored under oscillatory shear in the molten state. The electrical signal measured was oscillating exactly at the doubled frequency of the oscillatory shear deformation. Moreover, the experimental results gave a hint to the development of conductive structures in polymer melts under shear deformation. It was shown that the flow induced destruction of conductive paths dominates over the flow induced build-up in the beginning of the shear deformations. However, for longer times both competitive effects reach a dynamic equilibrium and only the thermally induced build-up of pathways influences the changes in the composite resistance during the shear. Moreover, the oscillating electrical response depends clearly on the deformation amplitude applied. Furthermore, a simple physical model describing the behaviour of conductive pathways under shear deformation was derived and utilized for the description of the experimental data.

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1. Introduction

The electrical properties of polymers are dramatically influenced by the incorporation of conductive fillers, such as carbon black or carbon nanotubes [1,2]. It is well known from the literature that the incorporation of conductive fillers leads to the formation of conductive pathways when a certain concentration is reached. Therefore, the dependency of the conductivity on the amount of filler is treated as a percolation phenomenon and classical percolation theory is often adapted for its theoretical description [3,4]. To produce conductive polymer composites for industrial applications, melt processing techniques such as extrusion or injection moulding are usually used. The structure of conductive pathways in the final material is significantly influenced by shear and/or elongational forces applied during the processing [5]. Alig et al. have shown the impact of processing conditions on the conductivity of polycarbonate/carbon nanotube composites by in-line melt extrusion experiments [6]. In order to design materials with desirable properties, it is important to understand the development of the conductive structures during the melt processing. Therefore, simultaneous electrical and rheological experiments provide a unique tool and have been in focus of research for several years. Most of these investigations were performed using coupled electrical and shear experiments at a constant shear rate [7–10]. From these studies it was found, that shear forces can either destroy or build-up conductive pathways. Moreover, a thermal induced build-up attributed to the motion and aggregation of conductive particles has to be taken into account which is known as dynamic percolation [11,12].

However, only few investigations were performed using oscillatory shear experiments coupled with electrical measurements. In our previous work we have investigated the impact of filler concentration, stressing amplitudes and different types of filler on the conductivity during coupled amplitude sweeps systematically [13]. It was found, that conductive structures formed by microfillers are rather fragile compared with those formed by nanofillers. For both filler systems it was observed, that the stability of the conductive structures rises with increasing the filler concentration. Moreover, Krückel et al. confirmed the build-up and destruction mechanisms between the conductive fillers which were expected under shear [13]. Another electrical measurements on conductive polymer composites under oscillatory shear were performed by Dijkstra et al. [14]. The authors investigated the electrical resistance of polycarbonate/MWCNT composites under oscillatory shear, too. It was found, that the resistance shows an oscillating response as well, where the frequency of the electrical oscillations is twice as

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fast the frequency of the deformation. This finding was also confirmed qualitatively by Alig et al. [2] and Zeiler et al. [15] for polycarbonate filled with carbon nanotubes. Zeiler et al. [15] measured the oscillating electrical conductivity for different strain amplitudes and for different molar masses of the matrix polymer. They observed an increase in the conductivity amplitude by increasing the strain amplitude and lowering the molar mass. The effect of an oscillating electrical response is explained by the destruction and rebuilding of the conductive pathways which is driven by the mechanical oscillation. However, a systematic study on this phenomenon and its quantitative evaluation was not performed up to now.

In our previous study [13] we have focused on coupled electrical and oscillatory shear measurements using amplitude sweeps with a fixed angular frequency (6.28 s^{-1}) and different amplitudes. The aim of this work is to investigate the electrical properties of polymethylmethacrylate filled with carbon black by coupled time sweeps for lower deformation frequencies at a fixed stressing amplitude. For that purpose, we have investigated the frequency behaviour of the electrical resistance under oscillatory shear systematically. Moreover, a simple model is postulated which describes the electrical resistance of a conductive polymer composite under oscillatory shear flow. This model leads to analytical equations which describe the oscillating response of the composite resistance to oscillatory deformation and confirm the doubled frequency of the electrical signal.

2. Experimental

For the matrix polymer a commercial PMMA grade Plexiglas 7N with a density of 1.19 g cm^{-3} from Evonik Röhm GmbH (Germany) was used. The conductive filler was carbon black (CB) Printex XE2 from Evonik with a density of 2.13 g cm^{-3}. In this study, we have investigated PMMA composites containing 3 vol.-% CB. The rheological characterisation of the neat PMMA and the composite studied is shown in Fig. 1.

We have previously shown that the percolation threshold was already reached at this concentration and significant changes of the electrical resistance under shear are expected [13]. Further information about the materials and the composite preparation are given in [13]. For the simultaneous electrical and rheological measurements a stress controlled shear rheometer Gemini from Malvern Instruments (plate–plate geometry, diameter = 25 mm, gap = 2 mm) was combined with a Picoammeter 6487 from Keithley. A detailed description of the experimental setup can be found elsewhere [13]. In this work the rheological measurements were performed in the time sweep mode. A sinusoidal shear stress $\tau(t,\omega_0) = \hat{\tau}\sin(\omega_0 t)$ with a constant stressing amplitude of $\hat{\tau} = 8$ kPa and different angular frequencies ω_0 between 0.0628 and 0.628 s^{-1} was applied to the polymer sample. It was shown, that an amplitude of 8 kPa lead to pronounced effects in the response of the electrical signal [13]. The mechanical response measured is a time-dependent sinusoidal deformation $\gamma(t,\omega_0) = \hat{\gamma}\sin(\omega_0 t - \delta)$ with a deformation amplitude $\hat{\gamma}$ and a phase angle δ. The dc-resistance R was recorded simultaneously during the measurements at a constant voltage of 1 V applied on the specimen using Picoammeter 6487 from Keithley (USA). The coupled electrical and rheological experiments were carried out in the molten state at a constant temperature of 189 °C under nitrogen atmosphere. Detailed description of the experimental setup used can be found in [13].

3. Results and discussion

In our previous work dealing with coupled electrical and oscillatory shear experiments we have studied the electrical properties of conductive polymer composites with different fillers as a function of stressing amplitude and filler concentration [13]. In the following study, we investigate the time-evolution of the electrical resistance during coupled time sweeps at constant stressing amplitude for different deformation frequencies. In Fig. 2 the resistance of a composite filled with 3 vol.-% carbon black deformed at $\omega_0 = 0.075$ s^{-1} is shown exemplarily as a function of time.

Region I depicts the time evolution of the electrical resistance prior to shear under quiescent conditions. In region II, a time sweep with an angular frequency of 0.075 s^{-1} and a stressing amplitude of 8 kPa was applied to the molten sample while the resistance was recorded simultaneously. In region III no shear was applied to the sample and the resistance was further monitored under quiescent conditions.

As can be seen in Fig. 2 only slight changes in G′, which is believed to be the most sensitive rheological quantity to follow the changes in morphology of particle filled polymers, were observed. The same behaviour was found in all the experiments performed at different angular frequencies, although significant resistance changes were recorded. This fact, in agreement with our previous investigations [13], emphasizes once more that electrical measurements are very sensitive tool to follow the morphology development induced by mechanical deformation in conductive polymer composites.

The initial value of the resistance for this filler concentration at 189 °C is around 25 Ω which corresponds to a conductivity of around 10^{-3} S cm^{-1}. In comparison, the conductivity of the pure

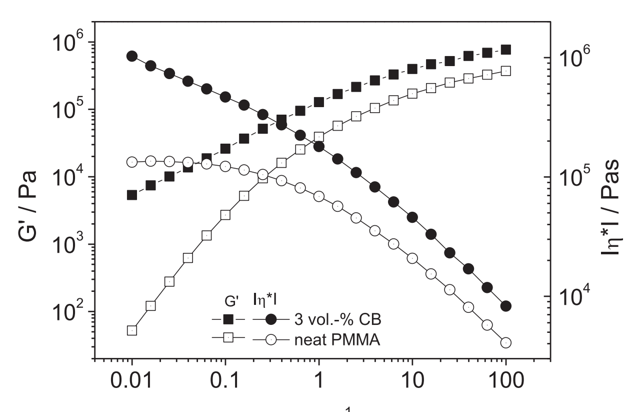

Fig. 1. Frequency sweeps of PMMA and PMMA filled with 3 vol.-% CB at $T = 189$ °C and $\hat{\tau} = 0.2$ kPa.

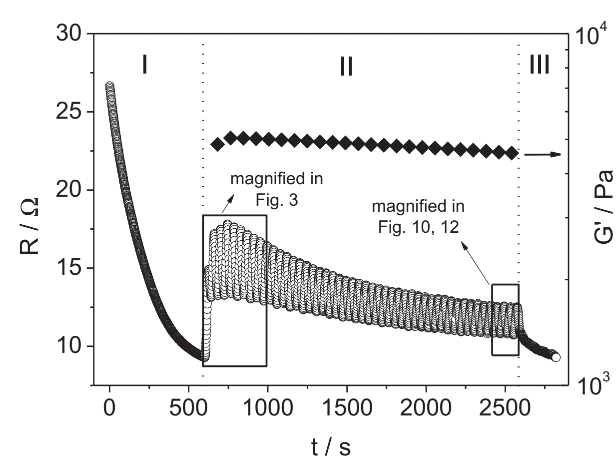

Fig. 2. Electrical resistance as a function of time for PMMA filled with 3 vol.-% CB at $T = 189$ °C (I quiescent melt, II shear ($\omega_0 = 0.075$ s^{-1}, $\hat{\tau} = 8$ kPa), III quiescent melt).

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