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Shear Induced Electrical Behaviour of Conductive Polymer Composites

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Abstract. The time-dependent electrical resistance of polymethylmethacrylate containing carbon black was measured under oscillatory shear in the molten state. The electrical signal 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. Furthermore, the oscillating electrical response depends clearly on the deformation amplitude applied. A simple physical model describing the behaviour of conductive pathways under shear deformation was derived and utilized for the description of the experimental data.

Keywords: Composites, Electrical resistance, Oscillatory shear.

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INTRODUCTION

The electrical properties of polymers are dramatically influenced by the incorporation of conductive fillers, such as carbon black or carbon nanotubes [1,2]. 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 [3]. Alig et al. have shown the impact of processing conditions on the conductivity of polycarbonate/carbon nanotube composites by in-line melt extrusion experiments [4]. 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 [5-7]. 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 [8,9].

Krückel et al. have investigated the impact of filler concentration, stressing amplitudes and different types of filler on the conductivity during coupled amplitude sweeps systematically [10]. Other electrical measurements on conductive polymer

composites under oscillatory shear were performed by Dijkstra et al. [11] on polycarbonate/MWCNT composites. It was found, that the resistance shows an oscillating response as well, where the frequency of the electrical oscillations is twice as fast the frequency of the deformation. This finding was also confirmed qualitatively by Alig et al. [2] and Zeiler et al. [12] for polycarbonate filled with carbon nanotubes. Zeiler et al. [12] 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.

Our previous study [10] has been 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.

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. Further information about the materials and the composite preparation are given in [10].

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 [10]. For the simultaneous electrical and rheological measurements a stress controlled shear rheometer Gemini from Malvern Instruments in plate-plate geometry was combined with a Picoammeter 6487 from Keithley. A detailed description of the experimental setup can be found elsewhere [10]. In this work the rheological measurements were performed in the time sweep mode. A sinusoidal shear stress with a constant stressing amplitude of $\hat{\tau} = 8 \text{ kPa}$ and different angular frequencies ω_0 between 0.0628 and 0.628 s^{-1} was applied to the polymer sample. The mechanical response measured is a time-dependent sinusoidal deformation with a deformation amplitude $\hat{\gamma}$. The dc-resistance R was recorded simultaneously during the measurements at a constant voltage of 1 V applied on the specimen. The coupled electrical and rheological experiments were carried out in the molten state at a constant temperature of 189°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

This study deals with the time-evolution of the electrical resistance during coupled time sweeps at constant stressing amplitude for different deformation frequencies. In Figure 1 the resistance of a composite filled with 3 vol.-% carbon black deformed at $\omega_0 = 0.075 \text{ s}^{-1}$ and a stressing amplitude of 8 kPa is shown exemplarily as a function of time.

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

Region I depicts the time evolution of the electrical resistance prior to shear under quiescent conditions. In region II, a time sweep 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 Figure 1 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 [10], emphasizes once more that electrical measurements are very sensitive tool to follow the morphology development induced by mechanical deformation in conductive polymer composites.

In region I and III the resistance decreases as a function of time. This effect is attributed to a dynamic percolation and is explained by the build-up of new conductive pathways due to the thermal motion and the aggregation of the carbon black primary aggregates [10,13]. Similar experimental results were obtained for polycarbonate filled

with carbon nanotubes [8]. This work was focused on processes occurring during oscillatory shear. As can be seen (Figure 1, region II), the resistance increases steeply at the beginning of the time sweep. Then, the resistance oscillates during the whole shear experiment. Regarding the oscillations of the resistance, several interesting effects are found.

Firstly, the amplitudes of the resistance increase with time at the beginning. After reaching a maximum, the amplitudes decrease again and finally reach a constant level. Secondly, the oscillating resistance is superimposed by a decrease of the resistance as a function of time. Finally, it was found, that the frequency of the electrical response is exactly twofold of the deformation frequency. In the following, the phenomena observed are discussed in more detail in order to obtain a deeper understanding of the development of conductive structures in polymer melts under oscillatory shear.

The coupled time sweeps were measured at different angular frequencies in the range between 0.0628 and 0.628 s⁻¹. As the decisive parameter for the behaviour of conductive pathways at a constant stressing amplitude is the amplitude of deformation $\hat{\gamma}$, the phenomena observed are discussed regarding the amplitude of deformation and not angular frequency itself. The relationship between these two quantities can be found in [16].

In the first part of the discussion we will focus on the effects observed at the beginning of the oscillatory shear experiment. During the first deformation oscillation it can be seen, that the resistance increases steeply. Then at the beginning of the shear oscillations the amplitudes of the electrical oscillations increase. This indicates that the destruction of conductive paths dominates at the beginning of the shear. After several oscillations, the amplitude decreases, which means that the build-up of new pathways takes place already during the shear which corresponds to the explanations given in the literature [5,6,14,15]. In order to get more information about the pathway destruction at the beginning of the oscillatory shear, this effect was evaluated for different deformation amplitudes. The ratio R_2/R_1 is taken as a measure for the destruction of conductive paths during the first mechanical oscillation. Here R_1 is the resistance at 600 s when the shear experiment has started and R_2 characterizes the resistance in the maximum of the first electrical oscillation. Figure 2 displays R_2/R_1 as a function of the deformation amplitude. For that purpose the experimental data from at least 5 coupled time sweeps per frequency were analysed.

FIGURE 2. Relative resistance as a function of deformation amplitude for PMMA filled with 3 vol.-% CB ($\hat{\tau} = 8$ kPa, $T = 189^\circ\text{C}$). Symbols – experimental data, solid line – Eq. 2.

As can be seen from Figure 2, small deformation amplitudes lead to a less pronounced destruction of conductive contacts. A decrease of the angular frequency leads to higher deformations in the composite. Therefore, the destruction of conductive contacts becomes more evident. For deformations higher than 0.15 the relative resistance reaches almost a constant value. Due to the fact, that the flow of electrons across a pathway can already be interrupted by breaking one contact, this effect can be treated according to a weakest link theory. Therefore, the experimental data were fitted using an equation which has essentially the mathematical form of a Weibull distribution (Eq. 1) [17].

$$\frac{R_2}{R_1} = 1 + \lambda \left(1 - e^{-\left(\frac{\hat{\gamma}}{\hat{\gamma}_c}\right)^m} \right) \quad (1)$$

Taking into account the standard deviation of each average value for R_2/R_1 , Eq. 2 describes the experimental data well. Such an ansatz seems to be reasonable regarding the limiting values of deformation amplitude. The critical deformation amplitude $\hat{\gamma}_c$ is a fit parameter and was determined as $\hat{\gamma}_c = 0.13$ for the given set of experimental data. The physical meaning of this parameter is explained by a simple model schematically shown in Figure 3. Let us idealize a primary carbon black aggregate as a sphere. In the left hand picture of Figure 3 a conductive pathway without shear is considered as a cylinder with a length l_0 and a cross section area A_0 filled with a certain number of primary aggregates. The interactions between the primary aggregates are purely

physical. The connections between the primary particles are sintering bridges build-up during the carbon black processing [1].

FIGURE 3. Sketch of a model for the morphology of conductive carbon black pathways for different shear states. A_0 , A_s , l_0 and l_s are the cross-sectional areas and the lengths of an unsheared and sheared pathway, respectively.

For $\hat{\gamma} \leq \hat{\gamma}_c$ the pathway is oriented in the shear direction but the primary aggregates still remain in contact with each other. For $\hat{\gamma} > \hat{\gamma}_c$ the conductive contacts between the blobs are interrupted and the primary aggregates can be separated from each other, as shown in the right hand picture of Figure 3. The interruption of conductive contacts occurs at the weakest link between the primary aggregates which leads to an increase of the electrical resistance immediately. During the backflow of the oscillatory shear the blobs are able to rebuild the broken connections. Furthermore, the separated primary aggregates can again build-up conductive contacts due to their thermal motion known as dynamic percolation. For that reason, the weakest link theory is suitable to describe the initial destruction of conductive contacts.

In the second part of this work, the time evolution of the resistance oscillations was investigated. It can be seen in Figure 1 that the resistance oscillation amplitude increase at the beginning of the shear experiment and after reaching a maximum the amplitude of the resistance oscillations R_A is decreasing and approaching a constant level. In order to study the resistance amplitude as a function of time, R_A was analysed from the maximum value (at 750 s) to the end of the time sweep (at 2600 s). Figure 4 shows the time evolution of the resistance amplitude R_A after the maximum for different deformation amplitudes applied.

FIGURE 4. Amplitudes for the electrical resistance as a function of time for different deformation amplitudes.

As can be seen from Figure 4, the amplitudes of the electrical resistance oscillations are exponentially decreasing as a function of the time reaching finally a constant value at long times. This result is interesting from the point of view of structure development of conductive pathways. At the beginning of the time sweep, the mechanical loading is applied on the material and the particle structures are destroyed (see Figure 1). This results in a high number of broken contacts between the aggregates. They can partially recombine during the back flow in the second part of the deformation oscillation. With time a stabilization of the broken structures occurs and both the flow-induced destruction and the flow-induced build-up take place. Then, these two counteracting processes reach a dynamic equilibrium expressed by a constant value of amplitude of the electrical resistance. From this point on, the flow-induced mechanisms of structure development do not contribute to the overall evolution of the resistance during the time sweep anymore. The slow decrease of the resistance (Figure 1) is then caused only by the structure build-up induced by the thermal motion of the free aggregates, i.e. by the same mechanism as in the case of dynamic percolation. Moreover, one can see that the amplitude of the resistance oscillations depends on the deformation amplitude applied on the sample. With increasing deformation amplitude longer times are needed to reach the dynamic equilibrium and the final constant value of resistance amplitude rises. Quantitative evaluation of these effects can be found in [16].

In order to describe and explain the changes in the conductive structures under oscillatory shear in more detail, equations showing a connection between the oscillatory deformation applied and the electrical properties were derived. The derivation is based on the model presented schematically in Figure 3 which describes the resistance oscillations at the end of the time sweep where the resistance amplitudes are constant and the flow-induced build-up and destruction have reached a dynamic

equilibrium. Considering the resistance of the sample as a sum of resistances of N individual conductive pathways in parallel connection and assuming the constant volume of the pathway V during the shear, one can derive the following equation describing the resistance of the composite under shear $R_{S,com}$ on oscillatory deformation (detailed derivation can be found in [16]).

$$R_{S,com} = \frac{\rho_f l_0}{NV} \left[1 + C_2 \hat{\gamma}^2 (1 - \cos(2\omega_0(t - t_1) - 2\delta)) \right] \quad (2)$$

In Eq. 2 ρ_f is the conductivity of the filler and l_0 is the length of unsheared pathway. Furthermore, two fit parameters t_1 and C_2 are introduced. The parameter t_1 shifts the periodic function on the abscissa to the experimental data and represents an experimental time between the rheological and the electrical measurement which are not exactly synchronized. In the case, where only a spatial rearrangement of the aggregates takes place i.e. when $\hat{\gamma} \leq \hat{\gamma}_c$, the value of the parameter C_2 is 1. Taking the interruption of conductive contacts and the separation of aggregates from the pathway into account, i.e. at $\hat{\gamma} > \hat{\gamma}_c$, the parameter C_2 should be a decreasing function of the deformation applied. In order to prove our model we have used Eq. 2 on a set of experimental data acquired at different angular frequencies. All the measurements were reproduced for at least 5 times at different specimens. Indeed, a clear dependency between the deformation amplitude and the parameter C_2 was found and is displayed in Figure 5.

FIGURE 5. Fit parameter C_2 as a function of deformation amplitude.

It is obvious that high deformation amplitudes lead to small values for C_2 . Contrary to that, for small deformations, C_2 is nearly 1. This finding is in good agreement with the expectation that the parameter C_2 can be explained as a measure of broken contacts and separated aggregates from the conductive pathways.

CONCLUSION

In this work we have investigated the time-dependent electrical resistance of PMMA carbon black composites under oscillatory shear in the molten state. The effect of different deformation amplitudes at a constant stressing amplitude on the electrical behaviour of the composites was studied in detail. During the shear a competition between flow induced destruction and flow induced build-up of conductive pathways was observed. Moreover, an overlaying build-up mechanism due to the dynamic percolation of carbon black aggregates has to be taken into account. If a certain critical deformation is applied, the flow induced destruction of the conductive pathways is the dominant process in the initial stage of the oscillatory shear. During the whole shear experiment, the electrical response showed an oscillating behaviour. At long times the amplitude of these oscillations becomes constant, which corresponds to dynamic equilibrium between destruction and build-up of conductive pathways. To describe and explain the experimental data a simple model was developed. This model is in good agreement with the experiments and it confirms the doubled frequency response in the electrical signal and explains the behaviour of conductive pathways under oscillatory shear for small deformations. Moreover, a parameter characterising the degree of destruction of conductive pathways induced by shear flow was introduced.

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