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Behavior of Conductive Particle Networks in Polymer Melts under Deformation

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Abstract. The electrical properties of the composites containing conductive fillers are given by the structure of the particle network. Therefore, the behavior of these networks under deformation in the molten state is of great interest in order to obtain materials with desirable electrical properties. In this work the composites containing carbon black or carbon fibers were exposed to a shear deformation in two different experimental modes – oscillation and creep and the electrical conductivity of the materials was measured simultaneously.

Keywords: Polymer composites, Rheology, Conductivity.

PACS: 83.80.Sg, 83.85.Cg, 72.80.Tm

INTRODUCTION

The electrical properties of polymer composites containing conductive particles are influenced considerably by their phase structure. As the final morphology of the composites is usually formed during melt processing, it is important to understand the behavior of the particle networks under defined deformation in the molten state. The electrical properties of the composites with conductive fillers can be described by percolation theory and its numerous modifications [1, 2]. It says that the conductivity increases steeply at a critical filler concentration called percolation threshold. At this concentration the filler particles form conductive pathways in the polymer matrix by which the electrons can be transported. Generally it is assumed that the final composite structure after processing is the result of the competition between destruction of the particle network induced by mechanical stress and rebuilding of the network due to reagglomeration of the particles [3, 4]. As the first studies on simultaneous rheological and electrical measurements appeared just few years ago, only the systems containing nanofillers were investigated. However, the quantitative characterization of nanocomposites morphology, i.e. degree of dispersion or size of the agglomerates, and its development under deformation is a difficult task which is still not solved satisfactorily. Then the explanations of the effects observed in electrical measurements are mainly just hypothetical and they are hard to verify. Contrary to that, the size, shape and orientation of microfillers can be described accurately. Moreover, the rebuilding of the network can be neglected because of the weak interactions between microparticles. Thus, only the destruction of the conductive

networks under stress can be studied. Such investigations on microfillers can help then in understanding of the behavior of the nanocomposites.

In this work the coupled rheological and electrical experiments were performed using a modified shear rheometer with a plate-plate-geometry enabling simultaneous measurements of rheological properties and conductivity of the composites. Polymethylmethacrylate (PMMA) was used as a matrix and carbon black (CB) or carbon fibers (CF) as fillers.

EXPERIMENTAL

The PMMA composites containing carbon black (CB) PRINTEX XE2 supplied by Evonik Degussa GmbH or carbon fibers (CF) PANEX 35 provided by Zoltek at different concentrations were prepared using an internal mixer (200°C, 60 rpm, 8 min). True concentrations of the fillers were estimated by thermal gravimetric analysis. The structure of the composites was then studied by means of electron microscopy.

For simultaneous rheological and electrical measurements a modified rotational rheometer CSM 50 with plate-plate geometry coupled with an amperometer Picoammeter 6487 was used. In this rheometer the rotor and bottom plate are isolated from the drive unit so the amperometer measures the current flowing through the specimen only. The experiments were carried out in two modes - oscillatory and creep measurements.

RESULTS AND DISCUSSION

Morphology of the Composites

The morphologies of the systems containing 5 vol.-% of the filler are shown in Figure 1 as an example.

FIGURE 1. Morphology of the PMMA composites containing 5 vol.-% of the filler: a), b) carbon black (TEM); c) carbon fibers (SEM).

As can be seen in Figure 1a) and b), the carbon black is homogeneously dispersed in the polymer matrix even at relatively high concentration of 5 vol.-% and the size of the CB particles is in the range of 50-200 nm. In the case of microcomposites with CF

no agglomerates can be observed in the material and the incorporated fibers are randomly oriented. In contrast to the CB nanocomposites the size and shape can be accurately estimated using image analysis. For this purpose the fibers were observed in a light microscope after dissolving the polymer matrix. It was found that the length of the carbon fibers decreases considerably with the increasing concentration as a consequence of higher viscosities of the composites with higher loadings and, therefore, higher shears forces during the mixing.

Rheological and Electrical Characterization of the Composites

The influence of the filler concentration on the rheological properties of the composites was determined by frequency sweep experiments. The results obtained are shown in Figure 2. It is obvious that the incorporation of the filler leads to the increase of the complex viscosity in all cases. The addition of only 2 vol.-% of carbon black results in the disappearance of Newtonian plateau at low frequencies. At higher CB concentrations this effect called flow restriction is even more pronounced. At the concentration of 10 vol.-% of CB the yield point was reached and no viscous flow can be observed anymore.

FIGURE 2. Influence of the concentration of carbon black (CB) and carbon fibers (CF) on rheological behavior of the composites.

In comparison with carbon black the incorporation of carbon fibers lead to much smaller effects on the composite flow behavior. Also in these cases the viscosity increases with the fibers concentration, but even in the composite containing 10 vol.-% of CF no flow restriction was observed and the Newtonian plateau was reached. The pronounced differences between the activities of both fillers can be explained by their different specific surface areas. Whereas the surface area of the

carbon fibers is in the order of $10^{-4} \text{ m}^2.\text{g}^{-1}$ the carbon black as a nanofiller has a specific surface area of about $10^2 \text{ m}^2.\text{g}^{-1}$. Therefore, the interactions between the CB nanoparticles and polymer molecules and particle-particle interactions are much stronger than in the case of carbon fibers. These interactions influence then the rheological properties of the composite considerably.

The conductivity of the prepared composites in the molten state under quiescent conditions is shown in Figure 3. The values reported were recorded 10 s after the temperature of the specimen reached measuring temperature 200°C . It can be seen that the conductivity of the pure PMMA is about $10^{-11} \text{ S.cm}^{-1}$. Incorporation of 1 vol.-% of CB has no effect on the composite conductivity. Raising the CB concentration to 2 vol.-% a dramatic conductivity increase of about five orders of magnitude is observed. The addition of more than 3 vol.-% of CB has only minor effect on the conductivity so the percolation threshold in PMMA/CB composites is in the range from 1.5 to 3 vol.-% of the carbon black. Contrary to that the percolation threshold in PMMA/CF composites is shifted to higher concentration of 3-4 vol.-% and also the conductivity values are few orders of magnitude lower than in the PMMA/CB systems. This is explained as a consequence of the stronger particle-particle interactions in the case of nanofiller (CB) in comparison with microfiller (CF). In carbon fibers composites no plateau above percolation threshold was observed and the conductivity increases with the CF concentration continually. To explain this behavior further experiments are needed.

FIGURE 3. Conductivity of PMMA/CF and PMMA/CB composites in the molten state at 200°C as a function of the filler content.

Behavior of the Particle Networks under Shear Deformation

Figure 4 shows the evolution of the conductivity during the oscillatory measurements of PMMA/CB composites. First no deformation was applied and the conductivity was measured under quiescent conditions (region I.). Then the amplitude sweeps with stressing amplitude from 0.5 to 12 kPa were performed (region II.). After the deformation the conductivity measurements continued to study the recovery of the particle network (region III.). At low concentrations below the percolation threshold, where no particle network is present in the material, the conductivity stays constant during the whole measurement. In the region of percolation threshold (concentration of 1.5 and 2 vol.-%) few interesting phenomena take place. A conductivity increase during the first stage of the experiment was observed. This effect known as dynamic percolation was found to be dependent on the voltage applied (not shown in the figure). During the amplitude sweep (region II.) the conductivity further increases until the critical stressing amplitude is reached. After this point representing the equilibrium between build-up and breakdown of the network, the destruction of the network is preferred and the conductivity decreases. This behavior is more pronounced in the systems with lower amount of CB where the particle network is rather fragile. With increasing CB concentration, i.e. with stability of the network, the critical stressing amplitude is shifted to higher values and also the conductivity drop is not so pronounced. At the concentration above percolation threshold the particle network is so strong that no destruction was observed in the range of stressing amplitudes accessible with the rheometer used. Third effect worth to study is the rebuilding of the particle network after cessation of the shear flow leading to the conductivity increase (region III.).

FIGURE 4. The evolution of the conductivity in PMMA/CB composites with different filler concentration during the amplitude sweep: I. quiescent melt; II. shear ($f=1$ Hz); III. recovery after shear.

A different behavior was observed in the systems containing carbon fibers (Figure 5). As the mobility of the fibers in the polymer melt is very small due to their weight and dimensions, no dynamic percolation during the first stage of the experiment was detected. During the amplitude sweep the breakdown of the network occurs and the conductivity drops nearly to the value of pure PMMA. This network destruction takes place at considerably lower stressing amplitudes than in the CB systems (Figure 4), which implies the fragility of the CF network given by weak particle-particle interactions compared to the CB network. After breakdown of the network the conductivity stays constant and no recovery of the network can be observed.

FIGURE 5. The evolution of the conductivity in PMMA/CF composite with 4 vol.-% of carbon fibers during the amplitude sweep: I. quiescent melt; II. shear ($f=1$ Hz, $t_A=20$ s); III. recovery after shear.

As the behavior of the particle network under oscillatory deformation can be affected by many parameters such as frequency, amplitude time or stressing amplitude, the experiments at constant stress (i.e. creep experiments) can reveal the basic answer how the particle networks answer the deformation. Similar to the findings from oscillatory measurements, the conductivity effects are more pronounced in systems with fragile particle networks i.e. with filler amount corresponding to the onset of the percolation threshold. Figure 6 shows the behavior of the composite with 2 vol.-% of CB at different shear stresses. As the conductivity in this region is very sensitive quantity and it can vary from sample to sample up to one order of magnitude, the curves were normalized with respect to the conductivity value at the beginning of the creep. Not surprisingly, the conductivity drop is more pronounced when higher stress is applied. However, it is obvious that the rebuilding of the particle network starts already during the creep. It seems also that the rate of this rebuilding is higher when the stress is applied compared to the consequent quiescent phase (region III.). Interesting effect was found by performing multiple creep tests when the second creep was started when the conductivity reached its initial value (Figure 7). It is obvious that the networks exposed to the creeps have completely

different properties. The network at the beginning of the second is much more stable than the original network so the conductivity drop is much less pronounced. The explanation lays probably in the rebuilding of the initial network which takes place partially during the first creep already. Then the new network is stable under this stress and can be destroyed only by applying higher stresses.

FIGURE 6. The evolution of the conductivity in PMMA/CB composite with 2 vol.-% of carbon black during the creep at different stresses: I. quiescent melt; II. shear; III. recovery after shear.

FIGURE 7. The evolution of the conductivity in PMMA/CB composite with 2 vol.-% of carbon black during two consecutive creep experiments at 5 kPa.

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REFERENCES

1. F. Lux, *J. Mat. Sci.* **28** (2), 285-301 (1993).
2. M. L. Clingermann, J. A. King, K. H. Schulz and J. D. Meyers, *J. Appl. Polym. Sci.* **83**, 1341-1356 (2002).
3. I. Alig, T. Skipa, D. Lellinger and P. Pötschke, *Polymer* **49**, 3524-3532 (2008).
4. T. Skipa, D. Lellinger, M. Saphiannikova and I. Alig, *Phys. Status Solidi B* **246**, 2453-2456 (2009).