Composites Science and Technology 100 (2014) 99–104

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Electrical conductivity behaviour of sheared poly(methyl methacrylate)/carbon black composites

Xianhu Liu [a,b], Johannes Krückel [a], Guoqiang Zheng [b], Dirk W. Schubert [a,*]

[a] Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nuremberg, Martensstr. 7, 91058 Erlangen, Germany
[b] College of Materials Science and Engineering, The Key Laboratory of Material Processing and Mold of Ministry of Education, Zhengzhou University, Zhengzhou 450002, China

ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 4 June 2014
Accepted 5 June 2014
Available online 13 June 2014

Keywords:
A. Nanocomposites
B. Electrical properties
C. Deformation
D. Rheology

ABSTRACT

The electrical conductivity behaviour of unsheared (static) and sheared poly(methyl methacrylate)/carbon black (CB) composite disc-shaped samples with various CB concentrations as a function of the radial position were investigated and analysed. It was found that the angular averaged electrical conductivity of the static samples is independent of the radius and CB concentration. In comparison to that, the angular averaged electrical conductivity of the samples with a shear history is decreasing as a function of the radius due to the linear increase of the deformation from the centre to the rim of the samples. It is shown, that this effect is less pronounced increasing the composite concentration. A simple model is proposed to explain this behaviour. The results obtained in this study are in a very good agreement with the investigations performed via coupled electrical and rheological measurements and provide a deeper insight into structural changes in conductive polymer composites induced by shear deformations.

1. Introduction

The incorporation of conductive fillers, such as carbon black (CB), carbon fibres or carbon nanotubes (CNTs) into insulating polymers provides the potential to create conductive polymer composites (CPCs) with desired electrical properties [1–30]. In the past decades, an enormous effort [4–11] has been devoted to the study of CPCs with very low filler concentrations both in experimental and simulative conditions. The following issues are mainly concentrated on: (1) electrical properties and percolation behaviour of polymer/CB system, (2) electrical properties of polymer blends with other conductive filler in the presence of CB, (3) positive temperature coefficient and negative temperature coefficient effects of polymer/CB composites and their alteration with various conditions, and (4) localization and morphology of CB in two or more polymer blends.

Recently, there has been increasing interest in so-called coupled electrical and rheological experiments, because the electrical properties of CPCs react very sensitively on changes of the conductive structure induced by shear deformation [12–24]. The linear viscoelastic behaviour and electrical conductivity of single-walled carbon nanotube/poly(methyl methacrylate) (PMMA) composites were investigated by Du et al. [12]. They found that the alignment and dispersion of the nanotubes have a strong influence on the rheological behaviour of the composites. Kharchenko et al. [13] have firstly reported the simultaneous electrical and rheological investigations on the polypropylene filled with multi-walled carbon nanotubes (MWCNT), and a decrease of the electrical conductivity over several orders of magnitude by increasing the shear rate was observed. Recently, Obrzut et al. [14] investigated the shear-rate dependence of the electrical conductivity in PP/CNT composites. It was observed that the critical percolation threshold value increased with the shear rate, indicating that shear field-induced alignment of the CNTs along the fluid flow directions can have detrimental effects on kinetic percolation under certain processing conditions. Alig et al. [15] investigated the sheared polycarbonate (PC)/CNT composites after the quiescent annealing. This shearing caused a drop in the electrical conductivity of more than 6 orders of magnitude. Krückel et al. [16] studied the electrical and rheological properties of PMMA composites with CFs and CB as a function of stressing amplitude and filler concentration. It was found that the particle networks in the composites filled with CFs were more sensitive to deformation than those of the CB composites. In addition, they confirm that the stability of the networks increased with growing amount of fillers. Skipa et al. [17,18] reported a shear-induced nanotube agglomeration in PC/MWCNT melts. It was shown that the electrical conductivity under steady shear can be increased, and destruction and build-up of a particle network are the competitive effects in PC/MWCNT

* Corresponding author. Tel.: +49 91318527752.
E-mail address: dirk.schubert@fau.de (D.W. Schubert).

http://dx.doi.org/10.1016/j.compscitech.2014.06.005
0266-3538/

composites under steady shear. This behaviour of the CPCs was attributed to the changes of the conductive filler networks, particularly to the destruction of contacts between the fillers or filler aggregates.

On the other hand, the electrical properties of CPCs depend on the size and the shape of the fillers (or filler aggregates) as well as their spatial distribution in the polymer matrix [23,31]. Moreover, the strong van der Waals attraction between CBs can result in the formation of large aggregates. Aggregation reduces the potential for property enhancement by reducing the interfacial surface area and creating non-uniformities that can result in a deterioration of electrical and mechanical properties. Therefore, in order to obtain materials with desirable electrical properties, the change of conductive filler network under shear deformation is of great interest. However, to the best of our knowledge, the literature on the distribution of electrical properties on the CPC samples themselves is very rare. The electrical properties (capacitance, resistance, and conductivity) of ion gel films were investigated as a function of film geometry (i.e., thickness and the area) by Lee et al. [32]. It was found that the electrical resistance was directly proportional to the thickness and the reciprocal top contact area of the sample. Nevertheless, there is no publication available on electrical properties distribution of the CPC samples prior to and after shear except our previously report [33]. Accordingly, as a part of continuous efforts to systematically understand the certain dependence of electrical properties as a function of position and different directions in the CPC samples prior to and after shear, in this work, the electrical conductivity of the PMMA/CB composite samples with different CB concentrations (high and low concentration above the percolation threshold) from the divided pieces using our proposed methodology was systematically investigated and analysed.

2. Experimental section

The PMMA used as the matrix material was Plexiglas 7 N from Evonik Röhm GmbH (Germany). The weight-average molar mass and polydispersity index are 86 kg mol^{-1} and 1.6, respectively. As the conductive filler a commercial carbon black, Printex XE2, from Evonik (Germany) was used. The specific surface area of this special conductive grade was determined to be 900 $m^2\,g^{-1}$ by the BET method (Brunauer–Emmett–Teller).

The composites were prepared for different concentrations by melt mixing at 200 °C using an internal mixer. The mixing time was 2 min at 20 rpm for inserting the polymer and the filler into the mixing chamber and additional 8 min at 60 rpm to obtain composites with a homogeneous distribution. In order to prepare cylindrical specimens, the composite materials were compression moulded at 100 bars and 200 °C using a hot press. In order to prepare samples with a shear history, a stress controlled shear rheometer Gemini (Malvern Instruments, UK) with a plate–plate geometry was used. Additionally the rheometer was equipped with an amperometer from Keithley (UK) in order to measure the electrical properties parallel to the rheological experiments. The composite samples were annealed for 5 min at 200 °C in order to create isothermal conditions. Afterwards, an additional annealing time of 10 min was carried out in order to monitor the electrical properties of the composite samples under quiescent conditions in the molten state. Then a short creep experiment was performed on the samples with a constant creep stress of 20 kPa and a creep time of 20 s. After the shear step, the samples were quenched down to room temperature using a cooling spray in order to freeze the sheared morphology. In order to measure the electrical properties of the samples at different positions along the radius and for different angles, the cylindrical samples were divided into small pieces and then the conductivity of each piece was measured at room temperature. A detailed description of this conductivity mapping and the experimental set-up used can be found in our work previously published [33]. In order to compare the mapping of the sheared samples with the conductivity mapping was performed analogously on the unsheared samples. The samples without a shear history are named static samples. Prior to the sample preparation and the measurements, the materials were dried at 80 °C under vacuum for at least 24 h.

3. Results and discussion

It is well known, that the mean distance between particles in a composite is decreasing by increasing the volume concentration. According to that, the following model sketch in Fig. 1 is proposed for three different scenarios in a CB composite. Assuming a statistical distribution of the particles in the composite, the mean distance $\overline{D}$ can be calculated [23,34–36]:

$$\overline{D} \sim \frac{D_0}{\sqrt[3]{\phi}} \quad (1)$$

where D_0 is the particle diameter, and ϕ is the volume fraction. In Fig. 1 the indices L, M and H characterize "low, medium and high content" of CB for the unsheared (static) samples. Taking into

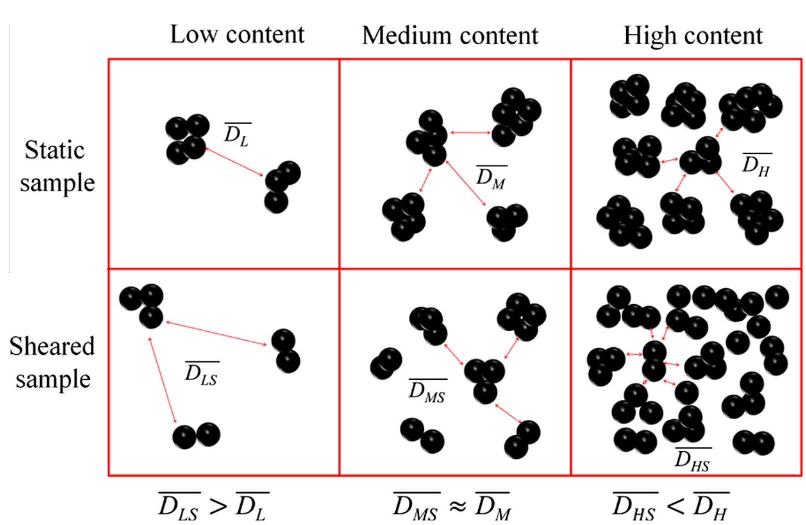

Fig. 1. Model of the mean distance between the CB agglomerates of static and sheared samples for different CB concentrations.