Polymer 139 (2018) 52–59

Contents lists available at ScienceDirect

Polymer

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

Conductive polymer composites with carbonic fillers: Shear induced electrical behaviour

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ARTICLE INFO

Article history:
Received 23 January 2018
Accepted 3 February 2018
Available online 8 February 2018

Keywords:
Polymer-matrix composites
Carbon fibres
Electrical properties
Rheology

ABSTRACT

Structural changes induced by defined shear deformation in conductive polymer composites containing carbon fibres or carbon black are investigated using simultaneous electrical-rheological measurements. This work presents first systematic study concerning the electrical behaviour of composites with anisotropic microfiller under deformation in the molten state. It was found that the electrical conductivity of composites with carbon fibres reacts very sensitively on the mechanical deformation. For instance, at a deformation amplitude of 0.1 the electrical conductivity oscillates over three orders of magnitude. On the other hand, the composites with carbon black display distinctly more stable conductive particle network resulting in only small variations in the conductivity under comparable conditions of deformation. The differences in the electrical and rheological behaviour of the composites are explained by distinctly stronger inter-particle interactions in the case of carbon black. The experiments presented show that conductive polymer composites containing micro-sized anisotropic particles could be a perspective material for deformation sensors or switches.

1. Introduction

Electrical properties of polymer composites containing conductive fillers are determined by the structure of conductive pathways formed by filler particles enabling an electron transfer inside the material. The conductive pathways are formed during the processing of the composite and their structure is influenced not only by the properties of the filler and the matrix, but to a large extent also by the processing conditions, e.g. flow fields and hydrodynamic stresses applied or thermal treatment [1,2]. The electrical conductivity of the composites with carbonic fillers lies typically in the range of semiconductors, which makes them suitable for applications in antistatic packaging or electromagnetic shielding [3,4]. The conductivity of the composite reacts sensitively on a change in the tunnelling distance between conductive particles. This change can be induced for instance by a swelling of the polymer matrix or by a deformation of the material. Thus, the conductive polymer composites (CPC) are tested also as perspective materials for liquid/vapour sensors [5,6] or strain sensors [7,8], respectively. A comprehensive review on CPC as sensitive electroactive materials was recently published by Deng et al. [1].

To get an insight into the behaviour of conductive particle structures in CPC under deformation, simultaneous electrical and rheological experiments were found to be a convenient tool. These experiments allow one to measure conductivity changes induced by a defined shear or elongational deformation [9–12]. The evolution of electrical conductivity during the deformation is a result of a competition between flow-induced destruction and build-up of conductive pathways [12]. Additionally in the case of nanocomposites dynamic percolation, i.e. thermally driven agglomeration of particles, contribute to the formation of conductive pathways [13–15]. Depending on the conditions of deformation the composite conductivity can either rise or decrease. Modelling the electrical conductivity as a function of time one can also obtain information about agglomeration kinetics of particles dispersed in a polymer matrix under defined deformation [16,17].

Nowadays the research in the field of polymer composites is focused mainly on nanocomposites. Fillers with nanoscale dimensions are preferred, because lower concentrations are needed to reach desired mechanical reinforcement in comparison with

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https://doi.org/10.1016/j.polymer.2018.02.008
0032-3861/

traditional microfillers. This is caused by large surface area of nanoparticles available for polymer-particle interactions. Moreover, highly anisotropic nanoparticles such as carbon nanotubes or graphene can be used. High aspect ratio of these particles allows efficient stress transfer in the material resulting in an enhancement in mechanical properties. Considering electrical properties of composites with random orientation of particles, percolation threshold decreases with increasing aspect ratio of the particles as predicted by excluded volume theory [18,19] and observed in many experimental studies [4,20,21]. Furthermore, dynamic percolation during the nanocomposite processing can lead to substantially lower values of percolation threshold than predicted theoretically. Smaller particles, i.e. those with larger surface area, are more mobile and form conductive pathways faster than the bigger ones at the same volume content. Thus, surface area of the particles and processing conditions affect the value of percolation threshold, too. However, to benefit from the low filler loadings, fine dispersion of the nanoparticles has to be achieved. This requirement is hard to fulfil using conventional melt-mixing techniques, however, due to high attractive forces between nanoparticles and their tendency to agglomeration in polymer matrices. When finely dispersed, the presence of nanoparticles often results in a tremendous increase in composite viscosity, which affects the melt processability negatively. These issues still limit the application of nanocomposites on a large scale seriously.

Up to now the electrical-rheological experiments described in the literature were performed only on systems containing nanofillers. In the first works of Kharchenko et al. [9] and in extensive studies of Alig and Pötschke [10,12,16,17] carbon nanotubes composites in PP and PC matrices, respectively, were investigated. The description and discussion of the behaviour of carbon black structures in PMMA under deformation can be found in the literature as well [22,23]. To our knowledge a systematic study concerning the electrical behaviour of microcomposites under deformation in the molten state has not been published.

In our previous work it was found that the particle structures formed by carbon fibres can be destroyed by considerably lower stresses in comparison with carbon black [23]. Moreover, the conductivity dropped down to the level of the neat polymer matrix during the shear, which was not observed in carbon black composites. In this work composites containing carbon fibres or carbon black with the same initial electrical conductivity are investigated. The electrical response of the composites on the oscillatory shear deformation at constant stressing amplitude is measured and evaluated. The rheological behaviour of the composites is discussed as well.

2. Experimental

2.1. Materials, sample preparation and characterization

The poly(methyl methacrylate) (PMMA) Plexiglas 7 N (Evonik Röhm GmbH, Germany) was used as the matrix material. The weight-average molar mass M_w of the polymer is 98.7 kg mol^{-1} and the polydispersity index M_w/M_n is 1.52. The conductive fillers were special conductive grade of carbon black (CB) Printex XE2 (Evonik, Germany) and chopped carbon fibres (CF) Panex 35 (Zoltek, Hungary).

The composites were prepared by melt mixing in an internal mixer PolyDrive (Haake) at 200 °C and 60 rpm for 10 min. Two composites containing 3 vol% of carbon black and 8 vol% of carbon fibres, respectively, are compared in this study. As found in our previous study, these composites show similar electrical conductivities of about 10^{-5} S cm^{-1} and their concentrations lie above the percolation thresholds [23]. Thus, they are suitable for investigations on changes in electrical properties induced by mechanical deformation. The real concentration of the fillers was determined by thermal gravimetric analysis. The specimens with a diameter of 25 mm and a thickness of 2 mm for electrical-rheological measurements were prepared by compression moulding (200 °C, 200 bar, vacuum). The specimens were dried under vacuum for at least 24 h at 80 °C prior to the measurements.

The morphological characterization of the composites prepared was performed by means of electron microscopy. The morphology of the CB composite was visualized by transmission electron microscopy (TEM) using an electron microscope CM30 (Philips) at an acceleration voltage of 300 kV. The 70 nm thin sections were prepared at room temperature using an ultramicrotome EM UC7 (Leica). Fracture surface of the CF composite was studied by the scanning electron microscope LEO 435 VP (Leica) at an acceleration voltage of 10 kV using a secondary electron detector. The composites were characterized rheologically at 190 °C by frequency sweeps in the linear viscoelastic region (stressing amplitude of 200 Pa) and amplitude sweeps at an angular frequency of 0.0628 rad s^{-1}. The PMMA matrix is thermally stable up to 50 000 s as determined by time sweep measurement in the linear viscoelastic range.

2.2. Simultaneous electrical-rheological 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 steel rotor was insulated from the driving unit of the rheometer by inserting a peg made of poly(ether ether ketone). The insulated rotor and the bottom plate of the rheometer were connected to a Picoammeter 6487 from Keithley (USA) using a 40 μm thin copper wire. The Picoammeter 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.

Simultaneous electrical-rheological measurements were performed according to the following protocol. After inserting the specimen between the plates of the rheometer with a gap of 2 mm and reaching the measuring temperature of 190 °C, the sample was kept for 10 min under quiescent conditions prior to shear. Then an oscillatory shear was applied for 2000 s with stressing amplitudes in a range between 0.1 and 10 kPa at a fixed angular frequency of 0.0628 rad s^{-1}. Every simultaneous measurement was performed 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. If not given otherwise, the error bars are shown in the figures only in the cases when they are larger than the symbols used. It is worth noting that the stressing amplitude is just a characteristic quantity because its value describes shear conditions on the edge of the specimen only and the material is exposed to smaller and smaller stresses in the direction to the specimen centre. Therefore, the electrical conductivity measured is an integral value including contributions of conductive particle structures exposed to different shear stresses.

3. Results and discussion

The structure of the PMMA composites visualized by electron microscopy is shown in Fig. 1. The carbon fibres are homogeneously dispersed in the matrix. The number average length of the fibres with a diameter of 7 μm was estimated as 182 μm giving the average aspect ratio of 26 [21]. Obviously, the interfacial adhesion between CF and PMMA is rather low as documented by the fibres pulled out or fallen out from the matrix (Fig. 1a). The carbon black particles of irregular shape are distinctly smaller with sizes between 50 and 100 nm.