



# Rheological and electrical behavior of poly(methyl methacrylate)/carbon black composites as investigated by creep recovery in shear



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## ABSTRACT

The rheological and electrical behavior of poly(methyl methacrylate) (PMMA)/carbon black (CB) composites has been studied as a function of CB concentration by simultaneous electrical and rheological measurements during creep and creep-recovery experiments in the linear and nonlinear regimes. The creep compliance and recoverable compliance were strongly influenced by the CB concentration in the linear regime, especially above the percolation threshold. The creep compliance remained almost unchanged in the linear and nonlinear regimes, but the recoverable compliance was strongly influenced by the creep stress. The electrical conductivity increased under low creep deformation, but under high creep deformation, the electrical conductivity decreased rapidly at the beginning of the creep experiment. After a sufficiently long creep time under shear, the electrical conductivity again increased. The results provide a deeper insight into structural changes in conductive polymer composites induced by shear deformation.

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## 1. Introduction

Conductive polymer composites (CPCs) have become increasingly interesting during the past decade because they can be used in antistatic packaging, electromagnetic interference shielding or sensor applications [1–28]. The filler network in the bulk polymer plays an important role in the electrical conductivity of the composites [1–9]. It is well known that the structure of the conductive pathways in the polymer composite is significantly influenced by the shear or elongation forces applied during the melt processing [10–29]. The shear deformation for different types of polymer processing operations is different [29–32]. In general, polymers in compression molding processes can experience shear rates as low as  $0.001 \text{ s}^{-1}$ , while polymers used for high speed injection molding can experience shear rates of  $50\,000 \text{ s}^{-1}$  or higher during the injection step [30]. Therefore, in order to fabricate a composite with the desired electrical properties, it is important to understand how

the conductive structure develops during the melt processing, since aggregate formation can be minimized by appropriate application of shear during melt mixing [27]. In this respect, coupled electrical and rheological experiments provide a unique tool which monitors sensitively the changes in composite phase structure induced by a defined mechanical deformation [10–21].

Many investigations have shown that the evolution of electrical conductivity during the shear deformation is the result of a competition between shear flow-induced destruction and the build-up of conductive pathways formed by filler particles [10–23]. The first simultaneous electrical and rheological investigations on polypropylene filled with multi-walled carbon nanotubes were reported by Kharchenko et al. [14] and Obrzut et al. [15]. A dramatic decrease by several orders of magnitude in the electrical conductivity was observed when shear rate was increased. Alig et al. [16] investigated sheared polycarbonate/carbon nanotube composites after quiescent annealing, and they found that the shear caused a drop in the electrical conductivity by more than six orders of magnitude. Bauhofer et al. [17] found that a given shear rate lead to a given conductivity of the CPCs, which was independent of the initial dispersion state of the filler and was determined by the competition between the build-up and the destruction of the conductive network under shear. In our previous works [18–23],

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we have confirmed the expected build-up and destruction mechanisms between the conductive fillers under shear, but to the best of our knowledge, the rheological and electrical properties of poly (methyl methacrylate) (PMMA)/CB composites under creep shear have not been reported. In this work, creep and creep-recovery experiments were performed on PMMA/CB composites in the linear and nonlinear regimes to elucidate the changes in elastic properties and electrical conductivity of the composite materials.

## 2. Experimental

### 2.1. Materials

Carbon black (CB) Printex XE2 with a density of  $2.13 \text{ g cm}^{-3}$  was provided by Evonik Röhm GmbH, Germany. Commercially available PMMA Plexiglas 7N with a density of  $1.19 \text{ g cm}^{-3}$  supplied by Evonik Röhm GmbH was used as the matrix material. The main advantage of PMMA is its high thermal stability, which allows investigations at elevated temperatures over long measuring times [33]. Additionally, PMMA is an amorphous thermoplastic polymer. It has been proved that the filler particles can be pushed out from the crystal region [34], and up to now, melt crystallization of PMMA has not been reported in the literature. Therefore, the influence of the crystallization on the distribution of the filler particles, electrical conductivity and rheological properties can be ignored in our case.

### 2.2. Sample preparation

The polymer matrix and CB were dried at  $80 \text{ }^\circ\text{C}$  under vacuum for at least 12 h and then mixed in a kneader at  $200 \text{ }^\circ\text{C}$ . Both polymer and CB were introduced directly in the mixer at a rotation speed of 20 rpm. After 2 min of mixing at 20 rpm, the rotation speed was increase to 60 rpm and kept constant for 8 min. After the melt mixing, the composites material was cooled down to room temperature and then granulated using a blade granulator (Wanner Technik). The obtained granulate composites were then compression molded at 100 bar and  $200 \text{ }^\circ\text{C}$  to 2 mm thick discs with a diameter of 25 mm and the discs were then dried at  $80 \text{ }^\circ\text{C}$  under vacuum for at least 12 h.

### 2.3. Characterization

The morphology of the PMMA/CB composites was studied by means of scanning electron microscopy (SEM, Carl Zeiss Microscopy, Germany). The samples were fractured in liquid nitrogen to obtain undeformed fracture surfaces and the surfaces were then coated with gold using Sputter Coater S150B from Edwards.

The simultaneous electrical and rheological measurements were carried out with the materials in the molten state at  $200 \text{ }^\circ\text{C}$  under a nitrogen atmosphere using a modified stress-controlled shear rheometer Gemini from Malvern Instruments with a plate-plate geometry. The insulated rotor and the bottom plate of the rheometer were connected to a Picoammeter 6487 from Keithley (USA). The DC-resistance  $R$  of the composite was recorded simultaneously during the experiment with a constant voltage of 1 V applied to the sample. The experiment was carried out under a nitrogen atmosphere. Before starting any experiment, the sample was allowed to equilibrate for 10 min in the measuring chamber at the chosen temperature. The electrical conductivity  $\sigma$  was estimated from the resistance  $R$  using the equation:

$$\sigma = d/R\pi r^2 \quad (1)$$

where  $d$  and  $r$  are the thickness and radius of the sample,

respectively.

## 3. Results and discussion

Fig. 1 shows the SEM images of PMMA filled with 1 vol% and 5 vol% of CB (the transmission electron microscopy of the composites can be found in Ref. [20]). It can be seen that the CB particles are mainly dispersed as small CB aggregates, but they are homogeneously distributed in the matrix. The CB particles consisting of primary aggregates have irregular shape. The size of the CB aggregates increases with increase of CB loadings and it is in the range of approximately 50–200 nm. Large CB agglomerates were not observed in the composite material.

Fig. 2 shows electrical conductivities of PMMA/CB composites with different CB concentrations during the electrical-rheological measurements including a shear step at a creep time  $t_c$  of 600 s under a constant stress  $\tau_0$  of 500 Pa. From the initial electrical conductivity values, the region of the electrical percolation threshold of the PMMA/CB composites can be determined. The pure PMMA and the composite with 1 vol% of CB are nonconductive materials, but when the CB content was increased to 2 vol%, a tremendous increase in electrical conductivity of about five orders of magnitude was observed, indicating that a CB conductive networks was formed. A further increase in the filler amount led to higher conductivity values, but the increase was not so pronounced as before. This finding is in a good agreement with our previous study [20,22], where the percolation threshold was estimated to be 1.8 vol%.

The electrical conductivity of the composite with 2 vol% of CB increased over time under the quiescent conditions due to the formation of conductive pathways. The driving force of this effect called “dynamic percolation” was the thermal motion of the particles in the melt and attractive forces between them [19–37]. It is often found for composites containing conductive nanofillers around the electrical percolation threshold. Nevertheless, the changes in the electrical conductivity became less pronounced with increasing CB concentration, which is attributed to the formation of more dense and more stable CB conductive pathways [20–23]. Furthermore, it was found that the CB concentration around the percolation threshold had a significant influence on the composite conductivity during the shear step. Under a shear stress of 500 Pa, the electrical conductivity of the composite with 2 vol% CB increased by about two orders of magnitude, implying that there must be a shear-flow induced build-up of conductive pathways which, together with the dynamic percolation, plays an important role in the development of a phase structure in the composite under shear. With increasing concentration of filler, the size of the CB aggregates increases as more particles are involved in the conductive pathways (see Fig. 1) and the CB particle structure becomes more stable; meanwhile, the number and size of the free separated agglomerates and/or individual isolated CB particles decreases, so fewer free separated agglomerates and/or individual isolated CB particles are involved in the conductive pathways under the same constant shear stress. Therefore the increase in electrical conductivity becomes less significant. As a CB content of 5 vol%, the electrical conductivity showed no increase during the creep stage.

The flow behavior of the PMMA composites during the creep is displayed in Fig. 3 as the times dependence of the creep compliance. As expected, in Fig. 3a, the incorporation of CB leads to a shift in the creep compliance curves to lower values. The ratio  $t_c/J_c$  is plotted as a function of time in Fig. 3b. After a sufficiently long time, when the slope of  $J_c = f(t_c)$  on a logarithmic scale attains the value of unity, the ratio  $t_c/J_c$  represents the shear viscosity of the material [38]. Fig. 3a shows that a slope of unity is reached with pure PMMA and composites with 1 and 1.5 vol% CB, as is confirmed by the

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