



# Is electrical percolation in carbon-filled polymers reflected by rheological properties?



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## ABSTRACT

It is well known that the electrical conductivity of particle filled polymers exhibits a distinct percolation behavior. In the literature it is stated that this percolation is accompanied by a comparable change of rheological properties designated “rheological percolation”. Evaluating dynamic-mechanical measurements from the literature and using own results from creep experiments on polymethylmethacrylate melts filled with graphite it is demonstrated that rheological properties change continuously as a function of particle concentration in the range of the threshold of electrical conductivity. A model is proposed and discussed, which describes the electrical and rheological properties. For rendering a polymer conductive, continuous pathways of conducting fillers are necessary. The rheological behavior in the percolation regime is determined by matrix molecules that become hindered in their mobility by an attachment to the particles.

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## 1. Introduction

A distinct percolation threshold widely known and thoroughly investigated is that of the electrical conductivity as a function of the concentration of conducting fillers in an insulating matrix. An example with some practical relevance is carbon black in thermoplastic polymeric materials. A typical percolation curve is sketched in Fig. 1. At low concentrations ( $\Phi < \Phi_c$ ) where the conducting particles are separated from each other by the insulating matrix, the conductivity is small. Within a certain concentration range ( $\Phi \approx \Phi_c$ ) the conductivity rises sharply and approaches another plateau of much higher conductivity.

As presented by the sketched model in Fig. 1, the steep jump in conductivity is usually explained by the formation of path-like particle structures running from the lower to the upper side of a sample and enabling electrons to flow. At still higher concentrations ( $\Phi > \Phi_c$ ), additional paths contribute to a further increase of electrical conductivity, but the overall effect is much smaller than in the transition zone. Such a behavior found for some other relations in physics is generally called percolation and electrical percolation in the special case of electrical conducting particles.

Another result of the addition of fillers to a polymer matrix is a change of rheological properties and in the literature papers are found that state a “rheological percolation” going along with the electrical percolation. Most authors define the “rheological percolation” by a more or less steep increase of the storage modulus  $G'$  with growing filler content in the concentration range of the electrical percolation. As shown later,  $G'$  is not a suitable quantity for the investigation of a percolation behavior, because it does not describe the liquid/solid transition unambiguously that should be taken as the criterion for a “rheological percolation”. Depending on the accuracy of the measurements performed and their interpretation, one finds various results in the literature with respect to the existence of a rheological transition.

In Ref. [1] it is stated for multi-wall carbon nanotubes dispersed in polycarbonate that a rheological threshold exists that coincides with the percolation of the electrical conductivity. For the same system in Ref. [2] a temperature-dependent “rheological percolation” is reported whose critical concentrations cover a wide range lying below or above the corresponding value for the electrical threshold. A model is suggested that neglects elementary knowledge on the configuration of macromolecules, however. In Ref. [3] it is stated for carbon black and in Ref. [4] for graphite dispersed in a high density polyethylene that there is an agreement between the electrical and “rheological” percolation found experimentally. A comparison between the “rheological” threshold on one side and

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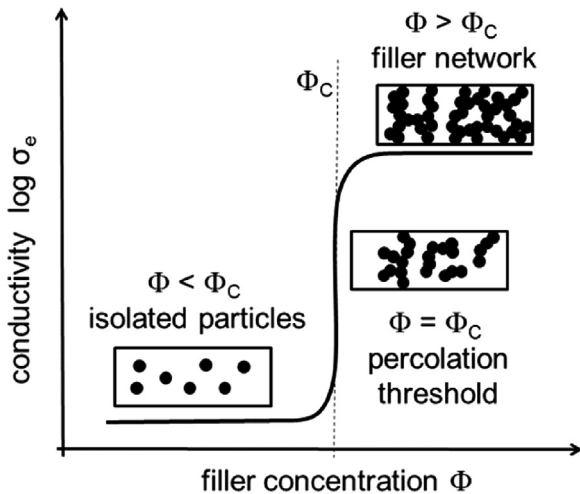


Fig. 1. Schematic percolation curve for the electrical conductivity of conducting fillers in an insulating matrix and particle morphologies in the different distinguished regions.

the electrical and thermal percolations on the other for multi-wall carbon nanotubes in polycarbonate is reported in Ref. [5]. The critical concentration for the “rheological” percolation determined from  $G'$  was found to be smaller than that for the electrical percolation. In addition, the thermal conductivity was measured as a function of the filler content. A “percolation behavior” was observed for this quantity, too, with a critical concentration between those for the storage modulus and the electrical conductivity.

These conclusions are misleading insofar as a “rheological percolation” should reflect the transition from a liquid-like to a solid-like behavior. As well known from the literature such a transition is designated by the storage modulus  $G'$  and the loss modulus  $G''$  running in parallel to each other in a double-logarithmic plot as a function of angular frequency. This feature corresponds to  $G''/G' = \tan \delta$  being independent of frequency [6]. It was not considered in the references cited, however.

These exemplary results from the literature demonstrate that the experimental basis for a comparison between the electrical and rheological behavior of particle-filled polymer melts is not very sound, even on a qualitative level. This situation makes it difficult to find out from the literature whether the threshold of the electrical conductivity, which is well established at least from a qualitative point of view, is mirrored by rheological properties. An answer to this question is of some relevance to set up a convincing model that is the base of understanding the experimental results. Furthermore, such a model may be used to support the specific development of electrically conducting polymeric materials for special applications.

In the following, some basics of measuring electrical conductivity and rheological properties are critically discussed. Making use of electrical and rheological experiments performed in parallel on one sample, it is shown that the electrical and rheological percolation is not necessarily correlated with each other. Rather, electrical and rheological properties based on different physical mechanisms exhibit dependencies on the filler morphology that are not comparable. A model is proposed and its conformity with the experimental results discussed.

## 2. Experimental

Most of the experiments reported in this paper were performed on a commercial polymethylmethacrylate (PMMA) filled with

electrically conducting carbonic particles. As conducting fillers, graphite platelets or carbon black were used. Specifications of the PMMA matrix and the carbon black are given in Ref. [7] together with information on the manufacturing of the composites. An experimental device was built up to determine the electrical properties just in the same states as the rheological measurements are performed. The direct current electrical conductivity of the blends in the molten state was measured directly in the rheometer (Gemini, Malvern Instruments) using an ampere meter (Picoammeter 6487, Keithley) as a source of the constant voltage of 1 V and a unit measuring the current flow through the specimen. More details of this special equipment can be obtained from Fig. 2 and the description found in Ref. [7]. The two steel plates act as the electrodes of a capacitor, which are electrically insulated from each other by replacing one part of the steel shaft by the high-temperature resistant polymer polyetheretherketone (PEEK) (see Fig. 2).

## 3. Electrical percolation curves

In most publications, electrical conductivities of filled polymeric materials at ambient temperature are presented for the experimental reasons of handling of samples and measuring equipment that is easier than at elevated temperatures. If compared to rheological properties, which are investigated at higher temperatures typical of polymer melts, the question arises in which way the electrical conductivity and its percolation behavior commonly obtained at ambient temperatures correspond to the states within the melt. It can be imagined, for example, that a crystallization process like in semi-crystalline polymers changes the distribution of particles. In amorphous polymers the cooling effect on the filler morphology should be much smaller, because no changes of supramolecular order occur during solidification. Reliable measurements of this kind are very rare in the literature, however.

A comparison between percolation curves in the molten and solid state is given in Fig. 3 for a PMMA filled with graphite [8]. The electrical conductivity is plotted as a function of the volume concentration at ambient temperature and in the melt at 210 °C.

The measured data are fitted according to Eq. (1) proposed by McLachlan [9], [10].

$$(1 - \Phi) \cdot \frac{(\sigma_m^{1/s} - \sigma_e^{1/s})}{\sigma_m^{1/s} + \left[\frac{(1-\Phi_c)}{\Phi_c}\right] \cdot \sigma_e^{1/s}} + \Phi \cdot \frac{(\sigma_f^{1/t} - \sigma_e^{1/t})}{\sigma_f^{1/t} + \left[\frac{(1-\Phi_c)}{\Phi_c}\right] \cdot \sigma_e^{1/t}} = 0 \quad (1)$$

This equation has been successfully used to describe percolation curves of the electrical conductivity of various composites.  $\Phi$  is the volume fraction of the filler and  $\Phi_c$  is defined as the critical volume concentration for the percolation threshold.  $\sigma_m$  is the electrical conductivity of the matrix,  $\sigma_f$  that of the filler and  $\sigma_e$  stands for the conductivity of the composite.  $\Phi_c$ ,  $\sigma_m$  and  $\sigma_f$  are fitted to the experimental data, the exponents  $t$  and  $s$  are assumed to be universal constants taken as  $t = 2$  and  $s = 0.87$  for three-dimensional systems [10]. More details on the fitting procedure and its accuracy and the reproducibility of the electrical measurements can be found in a supplementary file. As can be seen from Fig. 3, both data sets are well described by Eq. (1). The critical volume ratios for percolation follow as  $0.032 \pm 0.03$  at ambient temperature and  $0.037 \pm 0.005$  at 210 °C. Within the accuracies of the experiments and the numerical description, the differences can be regarded to be small indicating that the threshold of the electrical conductivity may be largely independent of temperature. This result is consistent with the model sketched in Fig. 1 showing that the percolation transition is due to the formation of conducting

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