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Modeling the dynamic percolation of carbon nanotubes and revisiting critical exponents

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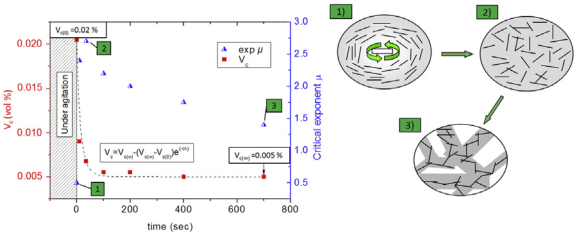
HIGHLIGHTS

- Percolation threshold and critical exponents are determined with an unmatched accuracy.
- The critical exponent strongly varies during dynamic percolation of carbon nanotubes.
- A correlation between critical exponent and particles dispersion is established.
- A new model depicts conductivity as a function of time and filler content.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, dynamic percolation of carbon nanotubes in silicone oil was probed by means of electrical measurements. Carbon nanotubes were first dispersed in silicone oils with ultrasounds. The obtained suspension was then slowly diluted. After each dilution, the changes in electrical properties was monitored over time. This procedure enabled to collect a large number volume fraction and define both the percolation threshold and the critical exponents with unmatched accuracy. The percolation threshold was found to decrease with time as a consequence of the already described aggregation of conductive nanoparticles. More surprisingly, the critical exponent also largely varied over time. This changes were correlated to the quality of the dispersion of carbon nanotubes within the host matrix. Finally, statistic percolation model was adapted into one that take into account for conductivity changes as a function of time and filler content.

1. Introduction

The electric properties of dielectric materials filled with conductive particles are known to depend strongly on the filler fraction and their arrangement within the host matrix [1–6]. The formation of a conductive path occurs at a critical filler content, well known and is usually described as a percolation threshold [7,8]. Above this amount of filler, the conductivity increases by orders of magnitude. In the case of 3D randomly dispersed systems, the percolation transition was modeled with great success as a power law by Kirkpatrick [9]:

$$\sigma = \sigma_0 \times (V - V_c)^{\mu} \tag{1}$$

with σ the conductivity, σ_0 the theoretical macroscopic conductivity of the filler, V_c the critical filler fraction, V the filler content and μ the critical exponent. This model has been widely employed by researchers to describe the conductivity changes of composite materials with increased filler content.

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Most of experimental measurements and numerical simulations led to a critical exponent μ close to 2 for 3D random systems; therefore assumed to represent a “universal value” [10]. However, scattered values from 1 to 6 have also been reported for μ in a wide variety of materials [11,12]. These results led to countless discussions on the universality of critical exponents. Several models and theories were in particular proposed to explain non-universality in polymer matrices mixed with carbonaceous fillers [11–22]. Though the origin of non-universality seems hard to determine, all agree that a physical meaning is hidden behind the critical exponent.

Non universal values may be explained with the random resistor network theory. Proposed by Kogut and Straley [13], this approach consists in imagining the fillers network as a distribution of resistances in the percolating network. This induces critical exponents higher than 2 especially if the distribution is broad. The Random-Void (RV) model, developed by Halperin et al. [14], consists in conducting media filled with void areas. Electron transport is achieved through a path between insulating spaces. This model predicts a critical exponent close to 2.5.

The non-universality might originate from anisotropy, but Celzard and coworkers clearly showed that universality could be obtained as well in anisotropic systems [16,17].

Non-universal values have been observed for angular particles and porous media by McLachlan et al. [18–22].

Vionnet-Menot [12] observed that high critical exponent values were usually found for composites with low percolation thresholds. In these systems, it was assumed that there is no direct contact between conductive particles. Electron transport is thus likely to result from tunneling and appears to govern “non-universal” values.

The application of thermal annealing on composites filled below the percolation threshold may lead to a restructuration of isolated particles into an infinite path. This formation of a conductive network with time is defined as dynamic percolation [23–29]. Recently, our research group [30–32] studied the changes in critical exponent values of composites submitted to dynamic percolation. A strong variation from 2 to 6 of the critical exponent during annealing was reported. These results were ascribed to filler aggregation processes in the melt. Then, non-universal values could be attributed to aggregated systems, in which the dispersion and distribution of conductive particles are not stochastic anymore.

Dynamic percolation was studied as a way to reduce the amount of filler necessary to achieve a conductive material. Many investigations described the mechanisms responsible for this process, however, only few scientists proposed quantitative models [33–37]. The following models from the literature are all based on Kirkpatrick's equation (cf. Eq. (1)), which was adapted with a kinetics term. In those models, the filler content V corresponds to the concentration of conducting filler truly participating in the percolating path. To describe the process of filler aggregation, kinetics equations were chosen by the authors. V is then substituted in Eq. (1) by an equation of the first or second order. Cao et al. [34,35] presented a model based on a first order kinetics:

$$\frac{dN_{(t)}}{dt} = -KN_{(t)} \tag{2}$$

where $N_{(t)}$ corresponds to the number of clusters over time and K is the reaction rate. Integrating Eq. (2) leads to Eq. (3):

$$N_{(t)} = cst \times exp^{(-Kt)} \tag{3}$$

Assuming that the fraction of clusters $V_{(t)}$ in the composite is proportional to the number of cluster ($V_{(t)} \propto n_{(t)}$), the authors adapted Eq. (3) into Eq. (4)

$$V_{(t)} = V_{(\infty)} - \left(V_{(\infty)} - V_{(0)}\right) \times exp^{(-Kt)} \tag{4}$$

$V_{(\infty)}$ and $V_{(0)}$ are respectively the fractions of percolated clusters at long and initial time. Combined with Eq. (1) results in:

$$\sigma_{(t)} = \sigma_0 \times \left[\left(V_{(\infty)} - \left(V_{(\infty)} - V_{(0)}\right) \times e^{(-Kt)}\right) - V_{c(\infty)}\right]^{\mu} \tag{5}$$

As mentioned by Cao et al. [34], V_c should be substituted by another term $V_{c(\infty)}$, corresponding to the minimum filler content required to achieve the percolation network. Alig and Skipa [33,36] proposed a similar model based on a kinetics of aggregation of the second order:

$$\sigma_{(t)} = \sigma_0 \times \left[V_{(0)} + \left(V_{(\infty)} - V_{(0)}\right) \times \left(1 - \frac{1}{1 + 4kt\left(V_{(\infty)} - V_{(0)}\right)}\right) - V_{c(\infty)}\right]^{\mu} \tag{6}$$

Later, Kruckel [37] proposed a more detailed model based on three distinct aggregation steps. In the first step, particles are dispersed in the matrix, the second one represents clusters not connected and the third one represents the formation of a percolation path. Calculations based on an equilibrium between three kinetics equations led to Eq. (7). Details of calculation can be found in the original paper [37]:

$$\sigma_{(t)} = \sigma_{1\infty} - \tilde{A}exp(-at) - \tilde{B}exp(-k_2 t) \tag{7}$$

In all these models, the critical exponent is arbitrarily set to the universal value. However, it was demonstrated [38] that the latter is altered by the aggregation process. This could lead to some mismatches between the proposed models and experimental data.

In the present paper, a new experimental process allowed us to accurately determine the critical exponent μ. A detailed investigation of the standard deviation on this value was performed in order to reduce the error and reveal meaningful differences over percolation time. The method was then applied to scout changes in the critical exponent over time. Finally, a model was proposed that quantitatively describes the measured conductivity as a function of filler content and time.

2. Experimental

2.1. Materials

The study was realized with a silicone oil, 47-V100, from Bluestar Silicones. The matrix was filled with multiwall carbon nanotubes, N7000, from Nanocyl, synthetized by chemical vapor deposition and characterized by a length of 1.5 μm and a diameter of 10 nm (aspect ratio ~150).

2.2. Suspension preparation

Carbon nanotubes were dispersed in silicone oil by ultrasonication for 5 min. To do so, a 750 Watt ultrasonic probe from Bioblock scientific was used. In order to prevent the suspension from heating during sonication, the latter was cooled in an iced bath during the process. The initial ”mother suspension” contained 0.048 vol % of CNT, should be taken well above all the measured percolation thresholds in these systems (0.01 vol %).