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Electric field as a tuning key to process carbon nanotube suspensions with controlled conductivity

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ABSTRACT

This paper describes the effect of electric field on the structuration of carbon nanotubes in silicone oil. The particles have been dispersed in the liquid by ultrasounds and diluted in order to vary the filler content. Electrical measurements were performed under different electric fields and over time on each filler content, in order to probe the particles structuration. From a critical value, the electric field was found to both increase the conductivity of the composite and reduce percolation threshold. This effect is further enhanced with time. Spectacular percolation thresholds, as low as 0.0024 vol %, have been evidenced. This result was attributed to a strengthening effect between filler contacts. More surprisingly, the conductivity remained high after the electric field was stopped, showing the irreversible nature of this effect. In addition, an analytical model has been developed to describe the conductivity of the composite as a function of three parameters: nanotubes content, time and electric field.

1. Introduction

Conductive particles, such as carbon black (CB) [1] or carbon nanotubes (CNT) [2], have been widely used to tune electrical properties of polymers [3–9]. The conductivity of such composites is governed by percolation. Above a given filler content, known as percolation threshold (V_c), a transition from insulating to conductive behavior occurs [10–13]. This transition is the result, at small scale, of the formation of an infinite network of filler in the matrix. The associated tremendous conductivity (σ) enhancement is commonly described by Kirkpatrick's equation [14]:

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

with σ_0 the theoretical macroscopic conductivity of the filler, V_c the percolation threshold, V the filler content and μ a critical exponent.

From the application viewpoint, percolation achieved at low filler content appears as a seducing route for manufacturing high added value smart materials at limited cost. Moreover, large amounts of filler may yield to reduced mechanical properties. The value of V_c depends on physical-chemical (matrix polarity [11,15]), fillers chemistry [16–18], geometrical (fillers shape ratio [19,20,18,21]) and process (dispersion distribution [22–26], temperature [27–30]) parameters. The overwhelming impact of processing conditions was specifically highlighted in the last decade in the case of extruded polymers compounded with high aspect ratio nanoparticles, such as CNT. Very low percolation thresholds in the range of 0.1 wt % were indeed expected for CNT nanocomposites due to their gigantic aspect ratio (up to 1000 and more).

However, extruded CNT composites have presented V_c values 10 to 100 times higher than the predictions [28,31].

This discrepancy between theory and experiment was finally explained by the scientific community: shearing prevents CNT from forming percolation networks [32,33]. Moreover, extrusion process can induce an orientation of particles with large aspect ratio through the flow direction [28]. This yields in a pattern of dispersion and distribution of CNT where the latter are isolated from one another. From this basic understanding, annealing of quiescent melts were successfully applied and resulted in significant decreases of percolation thresholds by dynamic percolation processes [29,30,34,35]. Percolation thus began being considered as a dynamic process that could be finely controlled, rather a than static and underwent one.

The impact of electric field on carbon particles has been already investigated [36–38] on epoxy filled with CB. By applying high voltage between two electrodes, the structuration from isolated CB to a network has been observed over time. As a result, the

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subsequent conductivity gained several orders of magnitude.

Electric fields are also known to induce filler orientation: for instance, Prasse [39] demonstrated that the conductivity of CB-epoxy composite was higher in the direction of the electric field than in the perpendicular direction. Wang [40] showed a similar behavior for polymers filled with graphite nanosheets. More recently, Pang [41] investigated both effects of electric field and annealing temperature on dynamic percolation in polystyrene matrix filled with CNT. The author showed that increasing the electric field leads to a significant reduction of the time needed (critical time) to obtain a percolation path.

In this paper, the effect of electric field during the dynamic percolation of carbon nanotubes was investigated in silicone oil. The use of a liquid media allowed to slowly dilute and precisely vary the filler content. The conductivity and percolation threshold were measured as a function of electric field, time and filler content. From these results, a quantitative model was developed to describe conductivity as a function of these three variables.

2. Experimental

2.1. Materials & samples preparation

Carbon nanotubes N7000 from Nanocyl were dispersed in silicone oil 47V−100 from Bluestar Silicones by ultrasonication for 5 min. To do so, a 750 W 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 process. The as-prepared mother suspension contained 0.048 vol % of CNT. As further described hereafter, the mother suspension is well above percolation threshold. The mother suspension was then diluted in order to get a series of 14 suspensions with varying CNT content from 0.002 vol % to 0.048 vol %.

2.2. Test method & electrical measurements

For each prepared suspensions, the change of conductivity was recorded as a function of time (from 0 to 170 s) and increased DC electric field (9 levels tested from 50 mV/cm to 150 V/cm, as it depicted). The suspension under test was homogenized by mechanical stirring before every experiment and between 2 steps in electric field (see Fig. 1). DC conductivity was measured using a in-house cell constituted of 2 parallel electrodes (area: 4.5 cm^2, gap: 2 mm) and plugged to a Modulab Materials Test System from Solartron Analytical. No temperature variation has been noticed, even at high electric field.

3. Results

3.1. Conductivity as a function of filler content

We will first present the sole effect of filler content. Percolation curve of CNT filled silicone oil is presented in Fig. 2. Experimental data were recorded after 17 s of application of an electrical field of 50 mV/cm. The percolation transition is evidenced by an increase of conductivity by 4 orders of magnitude. A good correlation was found with Kirkpatrick's model (Eq. (1)) with the following parameters: $\sigma_0 = 0.43 \pm 0.04$ S m^{-1}, $V_c = 0.009 \pm 0.001$ vol % and $\mu = 2 \pm 0.2$. The percolation threshold obtained in the silicone oil is one order of magnitude lower than the ones usually observed in polymer composites [31]. This may be explained by the ease of carbon particles to aggregate in low viscous media. The critical exponent μ has been determined close to 2, which is attributed to a statistical distribution of CNT [42].

3.2. Time dependence

The conductivity changes of CNT suspensions in silicone oil were

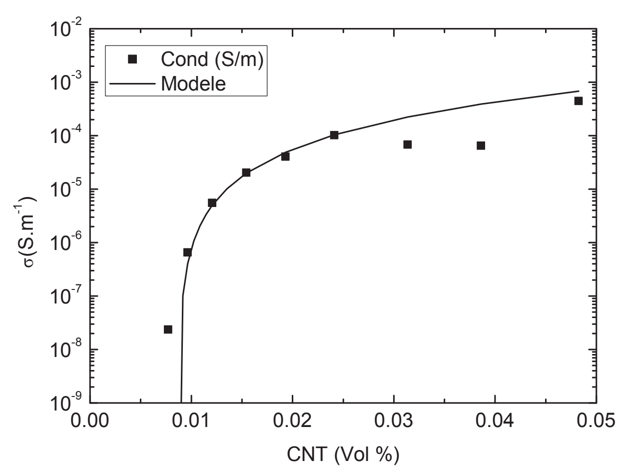

Fig. 2. Conductivity *versus* filler content with an applied electric field of 50 mV cm^{-1} measured 17 s after agitation was stopped. Data have been adjusted with Eq. (1).

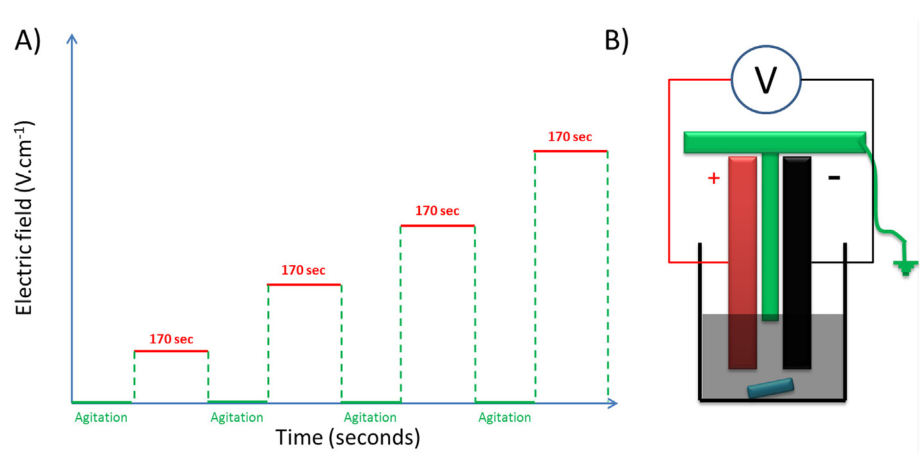

Fig. 1. A- Scheme of the electrical measurements performed on 14 filler contents. For each, 9 electric fields were applied over 170 s. B- Scheme of the electrodes immersed in silicon oil and connected to the dielectric spectrometer.