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Combined electrical and rheological properties of shear induced multiwall carbon nanotube agglomerates in epoxy suspensions

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ABSTRACT

In this work the rheological and electrical properties of semi-dilute carbon nanotube (CNT)–epoxy suspensions have been discussed. The suspensions are produced using two types of industrially available CNTs (Nanocyl 3150 and 7000) and using two different dispersion techniques, namely 3-roll milling and sonication. In-situ optical microscopic analysis and electrical conductivity measurements have been conducted. It is shown that despite using CNTs with similar aspect ratios, the dispersability of the raw material and the time stability of the suspensions are quite different. Additionally, viscosity measurements are used to evaluate the initial dispersion quality and time stability.

1. Introduction

By filling electrically insulating polymers with small amounts of conductive particles, the electrical conductivity of the system can be increased by some orders of magnitude due to network formation of the fillers throughout the matrix [1–3]. The formation of such a conductive network can be understood by using the percolation theory which describes the relationship between the filler content and electrical conductivity [4]. In the case of carbon nanotubes (CNTs), much evidence in literature cites the strong influence of production techniques and process parameters on the final electrical properties of CNT based composites [5–9].

The key problem with CNT based composites is the dispersability of the fillers in the matrix in order to utilize the properties of the pure material. The commercially available CNTs are constituted by several bundles of hundreds of carbon nanotubes that can become entangled or clumped together by amorphous carbon.

The greater than 1 μm long ropes further entangle into networks, due to van der Waals (vdW) attraction. This precludes the dispersion of carbon-powder insolubles in aqueous and organic liquids and thus hinders the nanocomposite production process. CNTs exhibit a surface area several times greater than the surface of conventional fillers [10]. Such a high surface area contributes to the difficulty with dispersing the tubes into matrices. Much effort has been made to incorporate CNTs into polymers in order to take advantage of the exceptional properties of the individual nanotubes, but effective dispersion has proven to be extremely difficult. Hence the resulting composites do not show the expected enhanced properties, in particular with respect to the mechanical performance. Various studies

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focusing on the improvement of CNT dispersion in different matrices for attaining good electrical properties are present in literature [5,11,12]. Recently, Pegel et al. [13] showed the different dispersion behavior of two commercially available CNT types in high viscous polycarbonate melts. In another study, McClory et al. [14] found a strong dependence of the electrical and rheological percolation threshold on the CNT geometry and functionality. Bauhofer and Schulz [15] showed the strong similarities between high viscous thermoplastic and low viscous epoxy systems.

Only the first part of this paper deals with the relationship between the dispersability of the CNTs in an epoxy matrix and the resulting electrical conductivity of the composite suspensions. Moreover, the dependence of the dispersion quality on the pristine tubes nature as well as on the processing technique has been shown and related to the rheological properties of the suspensions.

It is known that moderate shear can further improve the electrical properties by well-controlled shear induced agglomeration [16–19]. Depending on the applied shear rate and temperature, high and controlled conductivity values can be reached, if the initial filler dispersion is good. In fact, a coarse dispersion of CNTs in the matrix characterized by the presence of pristine, non disrupted bundles negatively influences the electrical conductivity because of the lack of free nanotubes that could contribute to the network formation [13,20–22].

As shown by Huang et al. [23], steady state shear flow measurements are able to directly characterize the dispersion state because the viscosity of the mixture is strictly related to the spatial and orientational distribution of the nanotubes in the matrix. Bad dispersion quality, due to too low forces or insufficient mixing time, results in erratic rheological values.

The work described in this paper is concerned with the simultaneous study of the rheological and electrical properties of a system where the nanotubes are suspended in a Newtonian epoxy matrix. The effect of two different mixing techniques and thus different dispersion qualities were investigated for semi-dilute epoxy suspensions containing two different types of commercially available multiwall carbon nanotubes.

The four different systems were compared regarding the rheological and electrical properties and the shear induced agglomeration tendencies. In this way, it was possible to obtain information about the dispersion abilities of the two production techniques as well as the time stability of the suspensions.

2. Materials and methods

2.1. Suspension preparation

In this study, two types of multiwall carbon nanotubes have been used. They are catalytic carbon vapor deposition (CCVD) grown CNTs purchased by Nanocyl S.A. (Belgium): NC3150 with an average diameter of 9.5 nm, an average length less than 1 μm and a purity exceeding 95 + % and NC7000 with an average diameter of 9.5 nm, an average length of 1.5 μm and a purity of 90%. The nanotubes have been used as received without any purification treatment. The matrix used for the production of the suspensions is an undiluted clear difunctional bisphenol A/epichlorohydrin (DGEBA), EPON™ Resin 828 purchased from Hexion.

The suspensions were produced using two common dispersion methods, which are sonication using a horn ultrasonicator (Misonix S3000) and milling by means of a 3-roll-mill (EXAKT® 120 E). Sonication is often used to produce small batches which makes it favorable for lab size applications [24–26]. In this work, a constant knob control setting of 1.5 has been chosen for sonication of the suspensions in order to have the same amplitude. Suspensions with several wt.% of CNTs have been produce for both types of nanotubes by using 20 g of EPON mixed with the correct amount of nanotubes. Two sonication times have been used for the suspension production, 10 and 120 min, with an average power of 20 W.

However, for larger amounts of material, sonication is not manageable due to the extreme reduction of the vibrational energy with increasing distance from the sonotrode. Here, milling is more favorable achieving good dispersion as shown before [27–29]. The dispersion of the nanotubes in the 3-roll-mill is based on high shear forces arising in the gap between the rolls. The fixed speed for the apron roll has been set at 300 rpm. In this work, the suspensions were produced by using a three cycle program with decreasing distances between the rolls for each cycle. The speed for the apron roll has been set at 300 rpm. The smallest gap size used was 5 μm. Suspensions at different nanotubes concentrations have been produced by milling from 0.02 to 0.1 wt.% CNTs for both types of nanotubes.

2.2. Rheo-optical-electrical experiments

The combined rheological and electrical measurements were carried out using a modified stress-controlled rheometer (StressTech HR, Rheologica Instruments). All measurements were performed in steady mode with an 35 mm parallel plate geometry. The lower rheometer plate is a glass plate with two evaporated rectangular gold electrodes (10 × 5 mm) with a 2 mm gap in between, which measures the conductivity parallel to the shear direction. The other rheometer plate was coated with a reflective, non-conductive coating to allow optical microscopy observations [30]. Optical, electrical and rheological in situ measurements are possible with this test setup. All conductivity and viscosity measurements were carried out with a gap size of 1 mm and varying shear rates between 0.1 and 100 s^{-1} were applied. For image capture, the gap had to be decreased to 0.5 mm to achieve better depth resolution.

All suspensions were pre-sheared with 100 s^{-1} for 60 s before measurement. The temperature for all measurements was set to 60 °C. This procedure and temperature were chosen in order to make the results comparable to previous experiments [15,17]. Additionally, temperatures above 45 °C are necessary to measure changes in the electrical conductivity [17].

Electrical conductivity was measured in AC mode using a HP 4284A LCR meter with a voltage amplitude of 1 V and a frequency of 100 Hz.