

ON THE EFFECT OF NON-COVALENT INTERACTIONS OVER THE DISPERSION STATE OF CARBON NANOTUBES IN EPOXY RESINS: FROM SUSPENSIONS TO CURED EPOXY/CNT NANOCOMPOSITES

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Abstract

In the present work we use a perylene derivative (PTCDA) as compatibilizer between epoxy resin and multi-walled carbon nanotubes (MWCNT). The electrical conductivity of epoxy/PTCDA/MWCNT suspensions (i.e. without any hardener) decreased, due to an improved MWCNT dispersion. On the other hand, a high electrical conductivity could be attained after curing the aforementioned suspensions with amine hardeners. A more pronounced improvement of conductivity was achieved by curing the resin at room temperature.

1 Introduction

Since the 90's a new family of nanostructures, based solely on sp²-hybridised carbon atoms (like those occurring in natural graphite) has gained considerable interest in the scientific community worldwide due to their unique set of properties[1-5]. In this context, multi-wall carbon nanotubes are very interesting fillers which bring together outstanding mechanical properties, electrical and thermal conductivity along with commercial availability with prices on-par with technical applications. The dispersion of carbon nanotubes in polymeric matrices has been extensively explored by several groups, since it enables the production of electrical conducting polymer nanocomposites at very low filler loadings [6]. Carbon nanotubes can be also incorporated in "conventional" fibre-reinforced composites providing not only electrical conductivity but also the possibility of structural health monitoring of such materials during mechanical tests [7]. In fact, many authors consider this might be the most boundary-breaking application of carbon nanotubes in a new area of functional fibre-reinforced polymer composites containing electrically-conducting nanoparticles [8].

This new application field relies on the electrical conductivity of carbon nanotubes reinforced polymers, a topic which is far away of being completely understood. In previous studies, we observed that the electrical conductivity of epoxy resins containing carbon nanotubes does not

depend solely on the type of the carbon nanotube, but also on its purity and more strongly on the processing conditions (including epoxy resin viscosity and curing temperature) [9,10]. From these studies, we also observed that the conductivity and dispersion state of carbon nanotubes in epoxy can be tuned by changing the processing conditions. In the present work, we evaluate the impact of non-covalent interactions between carbon nanotubes and the resin on the electrical conductivity of epoxy/multi wall carbon nanotubes nanocomposites. We modify the epoxy resin using an organic semi-conductor namely 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [11]. This additive should improve not only the dispersability of carbon nanotubes in the epoxy resin, but also the electrical conductivity of the nanocomposites.

2 Materials and testing methods

2.1 Materials

Catalytic Chemical Vapour Deposition (CCVD) MWCNT (Nanocyl 3150, hereafter coded as NC 3150), supplied by Nanocyl S. A. (Sambreville, Belgium) with an average diameter of 9.5 nm, an average length less than 1 μm and a purity exceeding 95%, have been used as received without any purification treatment. A bi-component epoxy matrix, based on bisphenol-A-co-epichlorohydrin (Epon 828) and triethylenetetramine (TETA) as hardener, supplied by Hexion, were used as polymer matrix. A dispersing agent, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), has been added in order to modify the resin prior to the addition of nanotubes.

2.2 Nanocomposite processing and characterisation

Epon suspensions have been produced by 3-roll milling, which assures a homogeneous and time stable dispersion of the nanotubes. A 3-roll-mill (EXAKT® 120 E), operating in a three cycles program has been used for this purpose. A fixed speed for the apron roll was set at 300 rpm and decreasing distances between rolls was used for each cycle, with the smallest gap size being 5 μm . PTCDA/Epon suspensions at different PTCDA concentrations were prepared by diluting a concentrated masterbatch at PTCDA 0.1 wt% with neat resin. A constant amount of 0.05 wt% of NC 3150 nanotubes was added to the as prepared PTCDA suspensions and NC 3150/PTCDA/Epon suspensions have been prepared using the same machine and three cycles program.

The curing agent has been added to Epon/NC 3150/PTCDA suspensions in stoichiometric ratio of 13 phr and mixed for three minutes by using a planetary centrifugal vacuum mixer (Thinky), which contemporary homogenously mixes the components and degasses the solution.

All the prepared suspensions have been cured using the same amount of curing agent and two different cycles: (i) 24 hours at 25 °C with a post cure of 2 hours at 120 °C and (ii) 2 hours at 120 °C.

Composites containing 0.05 MWCNT wt% in suspension, without PTCDA, have been prepared using the same curing cycles described above, as reference materials.

In the following, the composites containing only nanotubes will be named as “m-curing temperature” and the ones containing nanotubes and PTCDA as “mp- curing temperature”. For instance, the composite mp-120 contains MWCNT, PTCDA and it is cured at 120 °C. It is worth noting that the actual concentration of nanotubes in the final cured composites is 0.0442 MWCNT wt%, while, for sake of simplicity, the concentrations of PTCDA indicated in the following graphs and discussion are referred to the suspension without hardener. suspensions have been produced by milling, which assures a homogeneous and time-

Combined rheological and electrical measurements were carried out using a modified stress-controlled rheometer (StressTech HR, Rheologica Instruments). All measurements were performed in steady shear mode in a parallel plate geometry. The lower rheometer plate is a glass plate with two evaporated rectangular gold electrodes (10 mm x 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. All conductivity and viscosity measurements were carried out with a gap size of 1 mm. The rheometer electrodes were connected to an impedance meter (HP 4284A LCR meter), able to measure the electrical conductivity of the suspensions under shear with a measurement voltage of 1V and a frequency of 100Hz. The temperature for all measurements was set to 60 °C.

Bulk electrical resistance of cured composites has been evaluated by means of direct current (DC) measurements through the thickness of the sample, using a picoammeter connected to a two-probes station (Signatone 1160 probe station) at a constant applied voltage of 1 V.

3 Results and discussion

3.1 Epon 828/PTCDA/NC3150 suspensions

Figure 1 depicts the electrical conductivity of Epon/NC 3150/PTCDA suspensions at different PTCDA concentrations. In spite of the increase of electrical conductivity by decreasing shear rate, the suspensions containing PTCDA were always less conductive than Epon/NC 3150. This fact can be explained in terms of a better dispersion of carbon nanotubes in the presence of PTCDA. The perylene moiety of PTCDA can interact with carbon nanotube (or graphite-like surfaces) via pi-pi stacking[12], while the carboxylic anhydride functional groups of PTCDA can interact very strongly with the EPON 828 resin via dipole-dipole interactions and hydrogen-bonding. Therefore a better dispersion is expected for the suspensions containing PTCDA.

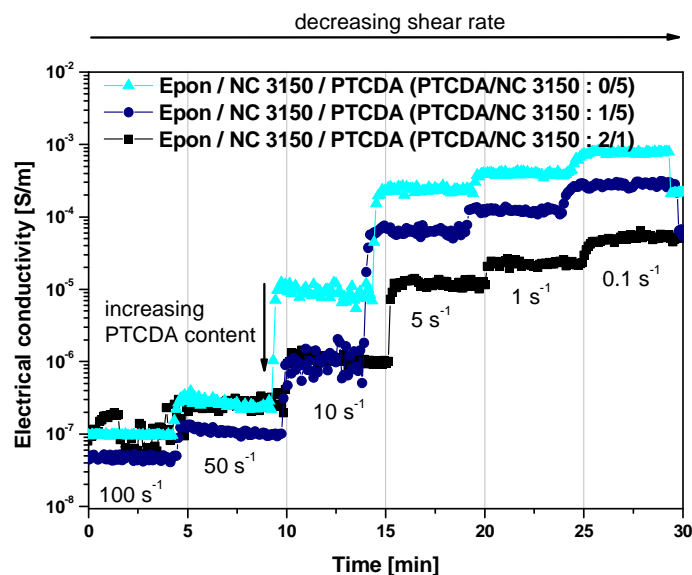


Figure 1. Constant shear rate step test of milled suspensions at different PTCDA contents, showing both shear-induced agglomeration and the effect of PTCDA to NC3150 ratio on the electrical conductivity (the NC 3150 content in the suspensions is kept constant at 0.05 wt%).

3.2 Cured composites

In order to study the effect that the addition of PTCDA has on the electrical properties of the cured composites, the electrical conductivity was measured. The ratio between the

conductivity of composites containing PTCDA over the conductivity of cured EPON/NC 3150 is reported in Figure 2.

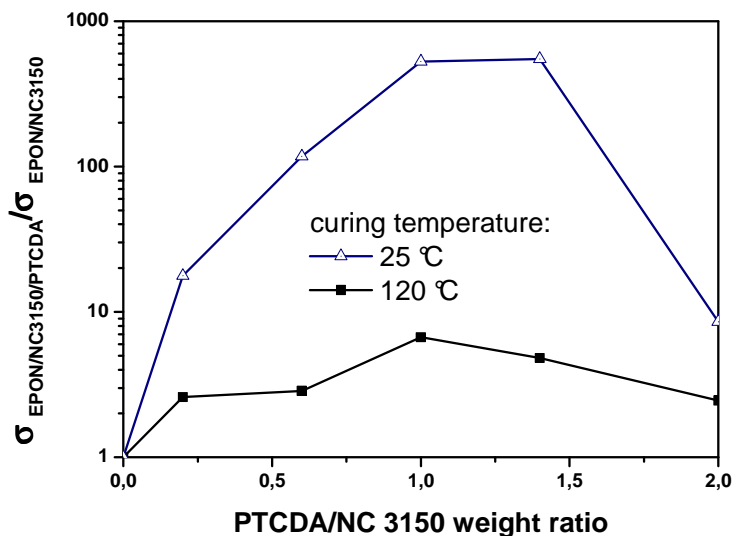


Figure 2. Relative conductivity (i.e. electrical conductivity of EPON/NC 3150/PTCDA divided by the conductivity of EPON/NC 3150, at the NC 3150 loading of 0.0442 wt%) as a function of PTCDA/NC 3150 weight ratio.

It is worth to mention that the effect of PTCDA in the composites is not univocally defined in terms of electrical properties, but it depends on the curing process used to produce the composites. An enhancement of electrical conductivity can be observed at all the PTCDA concentrations for the composites cured at room temperature, with a maximum in correspondence of 0.07 PTCDA wt% and a conductivity almost three orders of magnitude higher than the corresponding composite containing no PTCDA. The conductivity enhancement found in the composites cured at 120 °C is less than one order of magnitude for all the PTCDA contents, hence no significant improvement of the electrical properties can be noted by the addition of PTCDA if composites are cured at high temperature. On the contrary, the addition of PTCDA promotes the improvement of the electrical properties of carbon nanotubes composites.

4 Concluding remarks

We reported on the electrical and morphological properties of MWCNT epoxy composites modified by the addition of a perylene based dispersing agent. Electrical conductivity of epoxy suspensions and their agglomeration behavior is negatively influenced by the presence of PTCDA, resulting in lower conductivity values upon an increase of PTCDA content. This can be considered as an evidence for PTCDA to be a dispersing agent for nanotubes in epoxy. On cured composites, the effect of PTCDA is stronger for composites cured at room temperature, leading to an increase of electrical conductivity of almost three orders of magnitude with respect to the MWCNT epoxy composite without PTCDA. The semiconductor nature of PTCDA helps the conduction between tubes at room temperature, while the temperature induced agglomeration is hindered during curing at high temperature since PTCDA acts as a dispersing agent for tubes in epoxy.

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