

Evolution of carbon nano-tube dispersion in preparation of a fiber-reinforced epoxy-based composite: from a CNT masterbatch to a composite

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Keywords: Multiwall carbon nano-tube (MWCNT), dispersion, agglomeration.

Abstract

This work aims to offer an insight into the evolution of the CNT dispersion in preparation of a fiber-reinforced epoxy-based composite. This is done through a stepwise comparison of the dispersion qualities of multiwall carbon nanotubes (MWCNTs) in two epoxy based nanocomposite systems. The MWCNTs used in the two nanocomposites, experienced different histories in terms of the storage time while they were stored in the form of concentrated CNT/Epoxy mixtures (masterbatches). The study revealed that the older version contains large and difficult to break nanotube agglomerates. This significantly affected the rheological properties of the masterbatch in a liquid state as well as the electrical properties and glass transition temperature (T_g) of a solid nanocomposite. It is also shown that such an effect is further extended to the final fibre-reinforced composite where positioning of CNTs around the fibres seems to be controlled by the agglomeration/dispersion quality of the nanotubes in the original masterbatch.

1 Introduction

The potential of carbon nanotubes in increasing the performance of structural fiber-reinforced polymers has inspired a great deal of research on various aspects of these nano-engineered composites. It is generally accepted that the above mentioned potential largely depends on the dispersion state of CNTs in a composite. Many researchers have tried to assess the dispersion quality of CNTs in composite systems by different means. The latter are mainly composed of microscopic techniques and mostly considering only a specific phase such as a solid cured film or a liquid phase before the curing process [1-3].

The composite preparation process is a multi-step task, therefore a multi-step characterization is necessary to provide a realistic picture of the nano-tubes dispersion throughout the manufacturing process. That is because various factors can affect the dispersion/agglomeration of the CNTs during the composite preparation. These factors could not necessarily be anticipated and generalized through the characterization of any other step.

The focus of the present research work is to address this issue for the first time by utilizing various techniques for the assessment of CNT dispersion during the entire fibre

composite preparation process. Two resin systems containing multi-wall carbon nanotubes (MWCNTs) that underwent different storage histories are compared. To fulfill this goal, the characterizations have been conducted on three main levels: 1) the CNT masterbatch level, 2) the transition (curing) stage and 3) the solid state. Such a detailed analysis provides valuable information regarding the state of dispersion of CNTs in each step.

2 Materials and testing methods

2.1. Materials

Epoxy monomer used in this study (Epikote 828 LVELL) was a diglycidyl ether of bisphenol A (DGEBA). This was cured with 1,2-diaminocyclohexane (Dytek DCH-99) as hardener, which was added to the resin at 15.2 phr (parts per hundred resin). MWNTs were supplied by Nanocyl in the form of high concentrated, pre-dispersed mixtures (masterbatches) with a similar bisphenol-A epoxy resin (Epocyl NC R128-02). MWCNTs incorporated in this masterbatch have an average diameter of around 9 nm and a length of several microns, a specific surface of 250-300 m²/g and carbon purity > 90%.

2.2. Sample preparation

The two model systems under comparison were prepared using the same type of materials with equal compositions; however, the MWCNTs used in the two systems, experienced different histories in terms of the storage time. One system incorporates a fresh version of the CNT masterbatch, while the other one includes an older version of the same type. The latter was received and stored almost two years before the experiments. In both systems (hereafter being called “fresh CNT” and “old CNT”, respectively) nanotube masterbatches were diluted with DGEBA so that a final CNT concentration of 0.3 wt% in epoxy is attained. In order to homogenize the concentrated mixtures, prior to dilution, the masterbatches were thoroughly stirred using a marine type blade stirrer at 600 rpm for 10 minutes at room temperature. The same stirring procedure was repeated following dilution of the systems and the addition of the hardener. Samples were then degassed using a vacuum oven for 15 minutes.

2.3. Characterization methods

2.3.1. CNT masterbatch level.

Rheological measurements were carried out using an AR2000 rheometer, equipped with a 2° cone and plate geometry providing a gap distance of 51 μm. All measurements were carried out at room temperature. The oscillation time sweep was performed at sufficiently low strain and angular frequency (ω) values of 0.5 % and 0.5 rad/Sec respectively, to guarantee a linear behavior. This oscillatory test was performed in order to investigate the structure recovery behavior of the mixture by measuring G' evolution with time. The sample was subjected to pre-shear of 100 s⁻¹ for two minutes. The flow behavior of the samples was also characterized through shear viscosity measurements against the shear rate varying from 0.1 to 100 s⁻¹. A pre-shear protocol was applied to the samples before the measurements. It consisted of shearing the samples for two minutes at 100 s⁻¹ followed by a recovery period of 20 minutes.

2.3.2. Transition (curing) stage

Optical microscopy was used to observe the nanotubes behavior in the diluted system during curing. Imaging was carried out using an Olympus BHS Microscope. Milligrams of the samples were put between two glass slides and placed in a Mettler FP82-HT hot stage. The

micrographs were then obtained by a JVC TK-C1381 camera during the course of curing every 5 seconds programmed through Qwin software from Leica Company.

2.3.3. Solid state

Scanning electron microscopy was carried out by means of a FEI NOVA Nanolab 600 microscope with a TLD (through the lens) detector. This was done on 5 μm thick sections which were cut from bulk cured samples of epoxy. The cutting was done using a Leica Ultracut UCT microtome. No conductive layer was coated on the films to take the advantage of the contrast effect in electron charging (or “voltage contrast”) of the sample surface. This made possible to have a shallow insight into the slice and to observe the nanotubes embedded in the resin [4].

The electrical properties of the samples were measured by means of an AC impedance spectroscopy with a voltage amplitude of 2 V and a DC potential of 0.4 V at a frequency range of 0.1 to 10^6 Hz. Samples with a dimension of $1\text{mm}\times 10\text{mm}\times 10\text{mm}$ were cut and then the two wider surfaces of each sample were covered with a conductive silver paint.

3. Results and discussion

3.1 CNT masterbatch level

Our multi-stage investigation starts with the analysis of the nano-tube master-batches. Figures 1 and Figure 2 compare the rheological behavior of the CNT master-batches (before dilution with the epoxy resin), in terms of the shear viscosity vs. shear strain and recovery of the storage modulus respectively. Figure 1 shows the recovery behavior of the two concentrated systems.

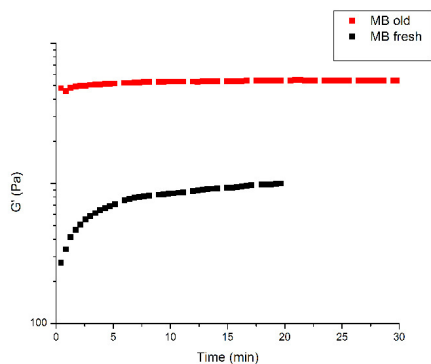


Figure 1. Evolution of the storage modulus during the recovery period of the master-batch samples following a pre-shear of 100 s^{-1} for 2 mins.

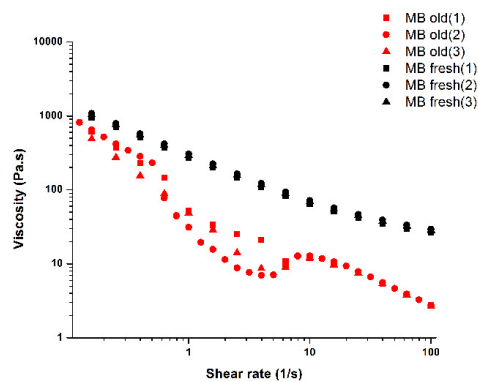


Figure 2. Shear viscosity vs. shear rate of the nano-tube master-batches following a 2 min. preshear at 100 s^{-1} .

A striking difference is observed between the two samples, where the fresh CNT version exhibits an obvious recovery over time for G' , while this is not the case for the old version. This suggests that CNT agglomerates existing in the old system are either very difficult to break under the applied pre-shear or they re-agglomerate extremely fast as soon as the shearing is stopped. The flow behavior of the two concentrated systems shown in Figure 2 also represents readily distinguishable shear-thinning trends which remain quite reproducible for each type. The shear viscosity of the fresh CNT remains higher than the viscosity of the older version especially at higher shear rates. This can be ascribed to a larger surface of CNTs

exposed to the resin in the fresh CNT masterbatch, where the higher interaction can cause a higher viscosity under shear. This indicates a finer distribution of carbon-nano tubes in this system, which confirms the findings of the oscillatory recovery analysis.

3.2 Transition (curing) stage

The second part of the analysis focuses on the behaviour of the two systems during the curing reaction where formation of the 3D crosslinking networks can affect the dispersion of CNTs in the final cured solid structure. The samples were monitored throughout the curing process using an optical microscope equipped with a heating element. Figure 3 shows the images obtained right after the curing reaction.

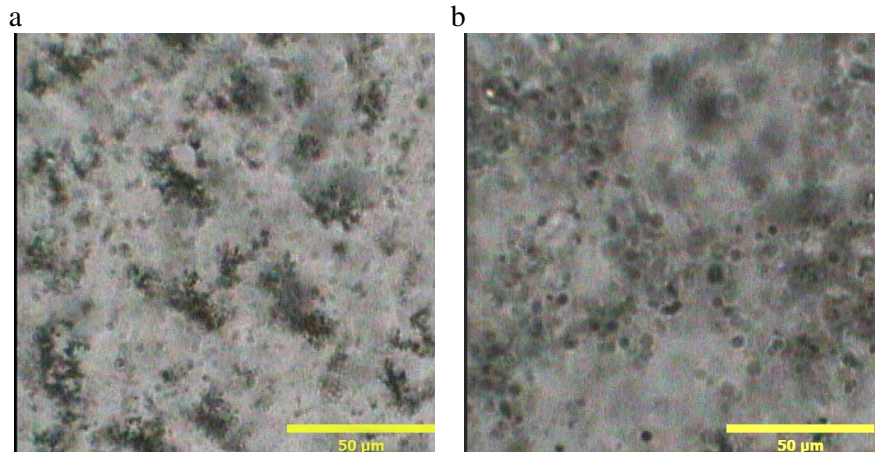


Figure 3. Optical micrographs of a) the fresh and b) the old diluted CNT samples right after curing.

When CNT/epoxy mixtures are heated, CNTs become very mobile and begin arranging themselves into larger structures. The formed CNT structures after curing are distinctly different in the two systems. In the fresh version, CNTs are organized in clusters/agglomerates that are individually separated. In the old version, CNTs are grouped in a network-like structure that runs thorough the material in a continuous fashion. These differences are striking considering that the two studied systems have the same composition..

3.3 Solid state

In order to facilitate the characterization of the CNTs dispersion in the matrix after completion of the curing process, at this step, fibre free solid samples were analyzed.

3.3.1 Electrochemical impedance spectroscopy

Specific conductivities of the solid samples are compared in Figure 4. The fresh CNT shows a significantly higher specific conductivity with a plateau region at lower frequencies. A frequency independent impedance (and hence specific conductivity), observed in the older version, is often considered as an indication of a percolated system; where conductive particles create a conductive path thorough the sample [5-7]. However, in the other system, which apparently has a better dispersion, the impedance is always increased as the frequency is lowered; indicating a non-conductive system with much higher resistance (lower conductivity).

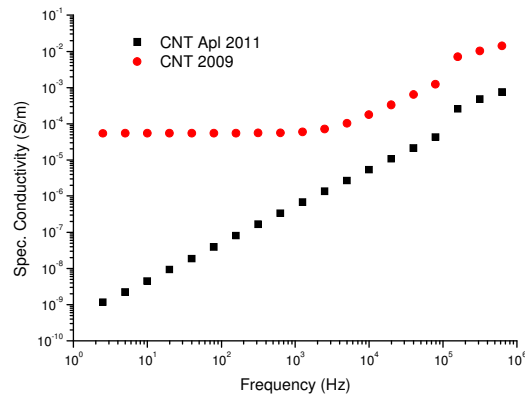


Figure 4. Results of the electrochemical impedance spectroscopy of the specimens in terms of the specific conductivity vs. frequency.

This is in excellent agreement with our previous microscopic observations where a network like structure was observed in the older system.

3.3.2 Scanning electron microscopy

Figure 5 presents SEM micrographs of the thin film specimens recorded with the through the lens detector. Using this technique, carbon nanotubes can readily be identified as bright tiny bundles lying inside the epoxy matrix becoming visible as a result of the charging.

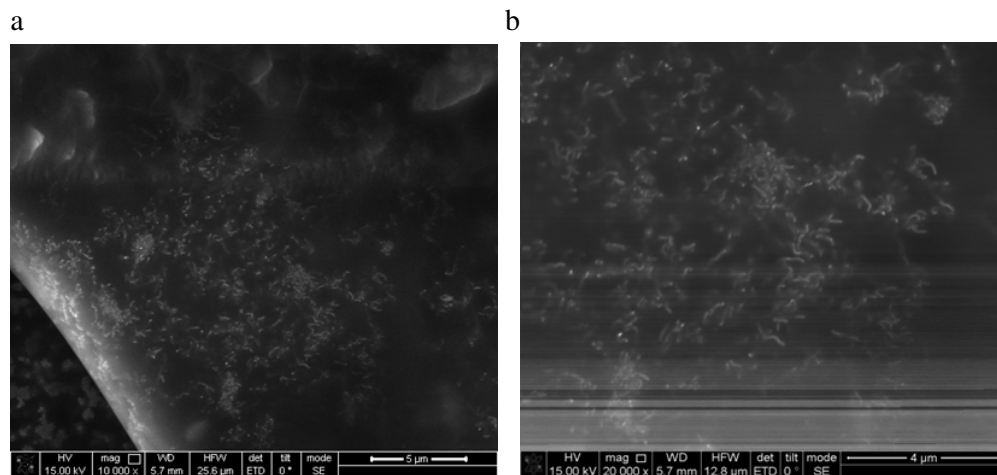


Figure 5. SEM micrographs of CNT dispersion in a) the old version and b) the new version recorded using an in lens detector.

Densely packed carbon nano-tube agglomerates can be clearly recognized in the older system, where a connected network of the CNT agglomerates has been formed.

3.4 Glass fibre reinforced composite

The dispersion quality of carbon nanotubes (CNTs) in a resin may influence position of CNTs in a fiber-reinforced composite produced from this resin. A higher concentration of CNTs in some areas (for example, in resin rich zones) combined with no CNTs in other areas (for example, inside fiber bundles) is likely to affect mechanical behavior of the composite. The topic is investigated in another paper presented at this conference [8] on the example of a woven glass fiber composite. It is shown that in the case of the fresh masterbatch a better distribution of CNTs throughout a composite is observed with CNTs also appearing inside fiber bundles. In the case of the old masterbatch, the network-like dispersion state, on the other hand, tends to localize CNTs in resin rich zones. The composite with CNTs in the resin rich zones has a higher strain-to-failure (by 12%) and lower density of transverse cracks (by 29%) in comparison with a virgin composite. In the meantime, a somewhat lower strain-to-failure and about the same crack density are measured for the composite where CNTs appear in small individual agglomerates. This once again emphasizes the importance of the multi-step characterization of the CNT dispersion.

Acknowledgements

The work in K.U.Leuven was done within GOA/10/004 project "New model-based concepts for nanoengineered polymer composites", funded by the Research Council of K.U.Leuven. The collaboration between K.U.Leuven and Nanocyl S.A was performed under the framework agreement between the Department MTM, KU Leuven and Nanocyl S.A. The help of Bart Pelgrims, Kris Van de Staey (Department MTM, KU Leuven) is gratefully acknowledged.

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