

# DISPERSION AND DIELECTRIC CHARACTERIZATION OF AN EPOXY RESIN REINFORCED WITH CARBON NANOFIBERS

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**SUMMARY:** Carbon nanofibers (CNF) have been recently developed and have shown to be promising materials which can lead to high performance composite parts. While these nanoparticles have a high potential in polymer composites, they have a tendency to agglomerate during processing, reducing the mechanical properties of the matrix. Dispersion of nanoparticles in the resin is a critical condition to obtain the desired properties. The characteristics of the dispersion when using electrically conductive fillers in polymers can be characterized by dielectric measurements. This research concerns the processing and characterization of an epoxy resin filled with carbon nanofibers. These nanoparticles, after different chemical treatments, have been added to the epoxy matrix in various concentrations. The resulting products were mechanically tested with a Dynamic Mechanical Analyzer (DMA). Samples were also electrically tested using a Dielectric Analyzer in order to measure the conductivity as a function of the carbon nanoparticles concentration. Optical Microscopy and Scanning Electron Microscopy (SEM) were performed to visualize the microstructure of the nano-reinforced material.

**KEYWORDS:** epoxy nanocomposites, carbon nanofibers, thermo-mechanical properties, dispersion, dielectric properties, electrical conductivity

## INTRODUCTION

Composite manufacturing is a growing field in aviation, automotive, medical or leisure applications. Carbon nanoparticles are used as fillers in polymer matrix nanocomposites. Many studies [1-3] have shown an effective reinforcement of the polymer mechanical properties at low filler contents. Achieving a good dispersion of the fillers in the polymer is well known to be a

critical condition to realize improvements [4]. The quality of the dispersion can be visualized using standard characterization tools like optical or electronic microscopy. Characterizing nano-modified resins containing conductive fillers through dielectric measurements can provide insight on the material's microstructure such as nanoparticles dispersion. Electrical conductivity measurement consist in evaluating the capacity of a material to transfer or store electrical loads. When conductive nanometric reinforcements are added to a matrix, the dielectric behaviour is modified. The change from an insulating to a conductive material is called the percolation threshold and is created by the formation of continuous pathways of conductive fillers through the sample thickness. Numerous industrial applications are dealing with electrostatic discharge or aptitude to conduct current and the challenge is to control the percolation threshold in order to minimize the filler content, therefore the material cost. Many studies on nanocomposite systems lead to the conclusion that percolation threshold greatly depends on the processing conditions used for dispersing the nanomaterial [5-9].

This work investigates the changes in mechanical properties as a result of conductive carbon nanofibers (CNF) addition, and characterizes the dispersion through dielectric measurements. DMA testing was performed to assess the thermo-mechanical reinforcement, microscopy was also used to visualize the quality of the dispersion and microstructure, and relate it to the dielectric measurements.

## **EXPERIMENTAL**

### **Materials**

The matrix material for the nanocomposites consists of a DGEBA epoxy resin used with two different curing systems, an anhydride hardener (80 phr) along with a tertiary amine catalyst (1.5 phr), and an amine hardener (23.9 phr). Stacked conical graphene sheet CNF were added to the matrices. Particles size distribution diameter varies from 13-144 nm and lengths vary between 10-100  $\mu\text{m}$ . CNF were functionalized with a 3:1 ratio of  $\text{H}_2\text{SO}_4$ : $\text{HNO}_3$  pure acids in ultrasonic bath. Nanofibers were washed using distilled water and dried prior use with epoxy systems.

For the preparation with the anhydride hardener, nanoparticles were first dispersed in ethanol using ultrasonication (US) at room temperature for periods varying between 1-3 hours. Then the mixture was embedded into the epoxy resin and sonificated again. Ethanol was evaporated on hot plate for 2 hours and the hardener and catalyst were added manually in stoichiometric proportions. Samples were cured in the oven at 145°C for 1 hour.

For the second preparation using the amine hardener, CNF were poured directly into the hardener. US dispersion was performed during 1 hour at 80°C. The resin was added to the cooled mixture in stoichiometric proportions. Samples were cured in the oven at 100°C for 2 hours, demolded and then post-cure at 165°C during 1 hour.

## Characterization

DMA Q800 from TA Instruments was used with the 3-points bending clamp for thermomechanical testing. The storage modulus was measured as a function of temperature over a range from 30°C to 200°C and a rate of 3°C/min. Strain amplitude of 0.08 % and frequency of 1 Hz were applied. The glass transition temperature ( $T_g$ ) was determined as well from these data.

The optical microscope was used to localize the agglomerate size and dispersion state. A drop of the liquid suspension was laid on a microscope slide and observed at magnifications from 50-200X. Morphology and dispersion of cured nanocomposites made from pure and acid-treated CNF were observed. Two different electron microscopes were used: a conventional SEM equipped with a Tungsten filament (JEOL JSM 840) and a high resolution SEM equipped with a field emission gun (Hitachi S-4700). Samples were prepared by polishing for the conventional SEM, and by ultramicrotomy for the high resolution SEM.

The dielectric measurements were performed using the Micromet device from NETZCH Instruments. The sensor consists in two rectangular copper electrodes placed on insulating holders. The sensors are positioned on each face of the cured sample, in order to get a measurement through its thickness. Since the percolation threshold can rise over several decades, the conductivity evolution was measured as a function of the filler content for large scale of conductivities. Since electrical conductivity is sensitive to the excitation frequency (insulating materials with low conductivity are detected at low frequencies whereas conductive materials are detected at high excitation frequency), therefore depending on the conductivity of the material, the measurements were done at different frequency ranges. The conductivity of the polished samples was measured for frequencies 1-10000 Hz and voltage of 1 V during 15 min.

## RESULTS

### Effect of CNF Concentration

The storage modulus ( $E$ ) evolution as a function of temperature for different concentrations of CNF from 0.3 to 5 wt% was studied. For this measurement, the time of CNF mixing in ethanol was kept constant at 1 h. The initial storage modulus values at 40°C and the  $T_g$  values were reported on Fig. 1. The glass transition temperature ( $T_g$ ) value is determined by the inflection point of the E-T curve.

As shown by the results reported in Fig. 1, improvement of 13% in storage modulus and 7°C in  $T_g$  can be observed for samples containing only 0.3% of CNF whereas the addition of 1 and 5% of CNF only induced a negligible decrease in storage modulus and slight improvement in  $T_g$  compared to the neat epoxy. These results could be explained by the constant time of 1 hour mixing in ethanol, which may be optimal to disperse small concentrations of CNF, but should be optimized for higher percentages, in order to minimize agglomeration.

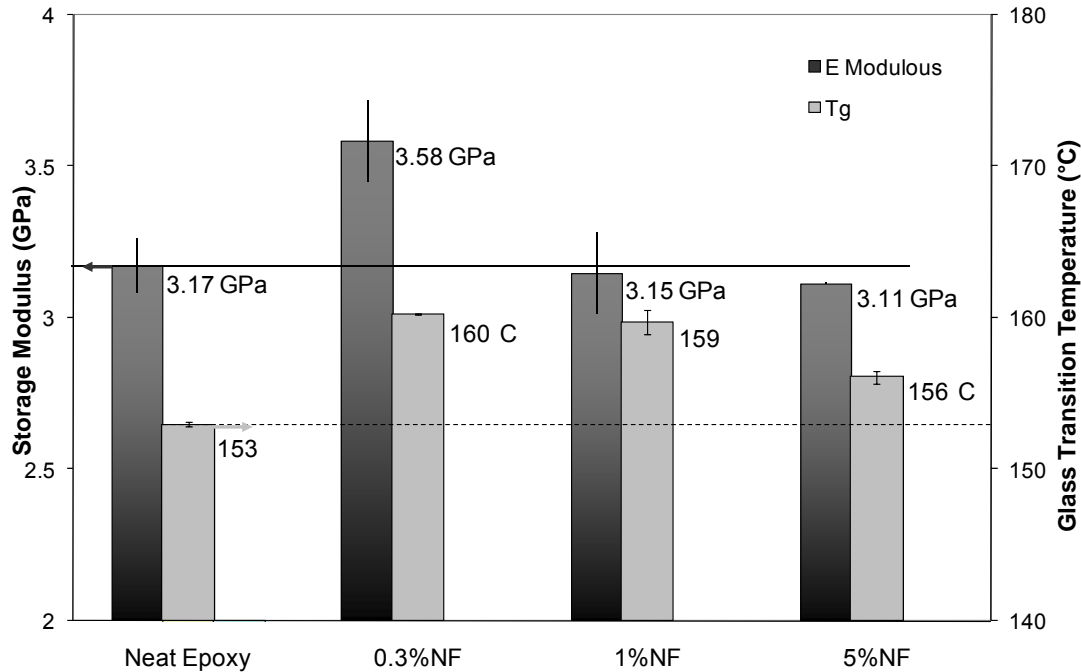


Fig. 1 Storage modulus and  $T_g$  values of epoxy/CNF for various concentrations (DMA flexural test).

### Evaluation of Dispersion Quality by SEM characterization

The SEM micrographs presented in Fig. 3 illustrate the dispersion of CNF in the epoxy-amine matrix. In Fig. 3 (a) pure CNF were used while in (b) functionalized CNF (5 min process) were embedded in the epoxy matrix. Some large agglomerates (about 20  $\mu\text{m}$ ) are present in the nanocomposite containing pure CNF. In comparison, the nanocomposite containing acid-treated CNF shows less agglomeration with clusters smaller than 10  $\mu\text{m}$ . In Fig. 4, a High Resolution SEM micrograph of 5 min functionalized CNF in epoxy-amine illustrates a good dispersion of the CNF in the matrix with exfoliated agglomerates close to the individual particle size. Based on these electron microscopy results, a functionalization time period of 5 min seems to help the CNF dispersion.

When comparing the SEM micrographs and DMA results (Fig. 2), large agglomerates in sample containing non-treated CNF could be associated to dramatic decrease of  $T_g$ . However, this microstructure is also associated to slight increase of the storage modulus, which could be explained by the purity of the CNF graphite layers, which induce a mechanical reinforcement of the matrix, compared to functionalized CNF, where graphitic structure may have been damaged by the strong acid treatment, resulting in a poorer reinforcement. Hence the functionalization of CNF decreases the storage modulus. However, the sample prepared with a 5 min functionalization shows enhanced  $T_g$  compared to non-treated CNF which is associated to smaller agglomerate. Acid functionalization is a compromise between de-agglomeration of the particles and increase of storage modulus.

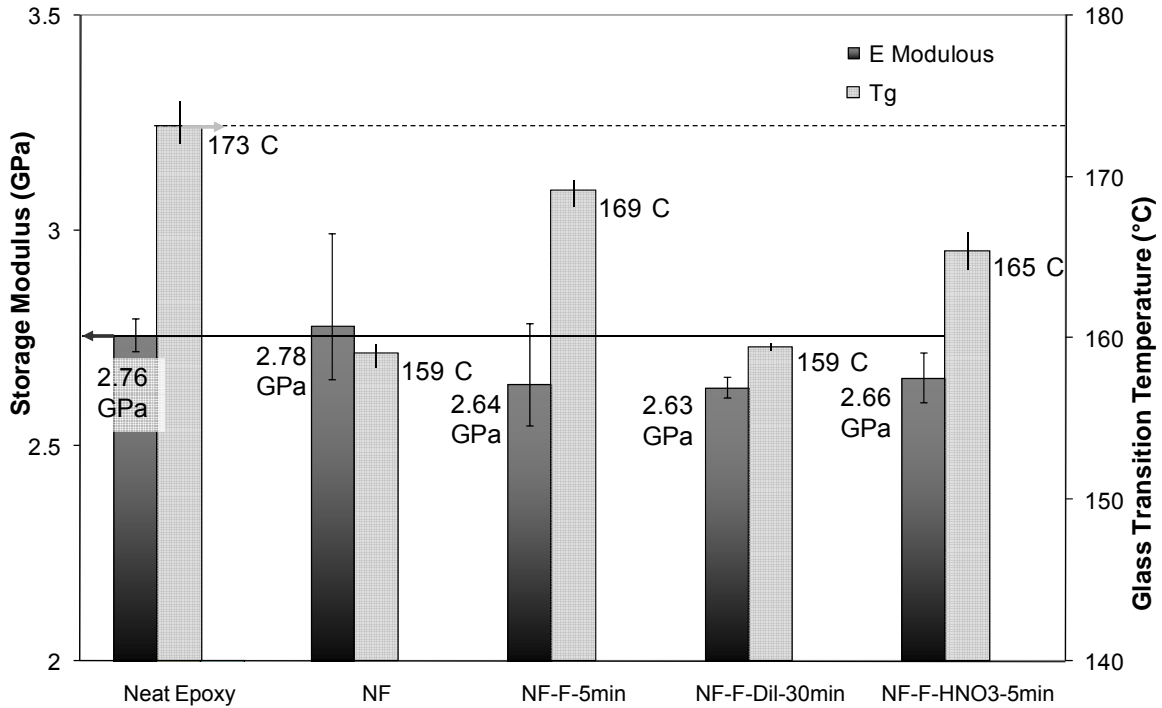
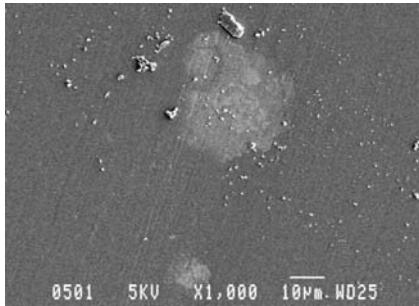
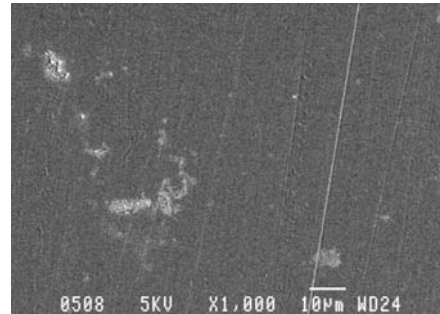


Fig. 2 Modulus and  $T_g$  values of epoxy/CNF for various types of functionalization (DMA flexural test).



(a)



(b)

Fig. 3 SEM micrographs of epoxy-amine/CNF nanocomposites containing non-treated CNF (a) and 5 min functionalized CNF (b).

### Evaluation of Dispersion Quality by Dielectric Measurements

To determine the value of the percolation threshold, the frequency dependant conductivity must be analyzed. The resulting value depends on many parameters such as the aspect ratio of the conductive fillers, the size of the agglomerates and the quality of connection between the particles. The shape of the percolating threshold curve depends on the orientation and shape of the agglomerates: when the agglomerates of conductive nano-fillers are large, the jump in conductivity from an insulating to a conductive state is progressive. On the contrary, the more

disentangled (smaller agglomerates), the more mobile are the nano-fillers, resulting in an accelerated rate of network formation and more drastic changes from insulating to conductive state [7].

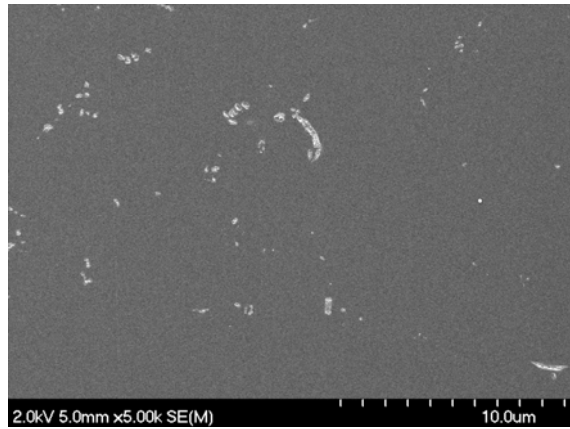


Fig. 4 High resolution SEM picture of 5 min functionalized CNF/epoxy-amine.

The system CNF/epoxy-anhydride was studied using dielectric measurements in order to analyze the quality of dispersion for varying dispersion time periods. Several concentrations of CNF/epoxy-anhydride system were investigated. Fig. 5 shows electrical conductivity as a function of CNF concentration and dispersion mode. The shape of the curve and value of percolation threshold are quite different. The CNF/epoxy prepared without US treatment in ethanol presents a slower transition than CNF/epoxy prepared with 3 h US dispersion. For non US dispersed nanocomposites, the electrical conductivity jump is initiated earlier (0.1 wt%) than the 3 h US dispersed nanocomposites (0.25 wt%). But for the latter the higher electrical conductivity plateau is reached at a lower concentration of CNF.

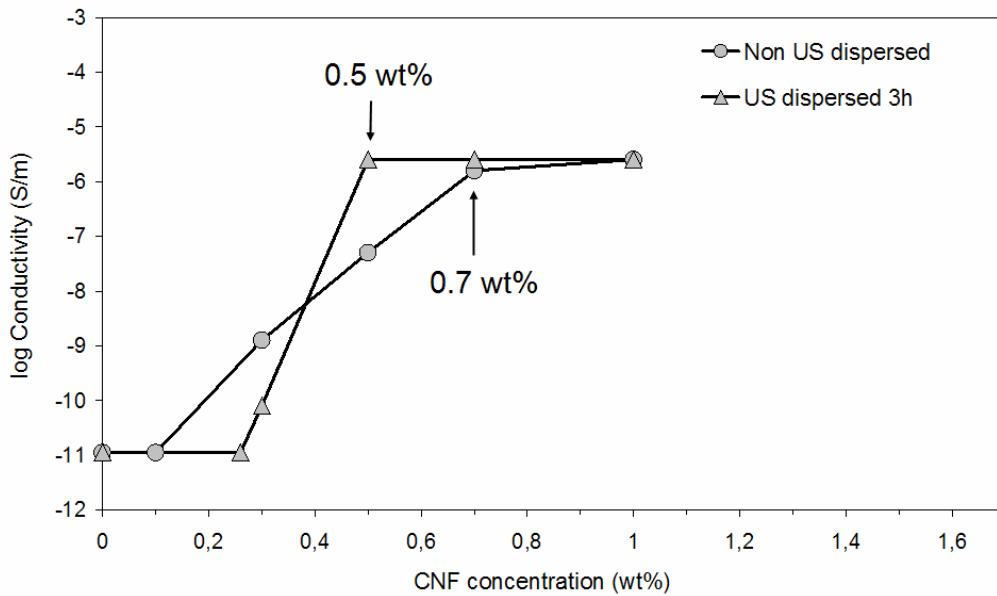


Fig. 5 Percolation threshold of epoxy/CNF nanocomposites depending on dispersion in US.

The percolation thresholds of both nanocomposites have been measured to differentiate their microstructure. As explained earlier, the percolation threshold value is estimated with the conductivity independence to frequency. The percolation threshold value for the CNF/epoxy non-dispersed in US is 0.7 wt% whereas this value is 0.5 wt% for the CNF/epoxy 3 h US dispersed (Fig. 5). A lower percolation threshold means that a lower concentration of conductive fillers is needed to create connection between fillers. This connection is a pathway to conduct the electrons, and finally reach the final value of electrical conductivity. Therefore, the 3 h US dispersion leads to a more disentangled microstructure of the CNF in the epoxy. This assumption coming from dielectric measurements is confirmed by optical microscope observations at concentration for which the electrical conductivity is rising. Fig. 6 shows optical micrographs of 0.5 wt% CNF/epoxy non US dispersed and 1 h and 3 h US dispersed in ethanol, which have been realized just after the embedding into resin and evaporation of the ethanol.

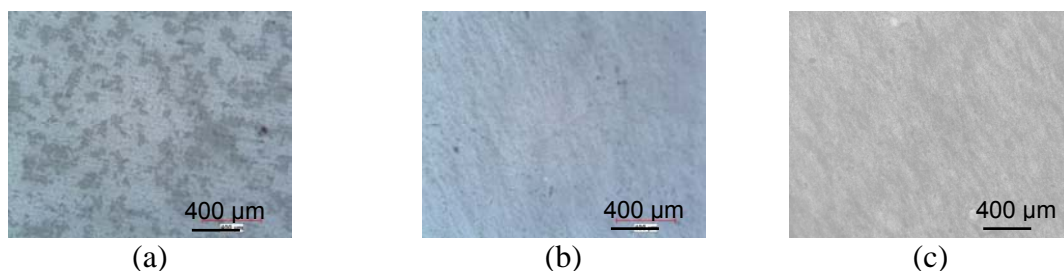


Fig. 6 Optical micrographs of 0.5 wt% CNF after several US dispersion times Non US-dispersed (a), 1 h US-dispersed (b) and 3 h US-dispersed (c).

CNF dispersion without the use of US in ethanol shows poor results (Fig. 6a), it shows improvement after 1 h of US (Fig. 6b) and particles are well distributed after 3h of US treatment (Fig. 6c). By comparing these results to dielectric measurements, it reveals that with good dispersion, small concentration of conductive fillers leads to a quick jump of the electrical conductivity. On the contrary, with a bad distribution, bigger amounts of nano-fillers are required in order to create a pathway for electrons and a significant increase of the electrical conductivity to reach the final value of electrical conductivity.

## CONCLUSIONS

Various nanocomposites were produced and their thermo-mechanical and dielectric properties were associated to their dispersion state. The CNF/epoxy-anhydride system showed that lower filler concentration creates better reinforcement. In the CNF/epoxy-amine system, the functionalization of CNF induces a higher  $T_g$  compared to the non-treated CNF. SEM observations revealed that 5 min functionalized CNF are much better dispersed in epoxy than non-treated CNF. Therefore, nanocomposites containing smaller agglomerates of CNF give higher thermal resistance. Dielectric measurements on the CNF/epoxy-anhydride system showed a quicker jump from insulated to conductive state for nanocomposites processed with longer US times. The percolation threshold is reached at lower concentrations for US dispersed CNF. Dielectric results were consistent with the DMA and SEM previous observations, showing that longer US time gives better dispersion and therefore more disentangled CNF.

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