ELECTRICAL AND DYNAMIC MECHANICAL PROPERTIES OF MWCNTs/EPOXY COMPOSITE FOR HIGH PERFORMANCE AEROSPACE APPLICATIONS

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Abstract
The present paper reports the results about a study of electrical, and dynamic mechanical properties of multiwalled carbon nanotubes (MWCNTs)/epoxy composite for structural applications. The composites were prepared by dispersing MWCNTs into an epoxy resin based on TetraGlycidyl-MethyleneDiAniline (TGMDA) and both epoxy precursor and composite were cured with 4,4'-diamino diphenil sulfone (DDS). Morphological investigation indicates good levels of CNT dispersion into the epoxy mixture. The electrical behaviour of the formulated composites and their high values in the storage modulus and glass transition temperature are very promising in the field of aerospace applications.

1 Introduction

In recent years, both academic and industrial researchers have focused considerable attention on the epoxy resin based composites since these materials, due to their excellent mechanical properties for structural stability, allow to manufacture a very versatile class of composites for structural applications in automotive, aeronautics, marine industry, electronics and others. In particular, an appropriate choice of the synthetic precursors and fillers as well as curing cycles and incorporation methods can allow to drive the material more and more toward desirable properties able to face the future challenges.

Among the fillers a particular attention has been addressed to carbon nanotubes. Indeed since Iijima's landmark paper in 1991[1], carbon nanotubes (CNTs) have spurred many researchers on developing advanced CNT composite materials to transfer some of their excellent physical properties [2-8] to polymeric matrices. Actually CNTs are considered one of the strongest materials known and very promising to manufacture a very versatile class of composites for structural applications. In addition, the inclusion of this filler into polymeric matrices stabilizes the polymer against the effects of UV and γ radiations [9-10]. This behavior seems to be of general validity and it is a very important prerequisite to apply these nanofilled

materials in the aerospace. The aim of this work is situated in this contest. We have tried to formulate epoxy composites for aerospace applications. In particular we have examined the properties of nanocomposites obtained by dispersing MWCNTs in the TetraGlycidyl-MethyleneDiAniline (TGMDA) cured with 4,4'-diaminodiphenyl sulfone (DDS). This system was selected among several solutions because it shows properties suitable for fibrous composites. The toughness of epoxy mixture has been increased by blending the epoxy precursor with a reactive modifier that performs a double function, as flexibilizer and regulator of viscosity for a best dispersion of carbon nanotubes. Preliminary results on the electrical and mechanical properties appear very promising.

2 Materials and methods

2.1 Materials

T*he epoxy matrix composite* was prepared by mixing an epoxy precursor (TGMDA) with an epoxy reactive monomer 1,4-Butandioldiglycidylether (BDE) that acts as flexibilizer and reactive diluent. These resins, both containing an epoxy, were obtained by Sigma-Aldrich. *The curing agent* investigated for this study is 4,4'-diaminodiphenyl sulfone (DDS). The MWCNTs (3100 Grade) were obtained from *Nanocyl S.A.*

2.2 Epoxy specimens manufacture

The epoxy matrix was obtained by mixing TGMDA with BDE monomer at a concentration of 80% : 20% (by wt) epoxide to flexibilizer. DDS was added at a stoichiometric concentration with respect to the epoxy rings. Epoxy blend and DDS were mixed at 120 °C and the MWCNTs were added and incorporated into the matrix by using a ultrasonication for 20 minutes *(Hielscher* model UP200S-24KHz high power ultrasonic probe). All the mixtures were cured by a two-stage curing cycles: a first isothermal stage was carried out at the lower temperature of 125 °C for 1 hour and the second isothermal stage at higher temperatures up to 180 °C or 200 °C for 3 hours. These samples are named TBD-CNT(X%)(Y °C) where X is the CNT percentage and Y is the temperature of the second stage.

2.3 Characterizations

In order to analyze the dispersion of the nanofiller inside the epoxy matrix, the samples were investigated by means atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM images were collected in tapping mode (TMAFM) which reaches lateral resolution < 1nm and height resolution of less than 1 Å. The data were acquired in an ambient atmosphere (30%-40% humidity) with a NanoScope V multimode AFM (Digital Instruments), Santa Barbara (CA), using microfabricated silicon tips/cantilevers. All the images have been recorded simultaneously in height and in amplitude. For AFM and SEM investigation, the composite sections were cut from the solid samples by a sledge microtome. These slices were etched before the observation by AFM and SEM microscopy. SEM pictures were obtained with a LEO 1525 microscope. The samples were covered with a 250-Å-thick gold film using a sputter coater (Agar mod. 108 A).

Dynamic mechanical properties of the samples were performed with a dynamic mechanical thermo-analyzer (TA instrument-DMA 2980). Solid samples with dimensions 4 x 10 x 35 mm were tested by applying a variable flexural deformation in dual cantilever mode. The displacement amplitude was set to 0.1%, whereas the measurements were performed at the

frequency of 1 Hz. The range of temperature was from -60°C to 300°C at the scanning rate of 3°C/min.

The measurements of the *dc* volume conductivity were performed by using disk-shaped specimens of about 2 mm thickness and 10 to 50 mm diameter. The measurement system, remotely controlled by the software LABVIEW®, is composed of a voltage generator FUG HCN 35-6500 (max output current 5 mA), a pico-ammeter Keithley 6514 (min current 10^{-13}A), and a suitable shielded cell with temperature control. For sensitivity purposes the applied electric field has been 5 MV/m for samples below the percolation threshold, whereas in order to avoid Joule heating of samples it has been set to 5.0 kV/m for specimen above the percolation threshold.

3 Results and discussion

3.1 AFM image analysis

Figure 1 shows the AFM micrograph of TBD-CNT(0.64 %)(200 °C); the height image is on the left and amplitude image is on the right. The formulated material has shown a strong ability to withstand chemical action of the etching solution, thus this image was collected after a strong etching procedure that has allowed the nanotubes to appear on the surface, forming a homogeneous structure in which CNTs uniformly cover the entire surface. The image clearly shows that the nanofillers were well dispersed in the polymeric matrix. Similar results have been obtained for lower concentrations of MWCNTs and curing cycles up to 180 °C. The obtained results demonstrate that the method used for CNT dispersion into the epoxy mixture was very efficient for this investigated composite.
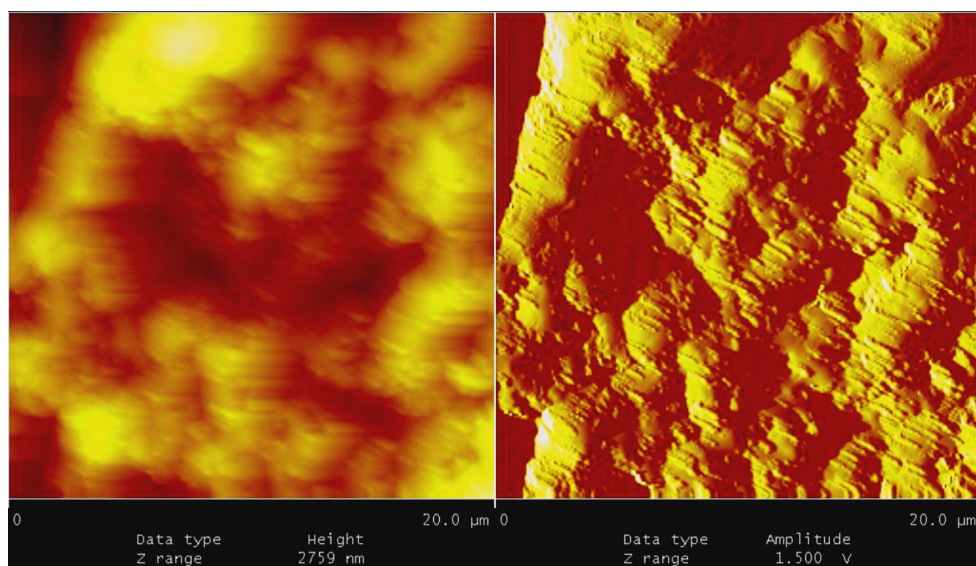

Figure 1. Tapping mode AFM image of TBD-CNT(0.64 %)(200 °C) sample.

3.2 SEM image analysis

The analysis was carried out on etched samples to remove the resin surrounding the nanofillers, leaving them bare. Figure 2 shows SEM images of nanofilled epoxy composites at loading rate of 0.64 (see Figure 2A), 0.32 (see Figure 2B) and 0.05 (see Figure 2C) per cent by weight. A careful observation evidences a homogeneous structure in the samples with nanofiller percentage of 0.64% and 0.32% in which the CNTs are uniformly distributed into the epoxy matrix (see Figure 2A and Figure 2B). In fact, for this CNT percentage, we observe whole lengths of the carbon nanotube segments released from the residual resin fraction.

Figure 2C shows the fracture surface of the epoxy composite at a nanofiller percentage of 0.05%. Individual nanotubes are not directly touching each other but are isolated by some fractions of polymer matrix forming small "islands" of carbon nanotubes. For this last sample the dispersion state is very different with respect to the previous samples. In the section of Electrical Behavior we will show that this different dispersion state strongly influence the nature of the interaction between nanotubes inside the epoxy matrix and therefore their conductive paths.
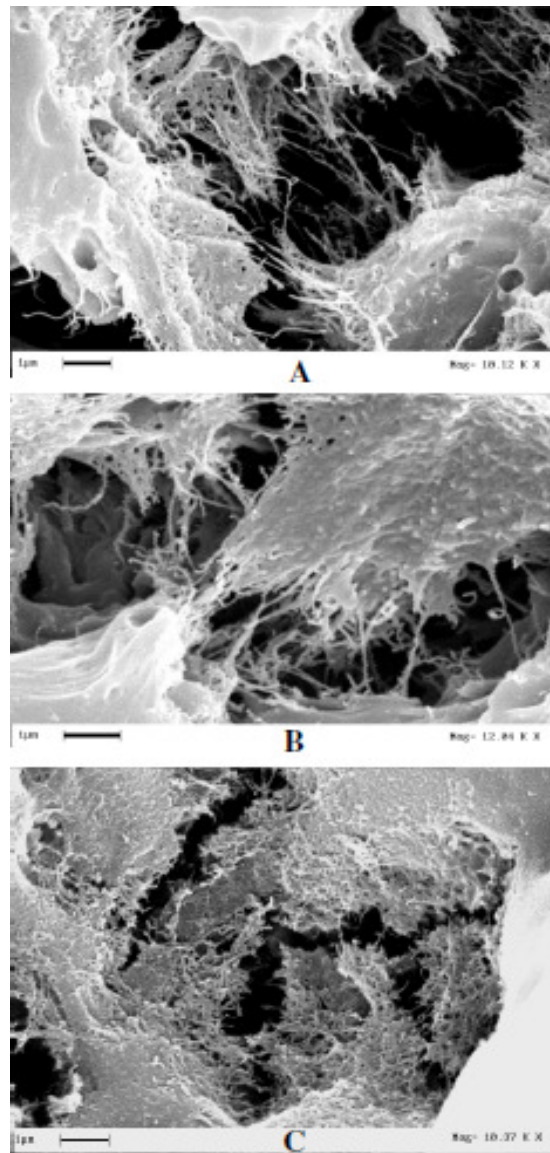

Figure 2. Fracture surface SEM images of the nanofilled epoxy composites at loading rate of **A)** 0.64, **B)** 0.32 and **C)** 0.05 per cent by weight.

3.3 Electrical Behavior

Figure 3 shows Dc volume conductivity of the nanofilled composites as a function of the nanofiller amount. An insulator to conductor transition takes place between 0.1 and 0.32 wt% of MWCNTs. The results on the conductivity above the percolation threshold are very promising because are among the highest values obtained for epoxy systems [8]. In the inset of Figure 3 the best fit of the power law $\sigma=\sigma_0(\Phi-\Phi_c)^t$ describing the conductivity behavior beyond the percolation threshold is shown. The calculated values of the parameters of the

percolation law are: $t = 2.13$, $\sigma_0 = 9 \times 10^3$ S/m and $\Phi_c = 2.23 \times 10^{-3}$ volume fraction (corresponding to 0.223 wt%). The value of the exponent t close to 2, related to the dimensionality of the system, reveals a 3D organization of the composite structure.
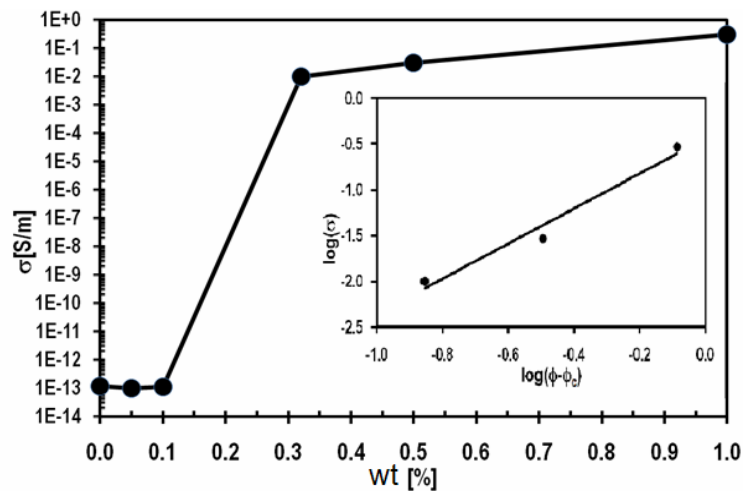

Figure 3. Dc volume conductivity of the sample TBD-CNT(% wt)(180 °C) vs. CNTs concentration

The first results concerning the influence of the cure temperature reveal that quite similar values of electrical conductivity can be obtained for the samples cured at 180 and 200°C. For example the conductivities of the samples TBD-CNT(0.32%)(cured at 200°C) and TBD-CNT(0.32%)(cured at 180°C) are 0.029 S/m and 0.023 S/m respectively.

3.4 Dynamic Mechanical Results

Dynamical mechanical data provide useful information on the relaxation processes that become operative in the polymer in a temperature range depending on the examined system.

The graphics in Figure 4 show that the incorporation of a small concentration of MWCNTs (0.32%) in the temperature range of -60 ÷ 180 °C causes an increase in the elastic modulus value with respect to the epoxy matrix (graphic at the top). The different temperature of the second stage of the curing cycle changes the curve profiles at temperature higher than 70 °C. For the lower temperature of the curing cycle (second stage), the nanofilled composite shows a non progressive decrease in the value of the elastic modulus with an unforeseen increase between 210 and 240°C before again decreasing. This behavior is very likely due to an increase in the cross-linking density during the heating. This increase is not observed from the pure resin (unfilled sample) with the same history of the curing cycle, see sample TBD(180 °C). We can explain this behavior if we assume that the inclusion of carbon nanotubes well dispersed inside the matrix causes a reduction of the cross-linking density in a fraction of the epoxy matrix in close contact with the nanofiller. This also explain two peaks in the tan δ of the sample TBD-CNT(0.32%)(180 °C) indicating the presence of a lower temperature glass transition (at 215 °C), beside the main transition at the same temperature as the pristine resin (260 °C).
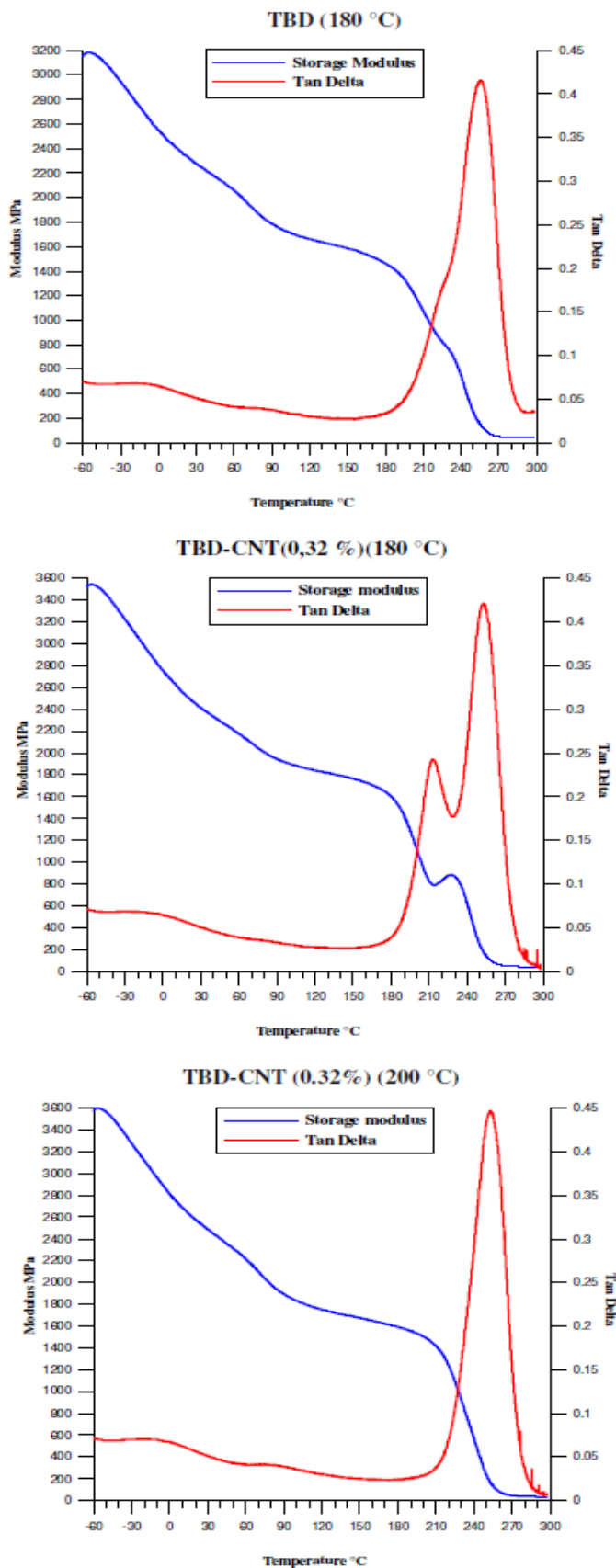
Figure 4. Storage modulus (MPa), and Loss factor (tanδ) of the pure epoxy **(graphic at the top)** and the composites 0.32 wt% MWCNTs solidified up to 180 **(graphic in the middle)** and 200 °C respectively **(graphic at the bottom)**.

We think the presence of this second lower transition is due to unreacted molecular segments that cause inhomogeneities from regions of varying crosslink density; since the samples TBD-CNT(0.32%)(180 °C) and TBD(180 °C) are formulated with the same stoichiometry and curing history the lower cross-linking density can be ascribed to the nanoinclusions only. This secondary peak, active at a lower temperature disappears for the same composite cured up to 200 °C (see sample TBD-CNT(0.32%)(200 °C). A more effective curing cycle at higher temperature up to 200 °C allows to overcome the drawback due to the inclusion of nanofiller inside the epoxy matrix. It was also observed that a different percentage of MWCNTs (data not reported here) is reflected in both the location and magnitude of the transition peak at lower temperature. These results indicate that, for the nanofilled composites, the curing history must to be optimized with respect to the unfilled formulations.

Conclusions

MWCNT/epoxy composites based on the TetraGlycidyl-MethyleneDiAniline (TGMDA) were prepared. The addition of MWCNTs causes the formation of resin fraction whit a decrease in the cure degree, as evidenced by the presence of a lower transition in the spectrum of tg δ. The incorporation of a small concentration of MWCNTs causes an increase in the elastic modulus value with respect to the epoxy matrix (graphic at the top) up to 180 °C. The reinforcement effect of MWCNTs with respect to the storage modulus is strong enough to compensate the decrease of the hydrogen bonding in the regular packing of the polymer chains due to the nanoinclusions that space out the polar sulfone groups (the proximity of these groups should favor hydrogen bonding contributing to an increase in the storage modulus).

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