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Thermal and rheological study of blended carbon nanotube/epoxy resin nanocomposites

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Abstract

Carbon Nanotube (CNT) / DGEBA epoxy nanocomposites with the (CNT) loading that varied from 0.5 to 2% by weight were prepared via melt compounding. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results showed that the presence of CNT could remarkably enhance the thermal properties of material. A very low CNT loading (0.5 wt%) increased the onset degradation temperature from 212°C to 228°C. The larger loading level of CNT gives the better thermal stability of DGEBA/NTC nanocomposites. Rheological investigation results showed that the amount and disperse of CNT were responsible for the improved thermal stability of nanocomposite.

Keywords: Nanocomposites**,** thermal stability**,** Rheology.

1. Introduction

Epoxy resins are widely used as matrix in the coating and encapsulation of electronic parts; that led to a requirement of material properties including those relating to improving the resistance to stress, the evacuation of the heat generated in the exhibit and the preservation from corrosion. One of the most common ways to increase performance is to add a load to the epoxy resin, which reduces the coefficient of thermal expansion CTE, increase the heat stability and improved mechanical rigidity.

The incorporation of a load in polymeric materials with the aim of giving them new properties or specific functions is a topic widely studied [1-5].

The behaviors of composite materials are influenced by the presence of dispersed particles inside. These insoluble additives such as carbon nanotubes (CNTs) are used to improve the properties of the photopolymer, including its mechanical strength and conductivity of heat or electricity. Bauer and Menhert [6] investigated the effect of nano-sized particles of silica on the properties of UV-curable acrylate, for example. They found that the addition of nanosilica improved the resistance of the acrylate coat to scratching and abrasion. Additives such as glass powder and carbon may also be used as fillers for the polymer composite. Such additives include carbon nanotubes (CNTs), which are well known to be an attractive material following their discovery by Iijima [7]. The mechanical, electrical, and rheological properties of the polymer and the CNT composites were reviewed by Moniruzzaman and Winey [8]. In order to optimize and control the dispersed system, it is important to clarify the influence of dispersion of these particles on thermal and rheological behaviors.

The present paper mainly focused on studying the influence of CNT on the thermal degradation behavior and rheological properties of nano composite based on DGEBA and CNT.

2. Materials

2.1. Epoxy resin

Epoxy resin diglycidyl ether of bisphenol-A (DGEBA) (Epon828). Filler based on multisheet carbon nanotubes

(MSCNT) with the following characteristics: Outer diameter (10-20 nm), Inner diameter (5-10 nm) and length (0.5 to 20 microns).

2.2. Sample Preparation

The protocol opted for the preparation of nanocomposites CNT/DGEBA is performed in two steps listed below:

Dispersion: The carbon nanotubes mixed with chloroform are placed in the ultrasonic unit for 20 minutes to remove aggregates and to ensure a better dispersion in the solvent. Then added to the epoxy resin and the mixture were allowed 25 minutes in the ultrasonic mechanical stirring at a temperature of 60 °C.
This mixture then undergoes vacuum evaporation at 75 ° C, after we allowed cooling slowly to room temperature.

The Curing: By adding a mass necessary to MDA and mixing, we conducted a cross-linking process followed by a heating cycle of the system at a temperature of 90 °C for 24 hours. nanocomposites were prepared containing 0.5wt%, 1.0wt%, 1.5wt%, and 2wt% of CNT in the epoxy resin.

The following table presents selected formulations in this study:

Table 1: Formulas of studied nanocomposites systems

Formulation N°	Weight percentage of CNT/ DGEBA/MDA
I	0,5%
II	1%
III	1.5%
IV	2%

2.3. Measurements and Characterization

Thermogravimetric analysis (TGA) was performed on a SETARAM TAG 24S thermal analyzer at a heating rate of 15 °C/min in N_2 atmosphere, with a scanning range from 30 to 600◦C.
The rheological properties of DGEBA and its nanocomposites were conducted on a controlled strain rheometer Haake Mars, rheometer system. The samples were pressed under 15MPa to get the disk like specimens with 25mm in diameter and 1.2mm in thickness. The isothermal dynamic frequency sweeps were performed under the condition of the frequency range, strain amplitude, and temperature being 100–0.1 rads^{-1} with the strain of 1% at 60°C. The dispersion of CNT in DGEBA matrix was observed by transmission electron microscopy (TEM, TECNAYT G^2 Series FET Company).

3. Results and discussion:

3.1. Thermogravimetric analysis of nanocomposites: CNT / DGEBA

Thermogravimetric analysis allows assessing the behavior of materials when subjected to the action of temperature, that's an essential tool for testing the heat resistance of polymeric materials, and therefore evaluating their thermostability.
The temperature scan is performed from room temperature to 600 ° C in a nitrogen stream, the heating rate was set at 15 ° C per minute and the weight of the samples was between 10 and 20mg. The results obtained for the nanocomposites thermodegradation CNT / DGEBA at different weight percentages of CNT, are plotted in Figure 1.

These curves have the look almost identical; the only difference is that the degradation takes place at different speeds. Taken together, these results show the influence of the rate of CNT particles on the thermal behavior of the composites studied. It is apparent that the incorporation of this filler in the organic matrix improves its thermal stability.

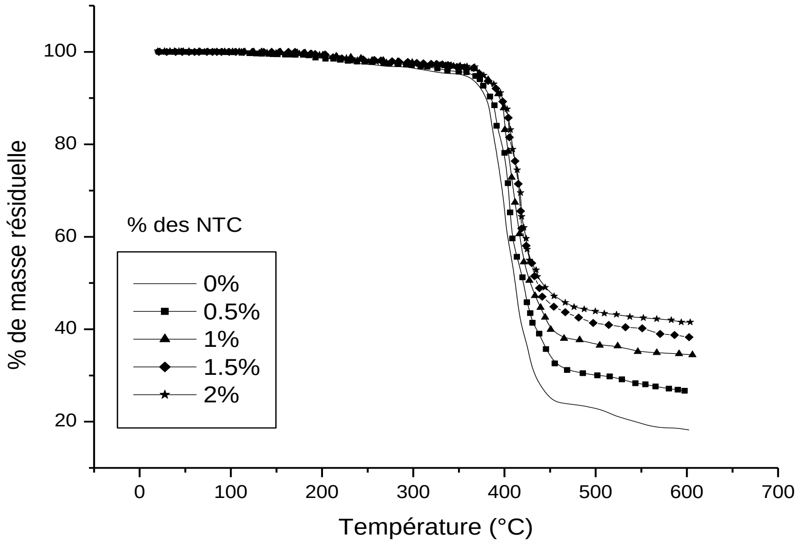

Figure 1: TG curves of (CNT/DGEBA) nanocomposites

In addition, we measured the characteristics of these materials, in accordance with conventional standards [9,10]:

- T_d: Temperature of onset of degradation corresponding to a loss of 2%.
- T_{10}: temperature at a reduction of 10%.
- T_{50}: temperature in the loss of 50%.
- S_{dr}: the threshold of rapid degradation.
- R_{500}: the residual at 500 ° C.

The main thermal characteristics of nanocomposites CNT / DGEBA, extracted curves are given in Table 2.

Table 2: Thermal properties of nanocomposites DGEBA / MDA / CNT

% Wight of CNT	T_d (°C)	T_{10} (°C)	T_{50} (°C)	S_{dr} (°C)	R_{500} (%)
0	212	285	372	342	22.6
0,5	228	291	385	354	31.1
1	232	298	393	360	37.5
1.5	238	309	401	365	40.3
2	240	314	412	372	42.7

We note that there is an analogy in these results because the thermostability increases when the percentage of CNTs increases. This improvement, which reaches its maximum 2% of CNTs is probably due to the dispersion of the filler that occupies the volume of the macromolecular network interchain obtained.

3.2. Differential scanning calorimetry nanocomposites CNT / DGEBA

The differential scanning calorimetry or DSC was used to study the behavior of our samples, when heated to determine the temperatures of phase changes occurring in the material as the melting temperature, crystallization temperature and the temperature glass transition temperature. For our part, we used this technique to determine the glass transition temperature (T_g) of our materials.

DSC analyzes were performed on samples containing mass percentages CNT from 0.5 to 2% in a temperature range from ambient to 400 °C under a stream of nitrogen.

The DSC curves are characterized by two main peaks; the first is the endothermic characteristic glass transition temperature, while the second is exothermic which is the thermal degradation of the material (figure 2).

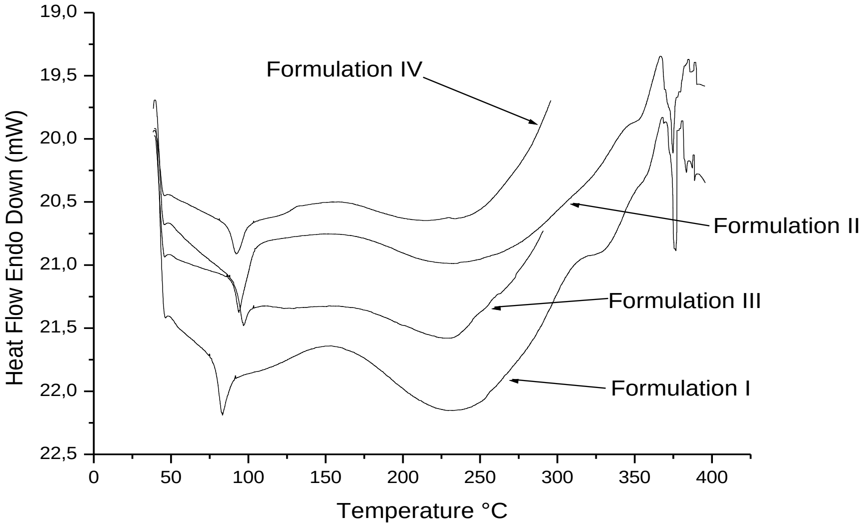

Figure 2: DSC of formulations (I to IV)

The results of the DSC analysis formulations I-IV are summarized in the figure 3, which includes all the glass transition temperatures obtained by different formulations.

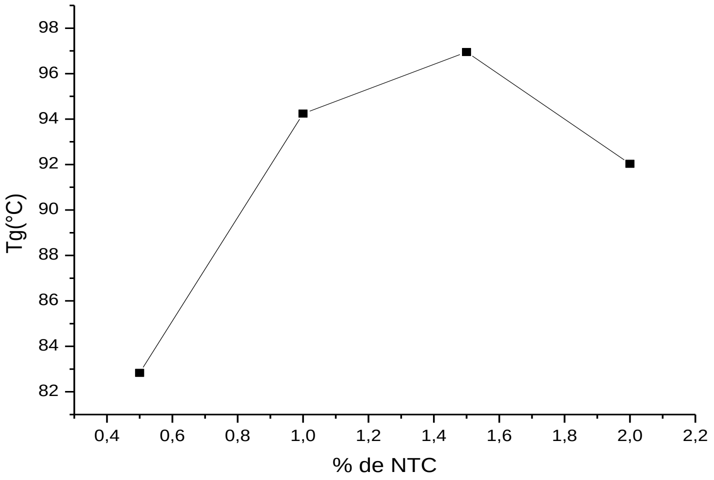

Figure 3: Evolution of Tg in function of NTC percentage

We note that the T_g increases to an optimum, which is 96 °C, corresponding to 1.5% of CNT. In our case after this value, any addition of NTC becomes useless since it helps any increase in T_g, but rather to its decline.
These results seem quite logical, because the fillers, when they exceed a threshold, tend to introduce a lot more space between nodes in the three-dimensional network formed, which has the effect of lowering the crosslinking density causing a decrease in glass transition temperature. It should be noted that the glass transition temperature is closely related to the crosslink density. More it is, the higher the T_g is high.

3.3. Morphological study of nanocomposites

According to observations by SEM of elaborated CNT / DGEBA nanocomposites, it's difficult to observe the CNT on the surface of materials, because of the density of the matrix is so high what not allow the observation of the fillers. Only clusters of tasks are visible as small white spots (Figure 4).

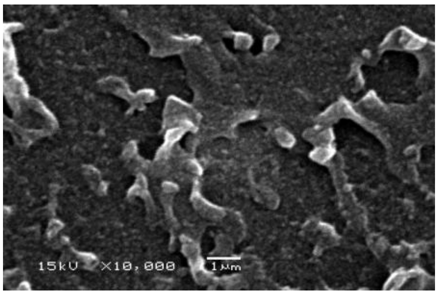

Figure 4: SEM of nanocomposites CNT/DGEBA

The resolution limit of the SEM led us to view these samples by TEM. Observations are made on nanocomposites already crushed beforehand using a porcelain mortar to have a very fine powder that can be better seen by TEM (Figure 5).

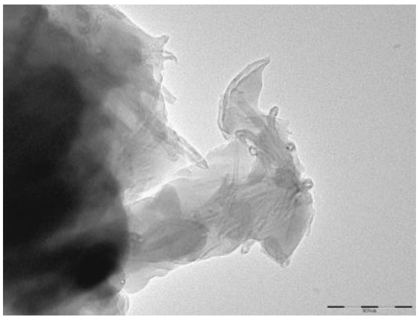

Figure 5: MET of nanocomposites NTC/DGEBA

TEM pictures show that CNT are barely visible in the ends of micrograin from grinding the composite, whose thickness can see the entanglement of these nanofibers in the matrix.

We note that these nanofibers are no longer grouped in bundles linear but they are oriented in a random manner within the matrix.

3.5. Rheological behavior of nanocomposites DGEBA / MDA / CNT

Literature on the rheological behavior of nanocomposites (viscoelastic behavior) often led to a better understand the structures and relationships responsible of strengthening of polymers by CNT.

Rheology is thus placed here on the border between structural determination and physical properties of nanocomposites; this technique is more often the key to understanding and improving the implementation.

In this part, we focused on the study of the rheological behavior of nanocomposites consisting of a dispersion of particles of CNT in an epoxy matrix (DGEBA). We sought to establish a link between at least qualitatively the thermal properties obtained for nanomaterials and their rheological behavior. The rheological analyzes of nanocomposites DGEBA / MDA / CNT were performed at 60°C and a frequency range of 0.1 - 100 rad/s.

Figures 6 shows the storage modulus G', and the loss modulus G", for the formulations CNT dispersions ranging from 0% to 2%. Whilst the addition of CNTs into the prepolymer DGEBA significantly increases G', there is only a modest increase in G". These changes in G' and G" are consistent with results obtained previously by Pötschke et al. [11] and Ma et al. [12] for CNT dispersions.

Ma et al. [13] observed microscopic aggregate structures of CNTs in a shear flow for dispersion of untreated CNTs . By contrast, however, they observed a uniform dispersion for treated CNTs. In the present study, the dispersed systems showed the aggregate structures which can be observed in TEM picture. The viscoelastic properties of CNT dispersed systems have been investigated by a number of different researchers. As discussed by Fan and Advani [14] the properties depend on the method of dispersion, the aspect ratio of the CNTs, the concentration, and the interaction between the CNTs. As mentioned above, the dispersed systems described herein have rheological properties that are in common with some other reported results, and are considered to have characteristics that are rheologically normal.

The rheological results are synonymous with improving the physical properties of our materials formulated. In agreement with the thermogravimetric results, we note that there is a correlation between the optimization of the rheological and thermal properties due to the increase of CNT in the matrix.

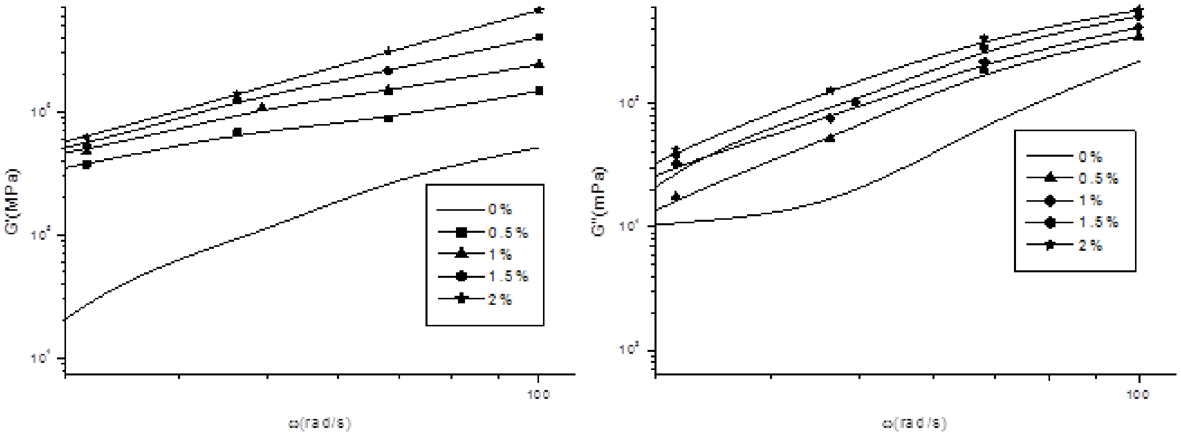

Figure 6: Rheological behavior of formulations DGEBA / MDA / CNT

Conclusion

Despite the complexity of the implementation of nanocomposites CNT/epoxy which has several technical difficulties, it is already possible to design samples in our laboratory and can achieve an optimum thermal stability. We showed that the formulation (III) is the most stable both at the level of thermal degradation at the level of the glass transition temperature. This improved thermal properties, synonymous with the stability of three-dimensional heterogeneous network (matrix - load) may have a positive impact on the mechanical strength of the material, the more rheological analysis formulated nanocomposites show an analogy between thermal and rheological behaviors.

The SEM and TEM led to improve the implementation, by the control of several factors that the dispersion of the filler in the matrix, including: the temperature of each stage of the process, the mixing time the quantities of the solvent and of the CNT, and the time of ultrasonic dispersion.

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