

PROCESSING USING REACTIVE AMPHIPHILIC MOLECULES, CHARACTERIZATION AND PROPERTIES OF DWCNTs CARBON NANOTUBES FILLED EPOXY NANOCOMPOSITES

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ABSTRACT

Nanocomposites made of a single component industrial epoxy resin developed for RTM and double-walled carbon nanotubes (DWCNTs) have been studied in the aim to assess the effects of amphiphilic molecules on the CNTs dispersion and on the resin processability. It has been shown that the amphiphilic molecules (HDA) used in this work facilitate the dispersion of DWCNTs into the liquid epoxy resin and enable to get a very low electrical percolation threshold at only 0.1 Wt% of CNTs. In addition, the use of HDA results in some modifications of the mechanical behaviour of the polymer at rubber plateau and induces some changes in the mechanical relaxation (α peak). At last, epoxy+CNTs rheological behaviour has been studied. As expected, the introduction of CNTs induces spectacular changes in the epoxy behaviour which exhibits a non-Newtonian liquid behaviour when filled with high contents of CNTs.

KEYWORDS: carbon nanotubes, epoxy resin, rheology, thermo-mechanical properties, MEB

1. INTRODUCTION

Carbon nanotubes (CNTs) have been studied intensively in the last decade for their applications as nanofillers in polymer matrix. Due to their particular geometrical characteristics (very high aspect ratio and high specific surface area) and unique physical properties, CNTs are very good candidates for the reinforcement of polymers and enhancement of their electrical conductivity with only a very low loading [1]. CNTs fit very well the new ambitions of composites engineering, i.e. multifunctional, lighter and long-life materials. However, to turn CNTs properties to advantage, their dispersion in the polymer matrix must be controlled. Although chemically-treated CNTs (such as amino-functionalized CNTs) could be easily dispersed and displayed good interfacial interactions with the polymer matrix, but such treatment is detrimental to the electrical conductivity level [2]. By contrast, we have shown in a previous work [3] that a dispersion process involving an amphiphilic molecule (i.e. palmitic acid) enabled to achieve a good dispersion and to have a lower electrical percolation threshold (i.e. 0.05 vol. %) and a higher electrical conductivity of nanocomposite. Electrical and rheological properties of Double Walled Carbon Nanotubes (DWCNTs) filled RTM6 epoxy resin has been investigated in this paper with various aims. An amphiphilic molecule, Hexadecylamine (denoted by HDA), has been used in order to facilitate the dispersion of the DWCNTs — resulting in lower electrical percolation threshold when introducing DWCNTs into the epoxy matrix — and to enhance the interfacial interaction between DWCNTs and epoxy based matrix.

2. EXPERIMENTAL METHODS

2.1 Materials

The DWCNTs used in this study are produced in CIRIMAT by catalytic CVD method and then characterized by M.E.T. analyses to determine the type of nanotubes and their average diameters. Also Raman spectroscopy and B.E.T. experiments have been carried out onto DWCNTs in order to determine their specific surface area [4]. Table 1 shows the characteristics of DWCNTs. Extraction and purification of DWCNTs were performed by a non-damaging soft soaking in H-Cl aqueous solution, to prepare a DWNTs suspension in water.

Table 1: DWCNTs average characteristics

Density	Specific surface area	Inner diameter	Outer diameter
1.3 g/cm ³	700 m ² /g	1.34 nm	2.01 nm

The polymer matrix used in this study is an epoxy resin (RTM6 produced by Hexcel Composites France). RTM6 is supplied as a mono-component resin in which stoichiometric quantities of prepolymer and crosslinking agent (i.e. hardener) are already mixed. An amphiphilic molecule hexadecylamine (HDA – C₁₆H₃₅N, see Figure 1) purchased from Sigma-Aldrich was used to help the dispersion of DWCNTs (which are initially in an aqueous suspension) into the liquid epoxy resin.

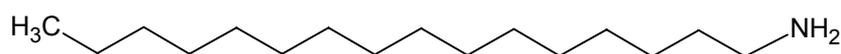


Figure 1 : chemical structure for Hexadecylamine

It is important to point out that the weight ratio of amphiphilic molecules (palmitic acid) to DWCNTs in an epoxy resin has been investigated by S. Barrau *et al.* [3]. These authors found that the optimal ratio was 1:1. This ratio is kept 1:1 in the present work.

2.2 Nanocomposites preparation

Our procedure to improve the interaction with the matrix, using surfactant-assisted processing, is comparable to the one settled in a previous work by Barrau *et al.* [3]. Nevertheless, the main difference here is that their work was performed on a bi-component epoxy system (in which resin and hardener come separately). To prepare our samples, the HDA was mixed to the suspension of DWCNTs in water and then sonicated in ultrasonic bath for 1 hour at room temperature. Then a tip sonication was applied using 20% of the maximum power amplitude (or 100 W) for 15 min. DWCNTs + water + HDA were mixed with the epoxy resin by mechanical stirring (3 blades pale - 1000 RPM) at 80°C for 30min. Mixture was degassed for 3 hours and 40 min at 80°C. These degassing conditions are necessary in order to remove all the water from the epoxy / HDA / DWCNTs mixture. Several tests were conducted by DSC and TGA at various times during the degassing process in order to determine the time from which all water was removed from the mixture (i.e. 3 hours and 40 min). After that degassing stage, the epoxy / HDA / DWCNTs mixture is poured into some Teflon molds (for manufacturing parallelepiped 1 mm x 10 mm x 40 mm and disk-like Ø 10 mm – 1 mm thick samples) and then cured according to the cure conditions recommended by Hexcel Composites: ramp at 2°C/min from 80°C up to 160°C followed by a 75 min isothermal dwell at 160°C. At dwell end the samples were then submitted to a post-cure treatment for 2 hours at 180°C.

2.3 Characterization methods

Dynamic mechanical characterization

Dynamic mechanical analysis (DMA) tests were performed on solid rectangular samples (epoxy+HDA+CNTs — dimensions: 1 mm x 10 mm x 40mm) using an T.A. Instruments ARES rheometer, operating in rectangular torsion mode at an oscillation frequency of $\omega = 1$ rd/s. A shear strain $\gamma = 0.1\%$ was fixed for all experiments. Dynamic thermal ramp test was investigated, from 0°C to 270°C at heating rate of 3°C/min for determining both the main mechanical relaxation peak characterized by its temperature (T_α) and its intensity (I_α) and the elastic shear modulus (G').

Rheology experiments

The final aim of our on-going work on nanocomposites is to use them as matrix reinforced by carbon fibres (T700 fibres). The candidate process is RTM and the shapes of the final parts (technological specimen) on which we are supposed to study the changes in electrical conductivity are rather complex. Consequently, simulations of RTM process will be made within a few months using a commercial simulation code (PAM-RTM). To this end, we need to determine various input parameters such as cure kinetics and rheological behaviour. In addition, beside the determination of RTM simulation input parameters, performing parallel plates experiments on our rheometer enables the changes in resin viscosities induced by DWCNTs and HDA to be determined. The rheological measurements were performed on liquid RTM6 samples containing various weight fractions of DWCNTs and HDA using \varnothing 50 mm plates at 80°C (injection temperature recommended for RTM6 resin). Oscillation and flow experiments were carried out. For oscillation the shear strain was fixed at $\gamma = 30\%$ while the frequency range analysed was lying between 10^{-2} up to 10^2 rd/s with a frequency step of $2.25 \cdot 10^n$ rd/s with n integer and $-2 < n < 2$. For flow experiments the frequency was fixed at 40 rd/s while strain remained at $\gamma = 30\%$.

Electrical conductivity measurements (DC & AC current)

The conductivity of our samples was investigated, first using a simple circuit. A direct voltage $U = 1V$ was applied directly to the sample. The current intensity (I) through the sample thickness (e) and contact area (S) was measured, using picoamperemeter (Keithley 617). DC conductivity σ_{dc} was then calculated using the following formula.

$$\sigma_{dc} = \frac{I}{U} \times \frac{e}{S}. \quad \text{Eq. 1}$$

AC impedance was measured using dielectric spectroscopy (Novocontrol BDS 4000). AC voltage amplitude was 1V. The frequencies ranged from 10^{-2} to 10^6 Hz with a step of $1.64 \cdot 10^n$ Hz with n integer and $-2 < n < 6$. From the results of the AC impedance spectroscopy, the specific conductivity $\sigma(f)$ of the samples was calculated according to:

$$\sigma^*(f) = \frac{1}{Z^*(f)} \times \frac{e}{S} \quad \text{Eq. 2}$$

Where S is the surface area, e is the sample thickness
and $Z^*(f)$ is the complex impedance of the sample as a function of frequency.

The real part, $\sigma'(f)$ of the complex conductivity $\sigma^*(f)$ was investigated. The DC conductivity (σ_{dc}) was taken as the value of $\sigma^*(f \rightarrow 0)$ at very low frequency (i.e. 10^{-2} Hz). To measure the electrical conductivity in the 3 space directions (through the thickness and along the two in-plan directions) bar-like samples (10 mm x 10 mm x 1

mm) were cut out from parallelepiped samples. \varnothing 10 mm disc-like with samples (1 mm thick) were also used for those electrical measurements. Figure 2 schematizes the electrical circuits used for σ (S/m) measurements. Before measuring, samples were polished on all sides to remove surface heterogeneities. Then the cross-sectional areas were coated with conductive silver paint.

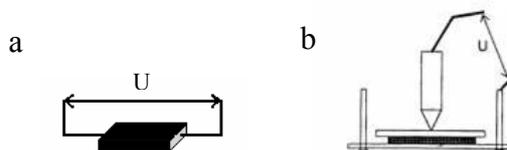


Figure 2: Measurement of electrical conductivity. (a) in plane (bar-like samples) and (b) through the thickness (disc-like samples).

HR-FE-SEM (High Resolution Field Emission Scanning Electron Microscope)

The quality of the carbon nanotubes dispersion was examined using a High Resolution Scanning Electron Microscope. Field Emission S.E.M. (JEOL JSM-6700 F) was used for these analyses. In order to get various surfaces to analyse, small samples were cut out from bar-like ones and then cooled into a liquid nitrogen bath for 5 min. As soon as the samples were removed they were fractured and the fracture surfaces were observed without any conductive coating at low voltage (0.7 kV).

3. RESULTS AND DISCUSSION

Assessment of the quality of DWCNTs dispersion by (HR-FE-SEM)

Dispersion and interfacial interactions are important issues in carbon nanotubes/polymer nanocomposites. Non damaging process to disperse carbon nanotubes in aqueous media by non-covalent adsorption of surfactants have been investigated by Hyeong *et al* [5]. The HDA was selected given the fact that NH_2 group of the amphiphilic molecule (Figure 1) could interact with the epoxy resin and the aliphatic chain with the carbon nanotube thus enhancing interfacial interaction and keeping stable the suspension of CNTs in an aqueous media.

The fracture surface images Figure 3 gives an illustration of how 0.4 wt% of DWCNTs are dispersed in RTM6. Pictures (a) and (b) show the nanocomposites obtained using HDA while the nanocomposites manufactured without HDA are shown in pictures (c) and (d). For a X1000 magnification when comparing (b-with HDA) and (d-without HDA) pictures, it is clear that HDA seriously improves the dispersion quality. Effectively, picture (d) shows many large aggregates of more than 5 μm diameter (if assimilated to spheres as a very first assumption) synonymous of rather poor-quality dispersion. Such large DWCNTs aggregates cannot be found among several tens of images randomly taken from specimen fractured surfaces when HDA is used to help the dispersion process. However, it can be noticed that in picture (d) the dispersion of DWCNTs without HDA enables to have numerous CNTs bundles ensuring the electrical percolation. When observing the (a) and (c) pictures taken under a X20000 magnification, it can be seen that even when using HDA it remains some DWCNTs aggregates. Nevertheless these latter are smaller than those exhibited by samples produced without this amphiphilic molecule. These elements show that HDA really helps deflocculating and hence individual DWCNTs can be seen in Figure 3 (a). The problem of CNTs dispersion has been widely studied in literature especially when using single-walled (SWCNTs) and double-walled CNTs. In fact, some authors have shown that SWCNTs and DWCNTs can have strong physical interaction between them then

forming large bundles and increasing the difficulty for their dispersion into a liquid polymeric media [6].

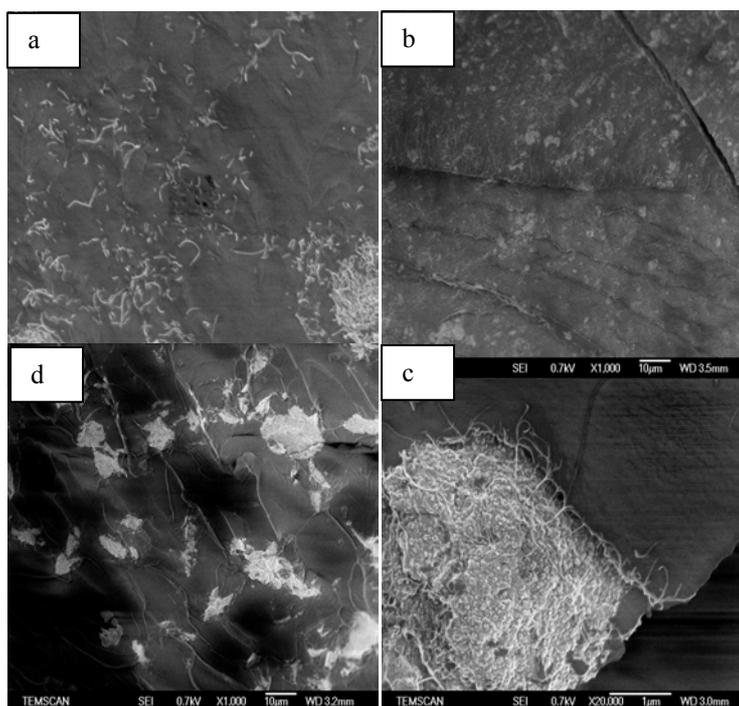


Figure 3: HR-FE-SEM images; (a) and (c) pictures: magnification X20000; (b) and (d) pictures: magnification X1000. Comparison between two RTM6 resin samples (a, b) filled with DWCNTs 0.4wt% plus HDA 0.4wt% and (b, c) DWCNTs 0.4wt% without HDA.

D.C. & A.C. conductivity of nanocomposites

For several years numerous authors have shown that the electrical conductivity level exhibited by polymers doped with CNTs is depending on the dispersion of CNTs and the network that they make inside the polymer. More especially, this demonstration has been made for a given weight fraction of CNTs [3, 7] varying only the dispersion process. For all the materials studied here, the electrical percolation threshold is reached for less than 0.1 wt% of DWCNTs introduced into the epoxy resin (Figure 4). For a filler content of 0.4wt%, the electrical conductivity of the DCWNTs-(HDA)-RTM6 nanocomposites ($\sigma = 10^{-4}$ S/cm) is one order of magnitude higher than ($\sigma = 10^{-5}$ S/cm) for the DWNTs- RTM6 nanocomposites. In-plane conductivity values do not differ from those obtained by out-of-plane measurements (through the samples thickness). This confirms that the percolating network is comparable in all directions and that there is no anisotropy in the electrical property.

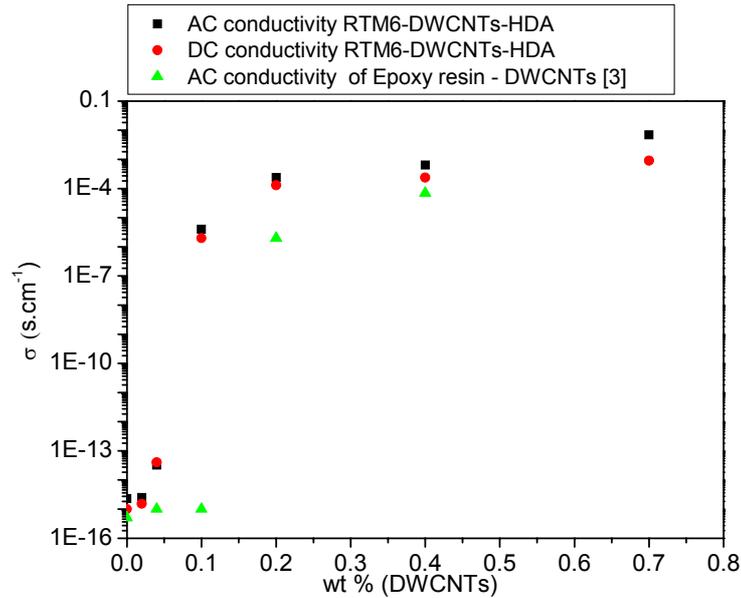


Figure 4: DC and AC electrical conductivity of RTM6 filled with different amount of DWCNTs and HDA (showing a percolation threshold). Green triangles represent percolation threshold from reference [3].

Rheology

Data about the rheological behaviour of unfilled and unreinforced RTM6 resin can be found in [8]. Polymers containing rigid fillers are important in many areas of polymers technology [9]. In order to optimise the different parameters of the manufacturing process to produce composite laminated parts by injecting (RTM) the resin doped by CNTs onto carbon fibres perform (future study), some rheological tests were performed both on unfilled and DWCNTS-filled resin.

The RTM6 epoxy resin exhibits a low viscosity at 80°C and a very slow kinetic reaction at this temperature. Flow tests performed at 80°C reveals that resin complex viscosity (η^*) increases dramatically and uniformly with respect to the DWCNTs/HDA weight fraction (wt%) introduced into the resin (Figure 5).

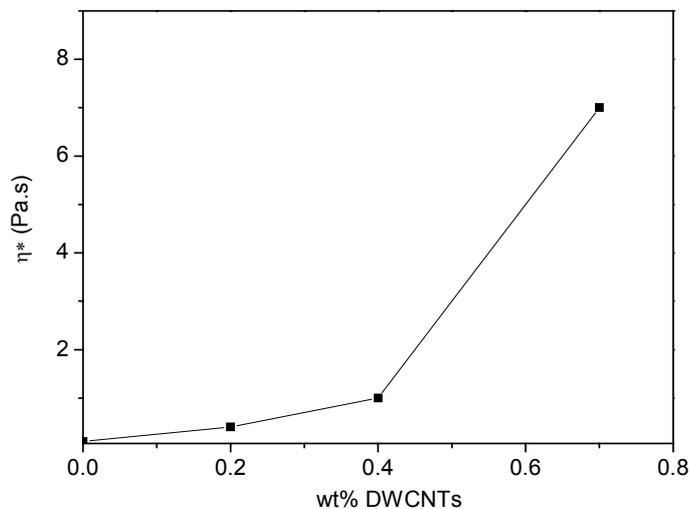


Figure 5: Complex viscosity η^* as a function of the weight fraction (wt%) of DWCNTs and HDA in RTM6 resin at 80°C.

The same behaviour was found for CNTs filled thermoplastic polymer [10]. The deviation of η^* from the linear regime (i.e. Einstein's like behaviour of suspension) for DWCNTs wt% above 0.4% becomes noticeable due eventually to entanglements in the dispersed composite.

The oscillation tests at performed at 80°C on the suspension media shows that the behaviour of unfilled RTM6 is Newtonian. The addition of DWCNTs/HDA modifies this behaviour to a non Newtonian one. It can be noticed in Figure 6 that when increasing the weight fraction of DWCNTs/HDA dispersed into the epoxy the changes in η^* versus ω (rd/s) becomes linear. This becomes particularly true when DWCNTs/HDA weight reaches 0.7%. For that suspension, the behaviour appears to be perfectly linear. For 0.2 wt% and 0.4 wt% DWCNTs/HDA suspensions, at high frequencies, it can be seen that the behaviour tends to reach a Newtonian plateau. Keeping in mind our final objective (injecting doped RTM6 on a dry fibrous carbon perform), those oscillation results mean that for process simulations the Darcy's law (assumption of a Newtonian fluid) will not be valid until the shearing rates (during injection) was sufficiently high.

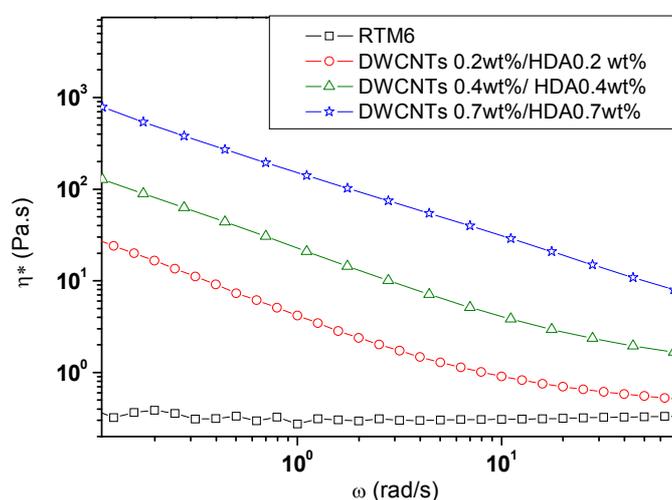


Figure 6: Complex viscosity η^* as function of frequency (ω (rd/s)) at 80°C for different DWCNTs and HDA weight percent (wt%) in RTM6 resin.

Dynamical Mechanical behaviour of solid nanocomposites

The experimental results of storage shear modulus G' and the loss factor $\tan(\delta)$ versus temperature are presented in this section: Figures 7, 8 and 9.

First tests were performed to evaluate the effects of DWCNTs/HDA concentrations on the mechanical performances of the RTM6 resin (figure 7). A special attention was paid to the effects of HDA. Some tests were carried out to evaluate those effects on nanocomposites containing 0.4wt% DWCNTs dispersed with and without HDA. As shown in Figure 7, the RTM6 resin seems to be somewhat strengthened by presence of DWCNTs at temperatures below T_α the temperature of the main mechanical relaxation peak (denoted by α peak – see $\tan(\delta)$ curves in Figure 8). The storage modulus G' values are given in Table 2. When trying to perform a very first analysis of these strengthening effects of DWCNTs, we should mention that some authors have attributed them to some residual curing stresses occurring between the epoxy matrix and the fillers [11]. F.H Gojny et Al. [6] have also recorded such reinforcing effects

with MWCNTs in an epoxy matrix and shown how the functionalization by amine groups of MWCNTs surfaces can contribute to these effects.

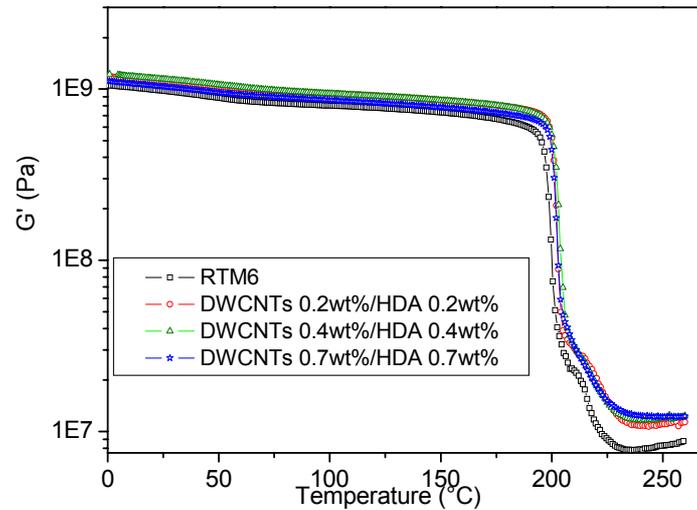


Figure 7: Storage shear modulus G' of RTM6 resin filled with different contents of DWCNTs and HDA wt% as a function of temperature.

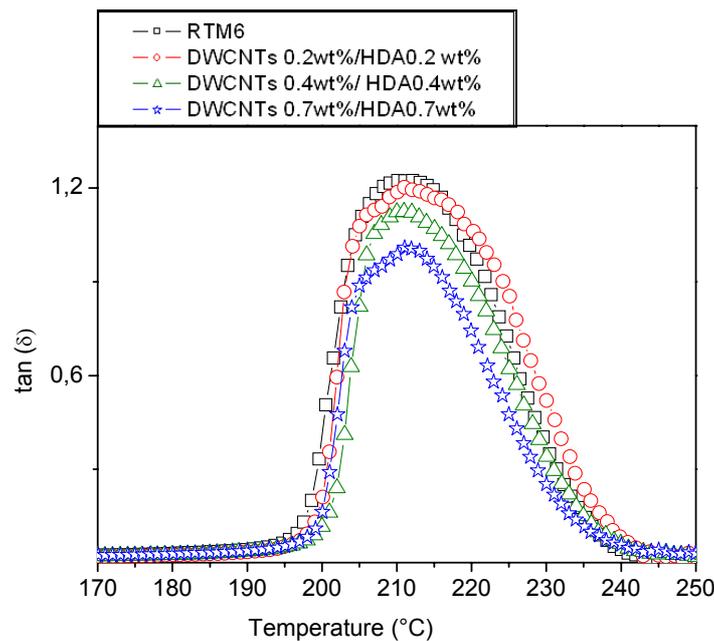


Figure 8: $\tan(\delta)$ as a function of temperature for RTM6 resin filled with different contents wt% of DWCNTs + HDA.

The study of G' at $T^\circ \geq T_\alpha$ reveals more information about the cured resin network density and mobility and about the interactions between the epoxy matrix and the fillers [11]. At $T^\circ > T_\alpha$ (in the rubber-plateau), the storage modulus G' values increase with respect to the DWCNTs/HDA weight fraction (figure 7). In order to perform a first assessment of the effects of HDA upon the epoxy network structure, some experiments were carried out on nanocomposites (0.4wt% DWCNTs) manufactured without HDA. The obtained results are shown in Figure 9. It can be concluded that for low HDA

contents (here 0.4 wt%) there are none effects upon the epoxy behaviour studied by DMA.

From a general point of view, introducing low quantities of DWCNTs/HDA into the epoxy resin do results in major modifications of the mechanical manifestation of the glass transition temperature (main mechanical relaxation α). Nevertheless, analysing the characteristics of the main mechanical relaxation peak (α), enables to see that its intensity (I_α) slightly decreases when filling the epoxy with DWCNTs/HDA (figure 8). Analysing the characteristics of a peak enables to get an idea of the kind of bondings established between the polymeric matrix and the fillers [11]. In our case, due to nature of RTM6 matrix (RTM6 is based upon tetradiglycidyl methylene dianiline and a blend of aromatic amine [8]) which has a strength network — when it is fully cured — the main mechanical relaxation always happens at a constant temperature $T_\alpha \cong 211^\circ\text{C}$ and only I_α undergoes small changes. A summary of the changes in G' , $\tan(\delta)$ and I_α , as functions of the DWCNTs content is given in table 2.

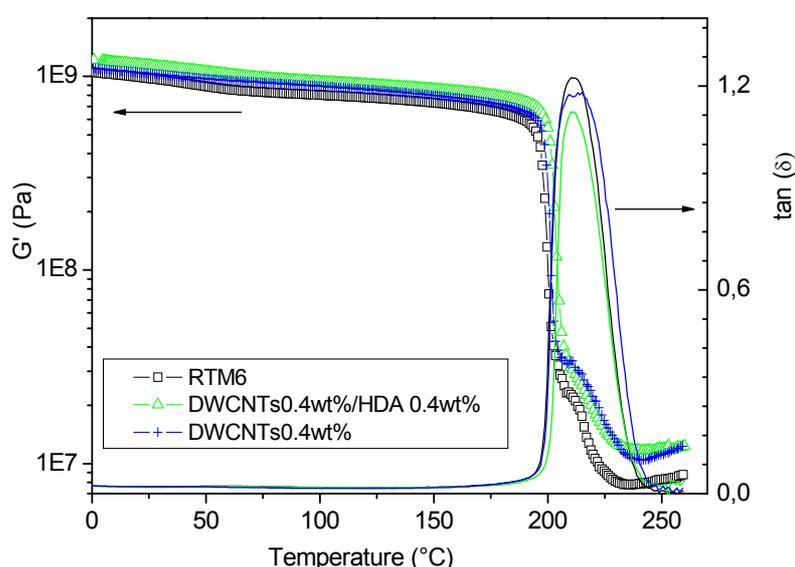


Figure9: Storage shear modulus G' and $\tan(\delta)$ of RTM6 resin filled with 0.4wt% of DWCNTs dispersed with or without HDA function of temperature.

Table 2: Summary of DMA results. G'_g : glassy and G'_r rubbery storage moduli.

	$\tan(\delta)$		G' (Pa)	
	T_α (°C)	I_α	G'_g at 25°C	G'_r at 250°C
RTM6	210	1.22	0.98 E9	0.83E7
DWCNTs0.2wt%/HDA0.2wt%	211	1.20	1.11E9	1.11E7
DWCNTs0.4wt%/HDA0.4wt%	210	1.17	1.14E9	1.19E7
DWCNTs0.7wt%/HDA0.7wt%	210	1.12	1.03E9	1.22E7
DWCNTs0.4wt%	212	1.01	1.11E9	1.11E7

4. CONCLUSION

Aiming to developing carbon fibres reinforced epoxy matrix filled with carbon nanotubes, this encouraging preliminary study has enabled the DWCNTs dispersion procedure to be defined. The results obtained show that HDA enables to get a lower

content of DWCNTs to reach the percolation threshold (0.1wt% when using HDA versus 0.2wt% without HDA).

In terms of conductivity level, it has been shown (Figure 2) that since HDA facilitates the dispersion of DWCNTs the nanocomposites with 0.4%wt of DWCNTs/HDA exhibit an electrical conductivity ten times higher than those obtained without using HDA for dispersion. These are very encouraging results.

As expected, from a rheological point of view, the addition of DWCNTs generates (depending on the weight fraction added) some increases in resin complex viscosity (determined in flow experiments). Furthermore, DWCNTs clearly modify the rheological behaviour of RTM6 resin from quasi-Newtonian to a non-Newtonian one. The epoxy/DWCNTs/HDA suspensions have to be submitted to high shearing rates to exhibit again a Newtonian behaviour. This point must be taken into consideration for our next works firstly on RTM process simulation and secondly on laminated parts manufacturing.

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