Thermal, Rheological and Electrical Characterization of MWCNTs/Epoxy Matrices for an Innovative Spray Process

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Abstract

Nanomodification of CFRP has the potential to increase electrical conductivity. However, a suitable processing method has to be found to produce hybrid composites. A proposed solution is to use an innovative CNT/epoxy spraying method on the dry carbon fibres. Using this technique requires good knowledge of the processing parameters. In this study, the cure kinetics, rheological and electrical behaviors of the MWCNTs/epoxy nanocomposites produced using a three-roll mill are studied. The shear-thinning effect caused by adding CNTs to the epoxy matrix is more pronounced at increased temperature and MWCNT weight content. At last the conductivity was investigated to characterize the percolation behavior and determine the best CNT content / electrical properties ratio.

1. Introduction

The high aspect ratio as well as the electrical properties makes Carbon Nanotubes (CNT) attractive when trying to improve matrix dominated properties of Carbon Fibre Reinforced Composites (CFRP) used in the aerospace industry. Inserting CNTs in the polymer matrix of CFRPs may lead to the increase in through thickness electrical conductivity expected in order to partially fulfill electrical conductivity requirements traditionally met by metallic structures.

A few methods to disperse carbon nanotubes in epoxy matrices in order to achieve the proper particle distribution have been presented in the literature. One of these methods consists in applying high shear forces with a three roll mill to break up the CNT agglomerates and disperse them in the epoxy matrix. Very good results have been reported using this equipment [2]. A major advantage of this technique is, beside the good dispersion state obtained, the up-scalability in order to efficiently manufacture larger amounts of nano composites. Therefore this will be the method of choice in this research.

A large number of papers have dealt with the effect of CNTs on the epoxy cure kinetics. El Sawi et al. [1] showed that double walled carbon nanotubes have an acceleration effect on the polymerization rate of an epoxy polymer but that no significant effect was noted on the glass transition temperature of the epoxy resin. This study revealed as well that a shear-thinning effect of DWCNTs was observed and was more pronounced at increased temperature.

Concerning the electrical conductivity behavior, Barrau et al. [3] have investigated the DC and AC conductivities of CNT/epoxy nanocomposites made by dispersing nanotubes in an ultrasonic bath in the epoxy matrix. Their investigations showed a frequency dependence of the measured conductivity followed by a DC plateau. The experimental results showed a DC conductivity percolation threshold at $p_c = 0.3$ wt%. CNTs. The behavior at low frequencies and above the percolation threshold follows an ohmic type law at room temperature.

In order to manufacture CNT modified CFRP using state of the art infusion processes (Resin Transfer Molding, Resin Transfer Infusion, etc…) a few challenges have to be overcome. Indeed the change in thermoset resin properties due to the insertion of CNTs (high viscosity, CNTs filtration effect) makes the use of such processes almost impossible. That is why alternative CFRP processing methods have to be developed. One of the alternatives could be to spray CNT/epoxy dispersions on the dry carbon fibres, followed by a controlled curing process. Manufacturing CNT doped CFRP with such a technique requires a good knowledge of the processing parameters involved, considering that the spray gun operates at higher processing temperatures and shear rates. That is why understanding the polymerization kinetics of CNT epoxy dispersions from the monomer state up to the final cured CFRP is crucial. Firstly, it is important to determine the influence of the spraying process on the polymerization kinetic and the time available to spray the CNT/epoxy dispersions on the dry fibres. Secondly, we need to assess the influence of the spraying process on the rheological behavior of the CNT/epoxy dispersion and define if the CNT doped resin is spray able from a rheological point of view. At last, these results (thermal and rheological analysis) need to be correlated with DC conductivity measurements, to find the best compromise between electrical performances and amount of CNTs inserted, which strongly influences the thermal and mechanical behavior.

2. Materials and Methods

2.1. Materials

The epoxy matrix used in this study is the commercially available MVR 444 provided by Cytec Industries Inc. This epoxy matrix is a single component resin where the epoxy prepolymer and amine hardener are already mixed together and degassed. It is typically used to manufacture aerospace composite components using vacuum assisted resin transfer molding and is usually cured at 180°C. The Carbon Nanotubes selected are Multi Walls Carbon Nanotubes (MWCNT) provided by Arkema (France). A masterbatch based on Cytec's MVR 444 resin was prepared by Arkema using their Graphistrength C S1-25 MWCNTs. With this method the CNT masterbatch is based on the same resin than the one used to dilute to the final CNT concentration, and by thus ensuring perfect compatibility. Carbon nanotubes dispersion was carried out using a three roll mill (Exakt 80E, EXAKT GmbH, Germany). The masterbatch was first diluted with uncured epoxy resin to the desired CNT concentration and then calendered. A calendering cycle developed in a previous work [4] was used. Mixtures were manufactured with a CNT weight content of 0.10 ; 0.25 ; 0.50 ; 0.75 and 1.00 wt%.

2.2. Methods

The cure kinetics of both unfilled and 1.00 wt% CNT doped epoxy has been studied using a TA Instruments Q2000 Differential Scanning Calorimeter. This study focused on two concentrations: 0 and 1wt.% CNT, as they represent the lower and upper limits of the CNT concentration domain investigated. First, temperature scanning measurements from -50°C to 320°C (heating rate: 5°C/min) have been performed in order to measure the total reaction enthalpy (ΔH_{total}) and the glass transition temperature of the uncured epoxy ($T_{g,0}$). Samples from both neat and 1.00 wt% doped epoxies were then placed in an oven at isothermal conditions for durations up to 175 hours. Temperature scanning measurements (similar to above mentioned conditions) were performed on small amounts of materials sampled (3 mg) and placed in DSC pans at regular time intervals to determine the residual enthalpy ($\Delta H_{residual}$) and glass transition temperature (T_g). Determining these two experimental parameters enabled the evaluation of the conversion rate as a function of time.

The rheological behavior of the unfilled and filled epoxy polymer was studied using an ARES Rheometer from TA Instruments. A Couette test setup was used. First of all, the linear response domain of the material as a function of the applied strain had to be experimentally determined for each temperature considered. In order to do so, strain sweeps were performed under isothermal conditions at 60°C, 80°C and 100°C in a range of strains from 10^{-2} to 8.10^{2} %. These measurements were performed each time for a few selected shearing frequencies: 10^{-2}; 5.10^{-2}; 10^{-1}; 1; 10; 80 Hz. It was chosen to record only the torsional moment as this is the only raw data not being processed by the rheometer software. The aim was here to determine the frequency and strain domains, for which the material exhibits a linear response to the stress applied: i.e. a requirement to determine the complex viscosity $\eta^*(\omega)$. As for the thermal analysis we chose to focus on the lower and upper limits of the CNT concentration domain (pristine epoxy and 1.00 wt% CNT doped). In a second time, the rheological behavior was investigated as a function of shear frequency. Frequency sweeps were performed at the selected isothermal temperatures (60°C, 80°C, and 100°C) for the selected strains and frequency domain, determined to ensure a measurement inside the linear response domain of the material. For this second part all of the CNT content range (from 0 to 1.00 wt%) was analyzed.

AC conductivity measurements were performed with a Solartron Schlumberger gain/phase analyzer SI 1260 together with a Novocontrol interface (broadband dielectric converter) in the frequency range of 10^{-1} to 10^{6} Hz. The measurements were performed in a temperature range of -150 to 150°C using a controlled nitrogen thermal regulation system (Quatro Novocontrol). Electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$. The real part, $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was investigated. The value of $\sigma'(\omega)$ at 10^{-1} Hz was considered as DC conductivity σ_{DC}.

3. Results and discussion

3.1. Cure kinetics

Figure 1 presents the conversion rate (α) graphs obtained through the residual enthalpy measured (○ symbol on the graphs), and the monitoring of the T_g (□ symbol).

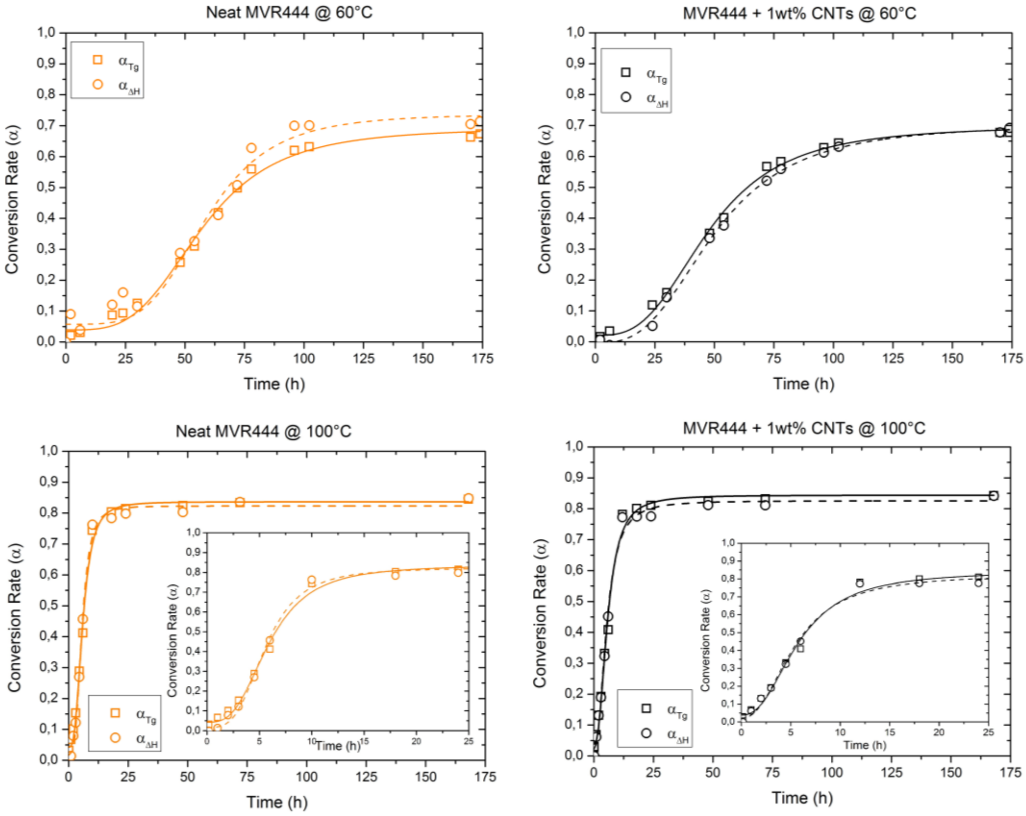

Figure 1: Conversion rate as a function of polymerization time

On Figure 1, two noticeable stages can be pointed out. First, for short times spent on the isotherm (i.e. between 0 and 75h at 60°C and between 0 and 10h at 100°C), we notice a strong and steady increase of α. This is directly related to the 3D cross-linking of the polymer. Indeed, in this first step (gelation), the amine and epoxy groups are free to react with one another. As the conversion rate continues to increase, it will eventually reach the point where T_g comes above the isothermal temperature ($T_g > T_{isotherm}$). We notice that as soon as it reaches this point, the increase in α is then slowed down. The polymer has then reached its vitrification state. In this state the molecular mobility is reduced and the chemical reactions are limited by the diffusion of the chemical species, which translates to a slower increase of the conversion rate. It finally stabilizes to a plateau, a final maximal degree of cure being reached ($\alpha(max)_{60°C} = 0.70$ and $\alpha(max)_{100°C} = 0.80$). The results indicate a very similar curing behavior to other epoxy amine systems. It was noticed experimentally that no noticeable influence of the CNTs on the evolution of the degree of cure could be observed. From Figure 1, we can also deduce the time available to process the resin without interfering with its chemical state. At 60°C this processing window has a duration of 20 h (at 100°C a duration of 2 h), which is useful information for the CNT/epoxy spraying process. It is essential to perform the rheological analysis inside this window in order to be sure to observe only molecular mobility induced phenomenon (and no chemical phenomenon such as gelation or vitrification).

3.2. Influence of the MWCNTs on the rheological properties of the epoxy polymer

In this subsection, the rheological behavior of the uncured epoxy is studied at three isothermal temperatures inside the processing range of the spray gun (60, 80 and 100°C) both for neat and CNT modified resin. The duration of the test does not exceed the durations mentioned in the previous section, so it can assumed that $\alpha \approx 0$ during the measurement. After defining the domain of linear response, the influence of temperature and MWCNTs on the shear viscosity will be presented.

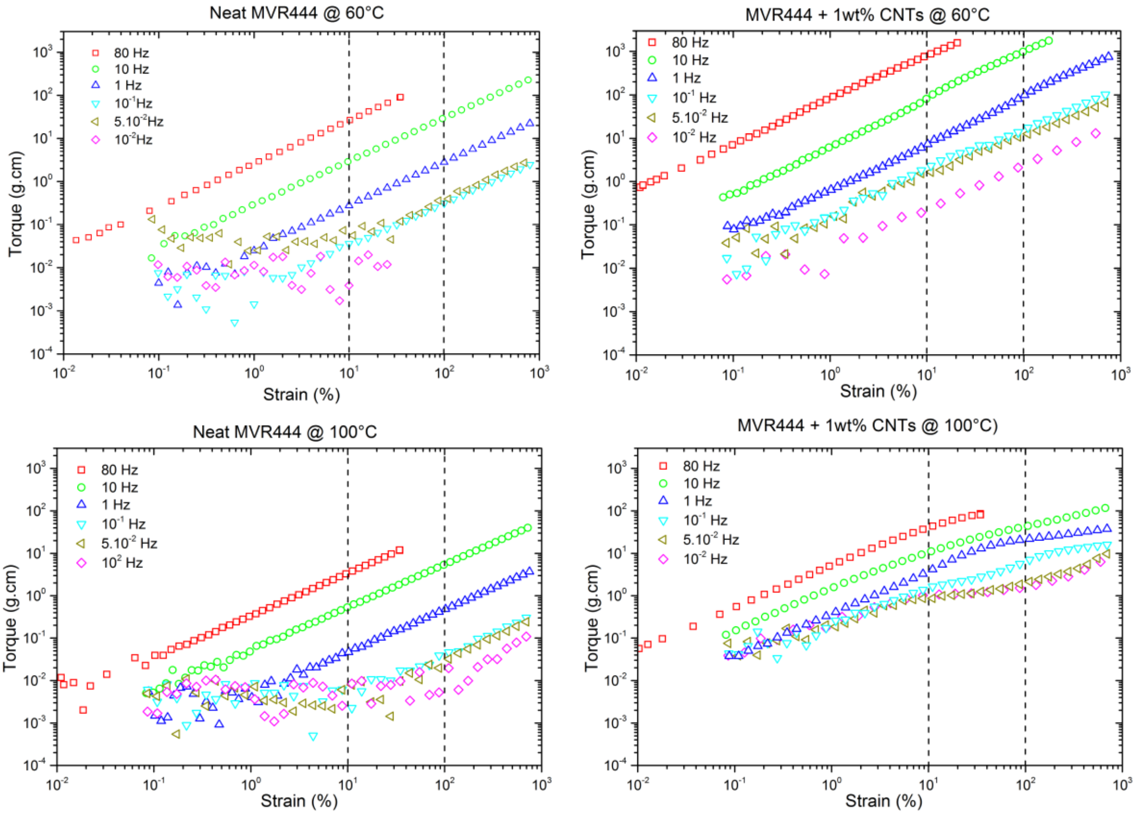

Figure 2: Torsional moment as a function of the applied strain

Figure 2 shows the strain sweeps (from 10^{-2} up to 8.10 % strain) for two of the three selected isothermal temperatures (60 and 100°C, as they represent the limits of the domain investigated), each time for the selected shearing frequencies. The vertical dashed lines are reading guides representing the two strain levels considered: 10 % and 100 %. The rheological behavior as a function of the applied strain can be divided in two parts. For the lower strain levels (low torsional moments measured), the response of the material is erratic and does not follow any linear trend. On the other hand, as soon as a critical strain level is achieved, the material follows a linear trend, characterizing the linear response of the material. Therefore, the material presents a linear response for the shearing frequencies from 5.10^{-2} to 80 Hz for both 10 % and 100 % strain and for all three temperatures considered (60°C, 80°C and 100°C). For the 1.00 wt% doped resin, two cases have to be distinguished. First, at 60°C (Figure 2 top right), the doped polymer exhibits the same type of response as observed for the neat resin. Here again, the material presents a linear response for the shearing frequencies from 5.10^{-2} to 80 Hz for both 10 % and 100 % strain and for all the range of temperatures considered. However, when testing at 100°C (Figure 2 bottom right), a different behavior is observed. For low shearing frequencies (100°C: 10^{-2} to 10 Hz), experimental points are not aligned and cannot be interpolated (with respect to strain level) by a linear function. A change in its slope and a curved form of the graphs with CNTs is observed. We are in the case of a nonlinear response of the material. As having a linear response of the material is required in order to define the viscosity function η* (shear modulus), one can only determine and represent η' for temperatures and strain rates where a linear response is observed. For the second part of the rheological study, it has been decided to work in the linear response domain by choosing not to investigate the rheological behavior at 100 % strain (to stay exclusively inside the domain of linear response).

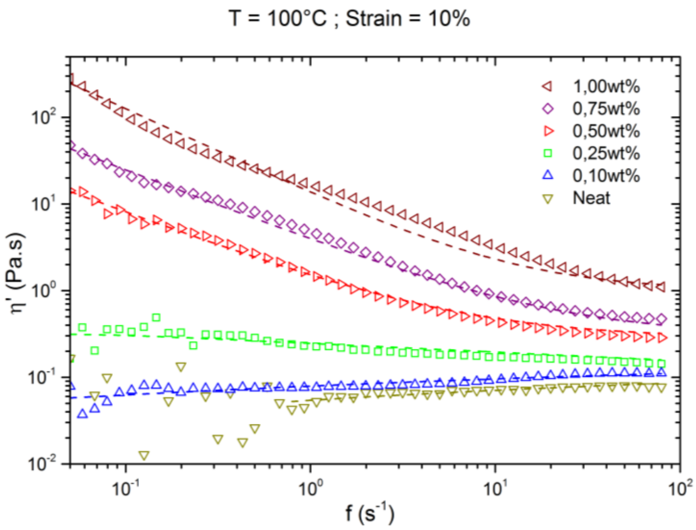

Figure 3: Logarithmic frequency sweeps for neat and CNT doped epoxy (100°C)

On Figure 3 is presented the real part of the complex viscosity η' as a function of the shearing frequency *f* for the epoxy resin doped from 0 to 1.00 wt% CNTs for one (100°C) of the three temperatures and for a strain rate of 10% (enabling to stay inside the domain of linear response, measurements at 60°C, 80°C as well as for 100% have been performed as well but are not represented in this paper, as some of them are outside the linear response domain). From the experiments it can be noticed that the behavior observed is different depending on the testing temperature. At 60°C and for CNT contents from 0 to 0.75 wt% the polymer exhibits a Newtonian or quasi Newtonian behavior, as the value of the real part of the complex viscosity remains almost the same for all the range of frequencies investigated. Only the epoxy dispersion containing 1.00 wt% CNTs undergoes a decrease in the η' value with increasing frequency, characterizing a shear-thinning behavior. At 80°C a different trend could be noticed. For CNT weight fractions from 0 to 0.25 wt% the behavior is still Newtonian as at 60°C, though for higher CNT contents the shear thinning behavior is more pronounced. Indeed the shear-thinning effect is already present from 0.50 wt% and up to 1.00 wt%. As for T = 60°C, the value of the strain applied does not seem to influence the results obtained. At last for the results at T = 100°C (Figure 3), the same Newtonian behavior is observed for concentrations from 0 to 0.25 wt% CNTs and shear-thinning behavior from 0.50 to 1.00 wt%. Although the same shear thinning behavior is observed here the trend followed by the shape of the curve is different compared to the one observed at 80°C. A deviation in the decreasing trend is observed as a sort of "bump" along the graph appears.

3.3. Electrical Conductivity

Figure 4 shows the measured DC conductivity at room temperature of the MWCNTs/epoxy nano composites as a function of the CNT weight fraction. It can be observed that the nanocomposite exhibits between a first plateau before and another one after the percolation threshold a clear increase in DC conductivity by 11 orders of magnitude. The percolation threshold was found to be around $p_c = 0.25$ wt% CNTs and the maximal conductivity was already achieved for a CNT content of 0,75 wt% is $\sigma_{DC}(\max) = 6 \times 10^{-3}$ S.m^{-1}.

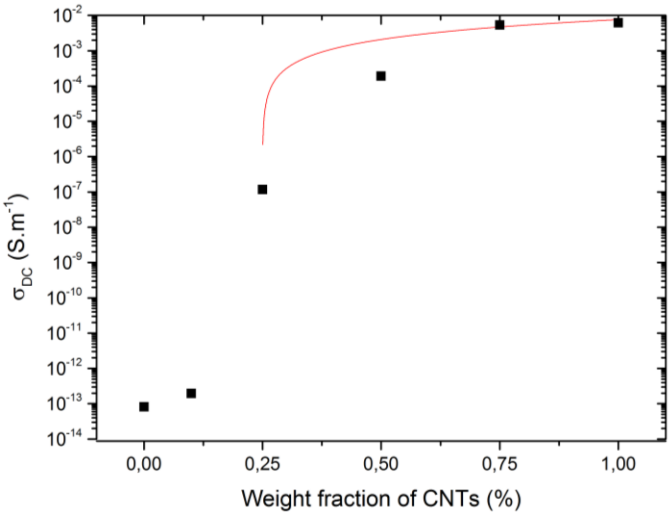

Figure 4 : Dependence of the CNT weight fraction on the DC conductivity of MWCNTs/epoxy

The presence of a percolation threshold indicates the existence of a percolation path for the electrical charges to travel through the material. Above this CNT loading, the conduction phenomenon is due to the formation of a connecting path thanks to the CNT bundles network inside the epoxy matrix. The state of dispersion of the nanotubes inside the epoxy matrix can be accessed via the measure of the DC conductivity of the nanocomposite. The lower the percolation threshold is, the better the CNTs are dispersed. A low percolation threshold signifies the presence of a homogeneous dispersion state, with few to no CNT bundles. Our percolation threshold obtained is similar to what is reported in the literature [1] [5] for mechanically dispersed nanotubes, indicating a very homogeneous, well dispersed three dimensional nanotube network.

4. Conclusions

In this study, MWCNTs were dispersed in an epoxy matrix using the calendering dispersion process and the cure kinetics, rheological and electrical behaviors of these dispersions were investigated. First, the curing reaction kinetics was studied. No clear influence of the MWCNTs on the curing reaction kinetics at the selected curing temperatures of 60°C and 100°C has been noted. We also were able to deduce the time available to process the resin without interfering with its chemical state.

Secondly, the linear response domain from a rheological point of view was determined by performing strain sweeps at the selected isothermal temperatures (from 60 to 100°C), each time for a few selected shearing frequencies. Parameters for which the torque measured followed a linear trend were next selected. Shear rate sweeps were consequently performed at the previously selected parameters and for short durations to avoid any chemical effect and focus only on rheological behavior. For temperatures ≥ 80°C, a shear thinning behavior was observed for concentration ≥ 0.50 wt% CNTs (dispersions with concentrations ≤ 0.25 wt% exhibit a Newtonian behavior, as for all dispersions ≤ 0.75 wt% CNTs when tested < 80°C). Focusing on a dispersion containing 0.75wt% CNT, it has been observed that at elevated temperatures (80°C and 100°C) a shear thinning behavior can be observed. This is useful for such a spraying process, which submits the sprayed material to high shear forces when operating. A short review of the literature available showed that shear levels of $10^3 – 10^4$ s^{-1} may be reached [6]. In this case of a shear-thinning behavior, the viscosity of the dispersion in then decreased and subsequently the spraying process is facilitated.

The dispersion state of the nanotubes inside the epoxy matrix was accessed by the measure of the DC conductivity, revealing a percolation threshold at around $p_c = 0.25$ wt% CNTs and that the maximal DC conductivity of 10^{-2} $S.m^{-1}$ was achieved for a CNT concentration of 0.75 wt% CNTs. This concentration will be chosen for the spraying process as it is the best CNT loading / conductivity achieved ratio.

This study helped settle the basic parameters in order to develop a method of spraying CNTs dispersed inside an epoxy matrix. In a more comprehensive way, this might be a more general way of inserting nanoparticules inside the matrix of CFRP materials either for Liquid Composite Molding processes as well as for prepreg materials.

Acknowledgements

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