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A B S T R A C T

In this study, the cure kinetics, rheological and electrical behaviors of the MWCNTs/epoxy nanocomposites produced using a three-roll mill are studied. After defining the domain of linear response, the influence of temperature and MWCNTs on the shear viscosity has been investigated. The shear-thinning effect caused by adding CNTs to the epoxy matrix is more pronounced at increased temperature and MWCNT weight content. Furthermore, a mechanical manifestation of the percolation phenomenon may have been observed. At last the electrical conductivity was investigated to characterize the percolation behavior and determine the best CNT content/electrical properties ratio.

Keywords:
A. Carbon Nanotubes
A. Nano composites
D. Rheology
B. Electrical properties
B. Curing

1. Introduction

The high aspect ratio as well as their good 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 an increase in through-thickness electrical conductivity expected in order to partially fulfill electrical conductivity requirements traditionally met by metallic structures.

Several methods to disperse Carbon Nanotubes in epoxy matrices in order to achieve a sufficient 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 [1]. A major advantage of this technique, beside the good dispersion state obtained, is the up-scalability in order to efficiently manufacture larger amounts of nanocomposites. 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. [2] showed that Double Walled Carbon Nanotubes (DWCNTs) 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 nano composites 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, $p_c = 0.3$ wt%. Furthermore, since then, the works of Gojny et al. [4] and Vavouliotis et al. [5] have shown that percolation thresholds as low as 0.1 wt% can be achieved by using untreated MWCNTs dispersed with a calendering device.

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 it 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, it is proposed in this work to study the thermal, rheological and electrical behavior of the CNT doped epoxy to pave the way for such a potential CFRP manufacturing process.

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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. Based on the information provided in the material data sheet, it can be assumed that this thermosetting resin is based on four chemical components: tetraglycidyl 4,4′-diaminodiphenylmethane, representing between 50% and 100% of the resin preparation; 4,4′-Methylenebis(2,6-diethylaniline), (between 10% and 25%); 4,4′-Methylenebis(2-Isopropyl-6-Methylaniline, (between 5% and 10%) and Diethyltoluenediamine, (between 5% and 10%). 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-Walled 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 as an additive (25 wt%). With this method the CNT masterbatch is based on the same resin as the one used to dilute to the final CNT concentration, and by thus ensuring perfect compatibility. The as-received degree of cure of this thermoset masterbatch was determined to be $\alpha = 0.03$ (measured with differential scanning calorimetry).

2.2. Dispersion of CNT and processing parameters

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 [6] was used. Table 1 presents the different steps of the calendering process and their corresponding parameters. This cycle was developed and optimized in order to give the best dispersion results. The ratio of roll speeds is as following: feed/center/apron ≡ 1/3/9. A calibration run was performed before starting the mixing procedure, so as to calibrate both roll speed and roll gaps (δ_1 and δ_2). A water cooling system was used to keep the resin temperature close to room temperature when poured between the rolls and counterbalance the increase in temperature due to the high shear forces applied. DSC measurements performed before and after the complete process showed that the degree of cure of the dispersion after calendaring remains at a minor value of $\alpha = 0.03$. Mixtures were manufactured with a CNT weight content of 0.10; 0.25; 0.50; 0.75 and 1.00 wt%. In parallel to this study, the percolation behavior of the nanocomposites was investigated in order to assess the Carbon Nanotubes' state of dispersion in the polymer matrix (see Section 3.3).

Table 1
Calendering procedure used in this study.

Step	δ_1 (μm)	δ_2 (μm)	ω_{apron} (rpm)
1	120	40	100
2	120	40	300
3	45	15	300
4	15	5	300
5	15	5	500
6	15	5	500
7	5	5	500
8	5	5	500
9	5	5	500

2.3. Experimental methods

2.3.1. Differential scanning calorimetry

The cure kinetics of both unfilled and CNT doped epoxy have been studied using a TA Instruments Q2000 Differential Scanning Calorimeter. This study focusses on two concentrations: 0 and 1 wt% 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_{g0}). Samples from both neat and 1.00 wt% doped epoxies were then placed in an oven at isothermal conditions for durations up to 175 h. 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 through Eqs. (1) and (2).

The degree of polymerization of thermoset resin systems can be characterized by the recording of the residual enthalpy. For low reaction rates (long durations) the conversion rate can be determined via Eq. (1). This method enables the calculation of a good approximation of the conversion rate.

$$\alpha_t = \frac{\Delta H_{total} - \Delta H_{residual}(t)}{\Delta H_{total}} \tag{1}$$

The process of the epoxy prepolymer and amine hardener reacting together to form the three dimensional network can be as well characterized by an increase of the glass transition temperature. Eq. (2) presents the relation between T_g and the polymerization rate proposed by DiBenedetto [7].

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1-\lambda)\alpha} \tag{2}$$

$T_{g\,0}$ and $T_{g\,\infty}$ are the glass transition temperature of the uncured and completely cured epoxy resin (cured in this case: 2 h at 180 °C). In Eq. (2), $\lambda = \Delta C_P\,\infty/\Delta C_{p0}$, where ΔC_{p0} and $\Delta C_{p\,\infty}$ are the specific heat capacity step around T_g of the uncured and fully cured epoxy. Pascault and Williams [8] stated that λ should be considered as an adjustable parameter. In this study, values of $\lambda = 0.52 \pm 0.01$ for the neat resin and $\lambda = 0.53 \pm 0.01$ for the 1 wt% doped resin have been obtained (via DSC), which is coherent with values from the literature [2,8].

2.3.2. Rheological measurements

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. Parameters of the setup geometry include a gap of 1 mm between the lower (linked to the motor) and upper (linked to the torque sensor) part, the upper cylinder having a diameter of 32 mm and a fully immersed length of 34 mm. This specific test setup was chosen in order to achieve a larger surface of contact with the sample, which enables a more appropriate range of torsional moments to be measured by the sensor device because of the low viscosity of the resin at processing temperatures. Furthermore, the amount of material being tested remains the same during the entire measurement, which is not always the case with other geometries (for example: parallel plates).

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 $8 \cdot 10^{2}$%. These measurements were performed each time for a few selected shearing frequencies: 10^{-2}; $5 \cdot 10^{-2}$; 10^{-1}; 1; 10; 80 Hz. It was chosen to record only the torsional moment (Torque) as this is the only raw data not being processed by the rheometer software. The aim was here to determine the frequency domain and strains, for which the material exhibits a linear response to the stress applied: a requirement to determine the complex viscosity $\eta^*(\omega)$. In the same way as for the cure kinetics 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 temperatures of 60 °C, 80 °C, and 100 °C for the selected strains and frequency domain, determined to ensure measurements inside the linear response domain of the material (see Section 2.2). For this second part all of the CNT content range (from 0 to 1.00 wt%) was analyzed.

2.3.3. Dynamic dielectric spectroscopy

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}–10^{6} Hz. The measurements were performed in a temperature range of −150–150 °C using a controlled nitrogen thermal regulation system (Quatro Novocontrol). The nanocomposite samples (3 mm thick) were cured 2 h at 180 °C, coated with a silver paint, and placed between two gold plated brass electrodes. 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}. The complex conductivity obtained from the complex impedance can be written as follows Eq. (3), where σ_{DC} is the direct current conductivity [9].

$$\sigma^*(\omega) = \sigma' + i\sigma'' \quad \text{with } \sigma'(\omega) = \sigma_{DC} + A\omega^s \tag{3}$$

3. Results and discussion

3.1. Cure kinetics

Fig. 1 presents four of the conversion rate (α) graphs obtained through the residual enthalpy measured (○ symbol on the graphs), and the monitoring of the T_g (□ symbol), for pristine (left-hand side of the picture) and 1 wt% CNT doped epoxy (right-hand side) at the 60 °C (top of the figure) and 100 °C (bottom) isotherms. We first notice a good agreement between results obtained following the two methods. In the graph, these results were fitted using a least square fitting method (plain line for T_g and dashed line for $\Delta H_{residual}$). A comparison to an existing model can be found later in the paper.

In Fig. 1, two noticeable stages can be pointed out. First, for short times spent on the isotherm (i.e. between 0 and 75 h at

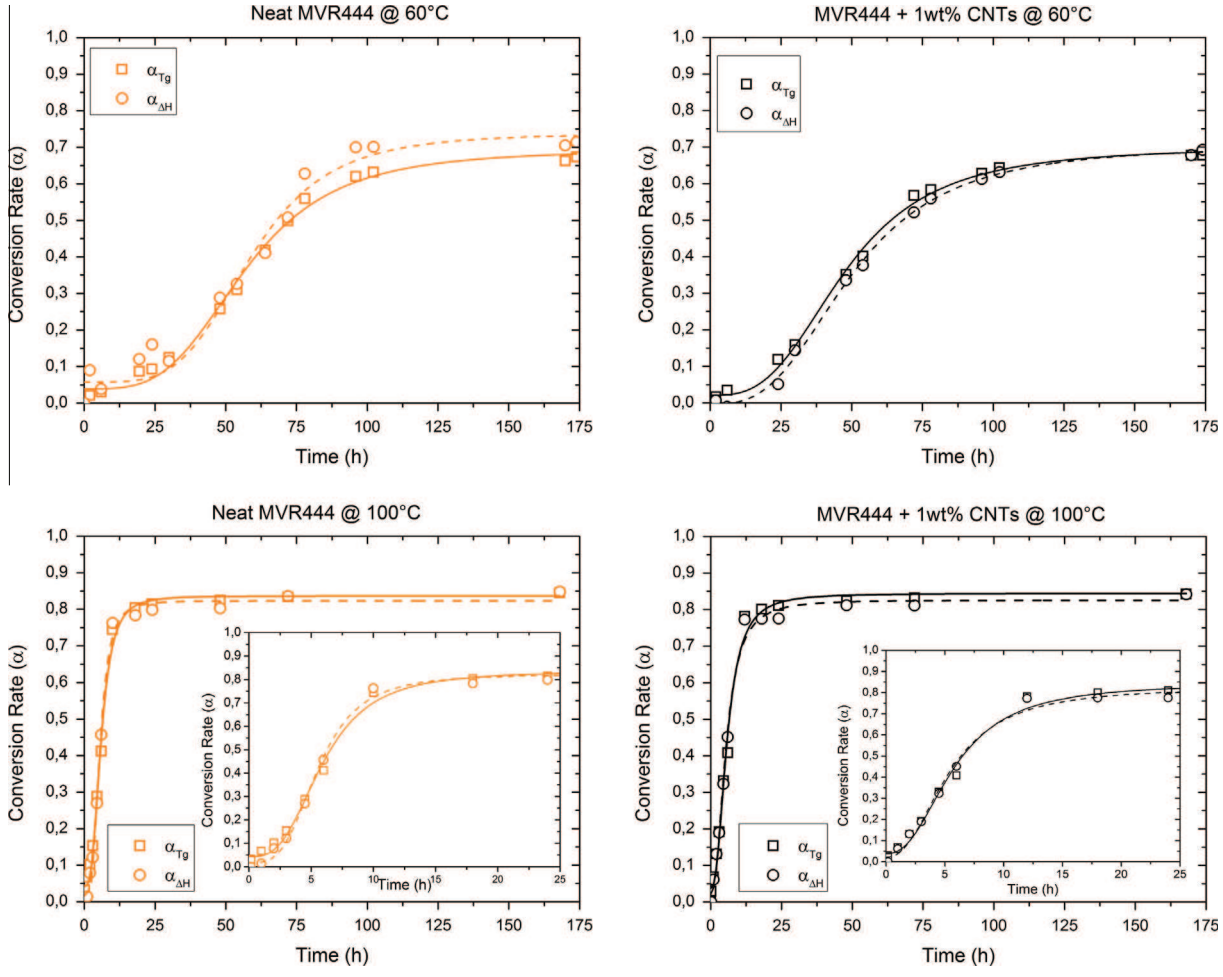

Fig. 1. Conversion rate as a function of polymerization time.

Table 2
Cure kinetics parameters for neat and 1 wt% doped MVR 444.

		m	n	k_1	k_2
60 °C	MVR 444	0.71	1.28	2.20×10^6	9.43×10^2
	MVR 444 + 1 wt% CNTs	0.70	1.36	1.24×10^3	8.57×10^2
100 °C	MVR 444	0.70	1.34	1.00×10^{18}	6.72×10^1
	MVR 444 + 1 wt% CNTs	0.62	1.43	1.00×10^{18}	5.49×10^1

60 °C and between 0 and 10 h 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 selected isotherms ($T_g > T_{isotherm}$). 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 [10]. It can be noticed that no significant influence of the CNTs on the evolution of the degree of cure could be observed.

From Fig. 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 and 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.

The cure kinetics of epoxy resins can be modeled by a few catalytic and autocatalytic phenomenological models. The cure kinetics model developed by Kamal and Sourour [11,12] is based upon both catalytic and autocatalytic mechanisms, and is the most widely used in the literature for epoxy systems [13]. This model was therefore chosen in order to model the curing kinetics of the MVR 444. It is expressed by Eq. (4).

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (4)$$

where α is the degree of cure, $d\alpha/dt$ the curing rate. k_1 is the parameter describing the rate constant of the reaction with the partial order m and k_2 is the parameter corresponding to the autocatalytic reaction with the partial order n. In this study, the four parameters of the Kamal and Sourour model have to be determined; m, n, k_1 and k_2. A least square fitting algorithm using the Kamal Sourour equation was used on both set of data (60 °C and 100° isothermal curing). We observed that the Kamal Sourour equation fits the experimental data very well. The four parameters of the model determined using this method are summarized in Table 2. The reaction orders m and n are in good agreement with the literature on epoxies [14]. We notice that these orders of the curing reaction are not influenced by the curing temperature or by the addition of CNTs. It can be noticed that for the curing at 100 °C, k_1, which is the parameter describing the rate constant of the reaction with the partial order m is almost equal to zero for both neat and CNT doped epoxy. This means that the associated reaction (the reaction of an epoxide with a primary amine producing a secondary amine) is discriminated compared to the reaction represented by k_2 (with the partial order n). The parameter n is the parameter corresponding to the autocatalytic reaction of this secondary amine reacting with another epoxy group to form a tertiary amine. It has been noticed that at 100 °C, k_2 is increased by one order of magnitude compared to 60 °C. Furthermore, at 60 °C, we notice that k_1 is increased by the addition of CNTs confirming their acceleration effect on the curing kinetics at this temperature, having an acceleration effect on this first reaction only, as no effect of the nanotubes on k_2 could be noticed.

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

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

Fig. 2 shows the strain sweeps (from 10^{-2} up to $8 \cdot 10^2$% strain) for two of the three selected isotherms (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, indicating a linear response of the material. Therefore, the material presents a linear response for the shearing frequencies from $5 \cdot 10^{-2}$ 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 (Fig. 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 $5 \cdot 10^{-2}$ to 80 Hz for both 10% and 100% strain and for all the range of temperatures considered (from 60 °C to 100 °C). However, when testing at 100 °C (Fig. 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. This nonlinear response observed can be a manifestation of either the heterogeneity of the material or a homogeneous material but exhibiting a complex mechanical response. In any case, 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.

Fig. 3 presents the real part of the complex viscosity (η') as a function of the shearing frequency (f) for the epoxy resin doped

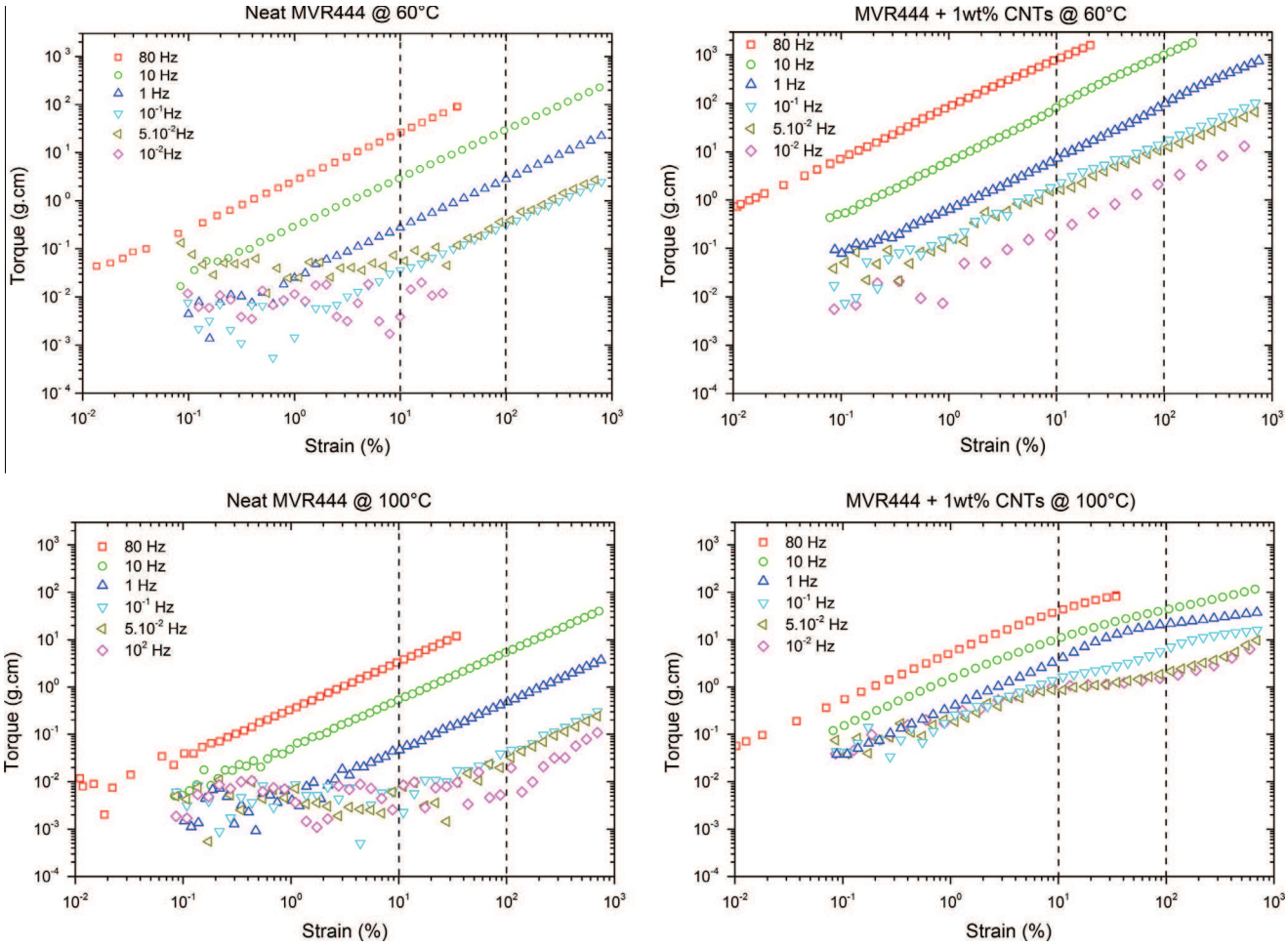

Fig. 2. Torsional moment as a function of the applied strain.

from 0 to 1.00 wt% CNTs for the three temperatures (60, 80 and 100 °C) and for a strain rate of 10% (enabling to stay inside the domain of linear response). 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%. At last for the results at T = 100 °C, 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.

To further investigate this shear thinning behavior observed, the Carreau Yasuda rheological model [15,16] (Eq. (5)) was used to fit the obtained experimental results:

$$\frac{\eta - \eta_0}{\eta_0 - \eta_\infty} = \left[1 + (\tau \cdot f)^2\right]^{\frac{n-1}{2}} \tag{5}$$

where η_0 and η_∞ are respectively the viscosity values at very low and very high shearing rates, n is the shear thinning index, characterizing the degree of shear thinning compared to a Newtonian behavior (where $n = 1$), and τ is a characteristic time of the shear thinning behavior.

For all temperatures studied, the data was fitted with this equation (see dashed lines in Fig. 3). In most cases a very good correlation of the experimental values with the Carreau Yasuda model is obtained. Only the experimental results at 100 °C seem to deviate from the theoretical model for the epoxy doped with 0.75 wt% and 1.00 wt% CNTs. For these two dispersions, as mentioned in the previous paragraph, a small "bump" can be noticed along the graph. This could be an expression of a re-agglomeration of the nanotubes. More experiments have to be done to investigate this hypothesis.

When examining the zero shear viscosity (low shearing rates: η_0) of the MWCNT doped epoxy in Fig. 3, a temperature and CNT amount dependency can be noticed. In order to make easier the investigation of this parameter, Fig. 4 presents the evolution of η_0 as a function of temperature (the dashed lines represent the linear trend followed by the experimental data). The zero shear viscosity η_0 seems to follow a different trend whether the CNT amount is below or above a critical loading (between 0.25 and 0.50 wt%). It shows a linear dependency of η_0 with the temperature T, however two different trends have been noticed. On one hand, for CNT concentrations from 0 to 0.25 wt%, η_0 decreases linearly while the temperature increases. On the other hand, for

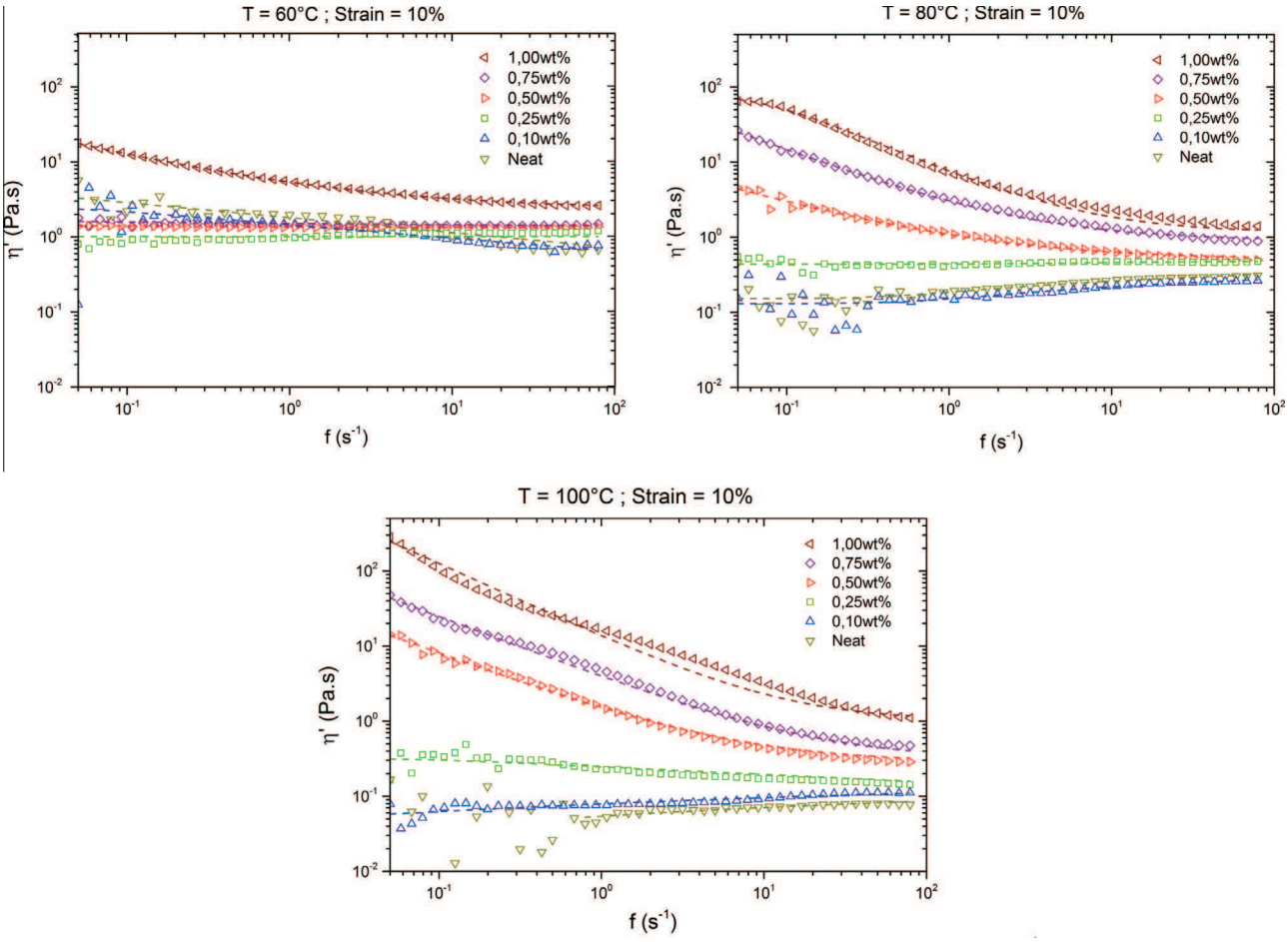

Fig. 3. Logarithmic frequency sweeps for neat and CNT doped epoxy (100 °C).

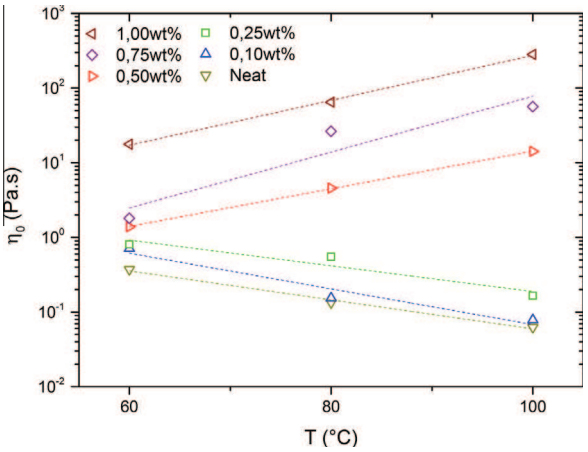

Fig. 4. Influence of the temperature on the viscosity at low shearing frequencies η_0.

CNT concentrations higher or equal to 0.50 wt%, η_0 increases while the temperature increases.

Earlier works [17–21,23] have reported that the viscoelastic properties observed are strongly dependent on the dispersion state and interactions of the nanofillers inside the polymer matrix. Pötschke et al. [17,19] suggested that the rheological behavior can be of use in order to identify the percolation threshold of CNT/polycarbonate composites. They observed that the resistivity threshold occurred in the same concentration range as the increase in melt viscosity found at low frequencies. Starting from a CNT loading of 2 wt%, the frequency dependence of the viscosity curves changed significantly and a step increase in viscosity was observed at low frequencies. In this study the percolation threshold was found at 2 wt%. Furthermore, Sumfleth et al. [20] also discussed the different percolation phenomena found in the electrical behavior of the cured epoxy/CNT nanocomposites as well as in the rheological properties of the CNT-filled suspensions. This comparison gave a comprehensive insight in the network forming process. The electrical percolation threshold of the cured samples was found to occur at lower CNT content than the percolation for the storage modulus of the uncured suspension (one order of magnitude: 0.025 vs 0.2 wt%). This was linked to the re-agglomeration process occurring during curing, which is usually promoted by high-shear forces and elevated temperature.

Based on Fig. 4 and these observations from the relevant literature, we presume that there might be a relation between the formation of the percolation network and the mechanical behavior of the CNT/epoxy suspension. In the uncured suspension, polymer chain interactions might be found (although negligible), the introduced CNT-monomer interaction and especially CNT–CNT interactions dominate and are responsible for the increase of η at low shear rates [17]. With the increase of nanofiller loading, an interconnected network structure is formed above a critical particle loading, this dense network prevents polymer chain and monomer mobility which might be the explanation of the increase in zero-shear viscosity with temperature (Fig. 4). On the other hand, below this critical particle loading, increasing temperature decreases the zero-shear viscosity as the thermal agitation promotes monomer

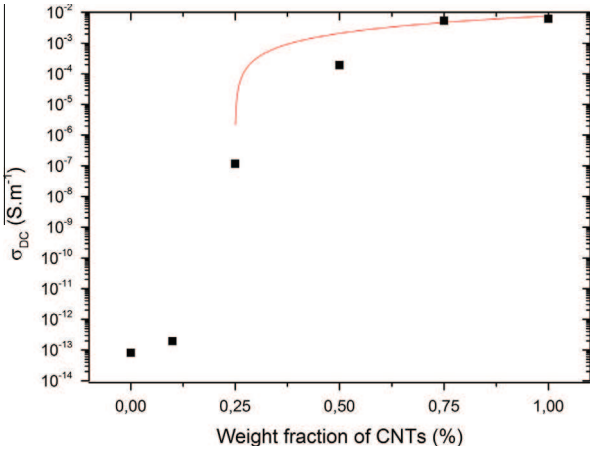

Fig. 5. Dependence of the DC conductivity on the CNTs weight fraction of MWCNTs/epoxy.

mobility in an environment where they are free to move (no CNT network obstruction). At last, in this study, a lower percolation onset in suspension could not be observed, as in Sumfleth et al. [20], which might be a manifestation of a re-agglomeration process occurring in the uncured suspensions at high CNT contents and temperature.

3.3. Electrical conductivity

Fig. 5 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 nano composite 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.

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 percolation theory [22] defines the insulator conductor transition and the corresponding percolation threshold achieved via Eq. (6):

$$\sigma = \sigma_0 (p - p_c)^t \quad for\ p > p_c \tag{6}$$

where σ_0 is a constant, p is the CNT weight fraction, p_c the CNT weight fraction corresponding to the percolation threshold and t the critical exponent. In Fig. 5, the data post percolation ($\geqslant$0.25 wt% CNTs) is fitted with Eq. (6) (solid red line). The interpolation of the experimental values leads to the determination of the above mentioned parameters: $p_c = 0.25$ wt%; $\sigma_0 = 1.07 \times 10^{-2}$ S m^1 and $t = 1.18$.

The state of dispersion of the nanotubes inside the epoxy matrix can be assessed via the measurement of the DC conductivity of the nanocomposite [22]. 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 slightly above the lowest percolation threshold achieved for these materials and dispersion process [4,5], but in the average range of what has been reported in the literature [14,24] for mechanically dispersed nanotubes, indicating that a very homogeneous, well dispersed three dimensional nanotube network was obtained.

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. It has been found that the curing kinetics at these temperatures is in accordance with the Kamal and Sourour model. 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 isotherms (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 $\geqslant$80 °C, a shear thinning behavior was observed for concentrations $\geqslant$0.50 wt% CNTs. Dispersions with concentrations $\leqslant$0.25 wt% exhibit a Newtonian behavior, as for all dispersions $\leqslant$0.75 wt% CNTs when tested <80 °C. This shear thinning behavior followed the Carreau Yasuda model. Furthermore we noticed a rheological manifestation of the percolation behavior. Indeed, we found out that the viscosity at low shearing rates seems to follow a different trend as a function of temperature, whether the MWCNT concentration is below or above the percolation threshold. Focusing on a dispersion containing 0.75 wt% 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 [25]. In this case of a shear thinning behavior, the viscosity of the dispersion in then decreased at higher shear rates 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 ration. The dispersion state of the nanotubes inside the epoxy matrix after the spraying process remains to be investigated.

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.

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References

[1] Gojny F, Wichmann M, Köpke U, Fiedler B, Schulte K. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – a comparative study. Compos Sci Technol 2004;64:2363–71.
[2] El Sawi I, Olivier P, Demont P, Bougherara H. Investigation of the effect of double-walled carbon nanotubes on the curing reaction kinetics and shear flow of an epoxy. J Appl Polym Sci 2012;126:358–66.

[3] Barrau S, Demont P, Peigney A, Laurent C, Lacabanne C. DC and AC conductivity of carbon nanotubes – polyepoxy composites. Macromolecules 2003;36:5187–94.
[4] Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, et al. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. Polymer 2006;47:2036–45.
[5] Vavouliotis A, Fiamegou E, Karapappas P, Psarras GC, Kostopoulos V. DC and AC conductivity in epoxy resin/multiwall carbon nanotubes percolative system. Polym Compos 2010;31(31):1874–80.
[6] Maillot AL, Luinge H, Schulte K. CNT modified carbon fiber Reinforced composites for aerospace applications. In: Proceedings of the 16th international conference on composite structures; 2011 June 28–30, Porto, Portugal.
[7] DiBenedetto AT. Prediction of the glass transition temperature of polymers: a model based on the principle of corresponding states. J Polym Sci. Part B 1987;25:1949–69.
[8] Pascault JP, Williams RJJ. Glass transition temperature versus conversion relationships for thermosetting polymers. J Polym Sci Part B 1990;28:89–95.
[9] Jonscher AK. The universal dielectric response. Nature (London) 1977;267:673.
[10] Puglia D, Valentini L, Armentano I, Kenny JM. Effects of single-walled carbon nanotube incorporation on the cure reaction of epoxy resin and its detection by Raman spectroscopy. Diam Relat Mater 2003;12:827–32.
[11] Kamal MR, Sourour S. Kinetics and thermal characterization of thermoset cure. Polym Eng Sci 1973;13:59–64.
[12] Sourour S, Kamal MR. Differential scanning calorimetry of epoxy cure: isothermal cure kinetics. Thermochim Acta 1976;14:41–59.
[13] Rabearison N, Jochum C, Grandidier JC. A cure kinetics, diffusion controlled and temperature dependant, identification of the Araldite LY556 epoxy. J Mater Sci 2011;46:787–96.
[14] El Sawi I, Olivier P, Demont P, Bougherara H. Processing and electrical characterization of a unidirectional CFRP composite filled with DWCNT. Compos Sci Technol 2012;73:19–26.
[15] Carreau PJ. Rheological equations from molecular network theories. J Rheol 1972;16:99.
[16] Yasuda K, Armstrong RC, Cohen RE. Shear flow properties of concentrated solutions of linear and star branched polystyrene. Rheol Acta 1981; 20:10.
[17] Pötschke P, Fornes TD, Paul DR. Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. Polymer 2002;43:3247–55.
[18] Kotsilkova R, Nesheva D, Nedkov I, Krusteva E, Stavrev S. Rheological, electrical, and microwave properties of polymers with nanosized carbon particles. J Appl Polym Sci 2004;92:2220–7.
[19] McClory C, Pötschke P, McNally T. Influence of screw speed on electrical and rheological percolation of melt-mixed high-impact polystyrene/MWCNT nanocomposites. Macromol Mater Eng 2011;296:59–69.
[20] Sumfleth J, Buschhorn ST, Schulte K. Comparison of rheological and electrical percolation phenomena in carbon black and carbon nanotube filled epoxy polymers. J Mater Sci 2010;46:659–69.
[21] Liu Y, Wilkinson A. Processing behaviour of a nanocomposite matrix for multiscale composites. In: Proceedings of the 16th European conference on composite materials; 2014 June 22–26, Seville, Spain.
[22] Stauffer G. In: Introduction to percolation theory. London: Taylor and Francis; 1985.
[23] Li J, Ma PC, Chow WS, To CK, Tang BZ, Kim JK. Correlations between percolation threshold, dispersion state, and aspect ratio of carbon nanotubes. Adv Funct Mater 2007;17:3207–15.
[24] Barrau S, Demont P, Perez E, Peigney A, Laurent C, Lacabanne C. Effect of palmitic acid on the electrical conductivity of carbon nanotubes – epoxy resin. Macromolecules 2003;36:9678–80.
[25] Barnes HA, Hutton JF, Walters K. In: An introduction to rheology. Amsterdam: Elsevier; 1989.