

PROCESSING BEHAVIOUR OF A NANOCOMPOSITE MATRIX FOR MULTISCALE COMPOSITES

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Abstract

A tri-functional epoxy resin was shear-mixed with different levels of multiwall carbon nanotubes (MWCNTs). The processability and dispersion of this nanocomposite matrix (NCM) for the formation of multi-scale composites was investigated in terms of the curing behaviour, rheology and thermal mechanical properties. NCMs suitable for the preparation of carbon fibre composites were developed. The rheological percolation limit for these epoxy-MWCNT NCMs was found to be approximately 0.1 wt. %. DMTA showed that E' was improved by 37% with the addition of MWCNT, while T_g is reduced by 8 °C at 0.5 wt. % MWCNT level.

1. Introduction

CNTs have excellent mechanical properties and are therefore expected to play an important role as a substitute for or as a complement to traditional carbon fibre (CF) composites. Multi-scale composites based on CNT are typically composed of two types of reinforcements, micro-scale fibres and CNTs, and have received significant attention in the field of advanced, high-performance materials [1]. The application of multi-scale composites can potentially offset the disadvantages of CF laminates and offers an opportunity to create multifunctional composites [2].

A common process to prepare multi-scale composites is to disperse CNTs into a resin matrix and then use the prepared NCM to produce the final composites [3]. In order to optimize the multi-scale composites, it is necessary to study the dispersion of CNTs in the NCM and the processability of the NCM. Most research in this area has focused on mixing CNTs with low viscosity epoxy resin systems, such as DEGBA based [4], with relatively few studies into epoxy resins of high-functionality, which have a much higher glass transition temperature (T_g). The main reason for this is that CNTs are difficult to disperse in high functionality epoxy resin systems due to their high viscosity.

In the present work, NCM with different MWCNT levels investigated as potential matrices for the formation of multi-scale composites. The dispersion state of MWCNTs in a tri-

functional epoxy resin was investigated using linear viscoelastic properties. The curing behavior was studied using thermal (DSC) and rheological techniques, and the mechanical properties and T_g were measured using dynamic mechanical testing.

2. Experimental

2.1 Preparation of MWCNT NCMs

A tri-functional epoxy resin triglycidyl-p-aminophenol (TGPAP, Araldite[®] MY0500) with a diamine hardener 4-Aminophenyl sulfone (4, 4-DDS, Aradur[®] 976-1) was used as the resin matrix. The MWCNTs (Nanocyl[™] NC7000 supplied by Nanocyl S.A), shown in Figure 1, were produced via the catalytic carbon vapor deposition (CCVD) process and have an average diameter and length of 7.5-9.5nm and 1.5 μ m, respectively. Six NCM systems were set with different MWCNT levels (wt. %) of; 0.0, 0.025, 0.05, 0.1, 0.25 and 0.5 wt. %.

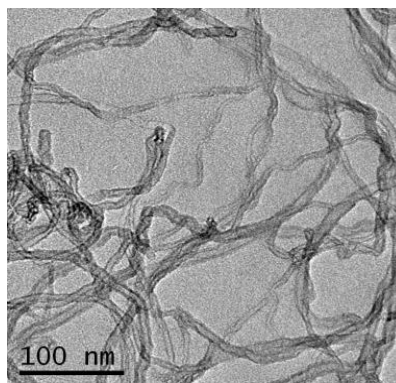


Figure 1. TEM micrographs of the MWCNTs used in this study.

To prepare the NCMs, 200mg of as-received MWCNTs were dispersed into 400mL of acetone using an ultrasonic bath (Elmasonic P70H) at a power of 650W for 1h. The solution was then left overnight to evaporate most of the acetone. The almost-dried MWCNTs were then ground using a pestle and mortar to further reduce the size of any agglomerates. Some residual acetone was retained to reduce MWCNT breakage during grinding. After grinding, the MWCNTs were dried in an oven at 80°C overnight to evaporate the residual acetone.

MWCNTs were dispersed into the TGPAP epoxy resin using mechanical stirring for 1h at 2000rpm in an oil bath at 80°C. The DDS hardener was then added into the MWCNT-TGPAP dispersion at a stoichiometry ratio of 0.71. The resin system was mechanically stirred at 130°C for 15 mins, then degassed in a vacuum oven at 130°C for 30min before being casted into a flexible mold for curing at 130°C for 1h, 150°C for 2h and 200°C for 2h.

2.2 Rheological Measurements

All rheological measurements were carried out using a Thermo Fisher MARS Rheometer equipped with a parallel plate geometry (20mm diameter and 0.5mm gap). A frequency sweep between 0.1 and 100 rad/s on the NCM system without hardener was conducted at a low controlled stress (1Pa), which is within the linear viscoelastic range (LVER), as determined by a stress amplitude sweep within the range from 0.1 to 1000Pa at a frequency of 1 Hz. The available time (or processing window) at 130°C was defined as the time for the resin viscosity to reach 30 Pa·s [5]. The processing window and viscosities at different temperatures (25°C

and 80°C) were measured using oscillatory-shear mode at a stress amplitude of 1Pa and frequency of 1Hz.

2.3 Thermal Analysis

Thermal analysis of the curing reaction was conducted by non-isothermal and isothermal differential scanning calorimetry (DSC), using a Perkin-Elmer DSC 8500. For non-isothermal scans, temperature increased from 30°C to 340°C at a scan rate of 10 °C/min. Isothermal tests were performed at three different temperatures: 150°C, 175°C, 200°C. The conversion (α) and reaction rate ($d\alpha/dt$) of the NCM systems were calculated using equation (1) and (2).

$$\alpha = \frac{\Delta H_t}{\Delta H_{iso} + \Delta H_r} \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{iso} + \Delta H_r} \quad (2)$$

Where: ΔH_t is the heat evolved up to time t, in the isothermal text; $\Delta H_{iso} + \Delta H_r$ is the total heat of reaction obtained from the isothermal scan and the dynamic scan. The degree of cure was calculated using equation (3).

$$\text{Degree of cure} = \frac{1 - \Delta H_r'}{\Delta H_{total}} \quad (3)$$

Where $\Delta H_r'$ is the residual heat measured using a non-isothermal scan after different curing times.

2.4 Dynamic Mechanical Analysis (DMA)

DMA was conducted using a Perkin-Elmer DMTA 8000. The cured samples were characterized in a dual cantilever mode at a frequency of 1 Hz. The measurement temperature ranged from room temperature to 300 °C at a heating rate of 5 °C/min.

3. Results and Discussion

3.1 Rheological Behaviour of NCMs

3.1.1 Rheological Percolation Characterization

Previous studies [6] have reported that viscoelastic properties are strongly dependent on the dispersion state of fillers and the interaction between fillers and the polymer matrix. In this NCM system, MWCNT-MWCNT and MWCNT-epoxy monomer interactions dominate and are responsible for changes in storage modulus, G' . Figure 2.a shows that G' increases with an increase of angular frequency (ω) and that the rate of increase is lower in the resin suspensions with higher MWCNT loading. G' is independent of ω in the low frequency range ($\omega < 5$ rad/s) at the MWCNT level of 0.1 wt. %, indicating elastic behaviour. At MWCNT levels of 0.25 wt. % and 0.5 wt. %, G' is totally independent of ω over the full experimental range due to the MWCNTs forming network structure.

Kotsilkova *et.al* [7] proposed that agglomerates of colloidal particles will form and as CNT content increases, these will form fractal clusters which will lead finally to the formation of an infinite network. As shown in Figure 2.b, Φ^* (~ 0.13 wt. %) depicts the MWCNT level of the formation of fractal clusters, while Φ^{**} (~ 0.15 wt. %) represents the formation of a continuous network composed of these clusters. Therefore, Φ^* is defined as the critical level, which represents the transition of the MWCNT/TGPAP NCM system from a cluster type to a network system. At this level, the particle-particle interactions among the MWCNTs are strong enough to form a percolated MWCNT network in this TGPAP epoxy resin [8].

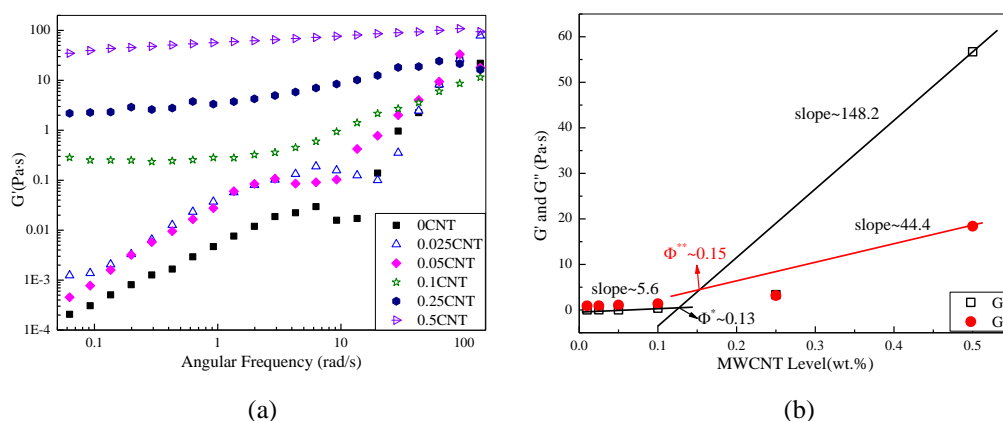


Figure 2. Rheological percolation analysis. (a), Shear storage modulus (G') data for NCM with various levels of MWCNT, showing the changes of G' along with angular frequency (ω); (b), Plot of G' and G'' at a low frequency ($\omega=1$ rad/s) versus MWCNT level for the TGPAP resin system. Linear fitting was used to measure different slopes in this graph. Point A was determined by the crossing point of the two slopes of G' , and point B was obtained by the intersection of G' and G'' [6].

3.1.2 Rheology during curing

In the processing of multi-scale composites using liquid resins, a low initial viscosity and a long gel time aids infusion of the fibre reinforcement [9]. Table.1 shows the viscosity increasing with higher MWCNT concentration. The viscosities of the NCMs are all ≥ 100 Pa·s at low temperature (25°C), which will hinder fibre infiltration. However, the NCM viscosity decreased almost 10-fold at 80°C is low enough ($\eta < 30$ Pa·s [5]) to apply to resin film infusion. For the purpose of achieving a better infiltration, the processing window was determined as the time required for the viscosity to be kept at 30 Pa·s at 130°C . As Table 1 shows, processing windows of different NCM in this work are all ≥ 50 minutes.

MWCNT concentration (%)	Processing Window at 130°C (min)	Viscosity at 25°C (Pa·s)	Viscosity at 80°C (Pa·s)
0	54.8	20	0.20
0.025	51.3	99	2.80
0.05	54.6	124	3.12
0.1	53.4	139	4.37
0.25	49.7	340	6.50
0.5	46.6	297	27.74

Table 1. Processing window and viscosity data of NCMs

3.2 Thermal Analysis

Table 2 shows the non-isothermal DSC results of NCMs with different MWCNT levels. Both the total heat of reaction (ΔH_{total}) and the exothermic peak temperature (T_p) of NCM are lower

than that of the neat resin and decrease along with the increase of MWCNT levels. The results indicates that the MWCNTs act to facilitate curing at the initial stage and lower the T_p , which can be ascribed to the extremely high thermal conductivity of MWCNT [10]. However, the addition of MWCNTs also reduced the value of ΔH_{total} , which may be indicative of a hindrance to the reaction of the epoxy resin.

MWCNT level (wt. %)	T_p (°C)	ΔH_{total} (J·g ⁻¹)	Curing Degree (%)
0	249	499	98.6
0.025	241	439	99.1
0.05	243	428	99.0
0.1	239	411	98.8
0.25	237	398	97.9
0.5	225	409	97.5

Table 2. DSC results for NCM at different MWCNT levels.

* T_g was obtained from the peak temperature of $\tan \delta$.

Isothermal DSC tests were used to study the curing behaviour and to determine the curing cycle. The NCM system with 0.1 wt. %, which is near the rheological percolation limit, was chosen to study the effect of temperatures on the curing reaction. As can be seen from Figure 3, the degree of conversion and the reaction rate increased along at higher temperature. The reaction rate reaches to a maximum of 28 min, 9 min and 4 min, whereas, the degree of cure reaches to 95.8%, 96.5% and 98.9% after 3h of curing in DSC at 150 °C, 175 °C and 200 °C, respectively. To obtain a high degree of cure and to avoid excessive exotherm, the curing cycle of NCM is determined as 130 °C 1h, 150 °C 2h and 200°C 2h. Table 2 shows that the degrees of cure of all the NCM systems under the determined curing cycle are all above 95%.

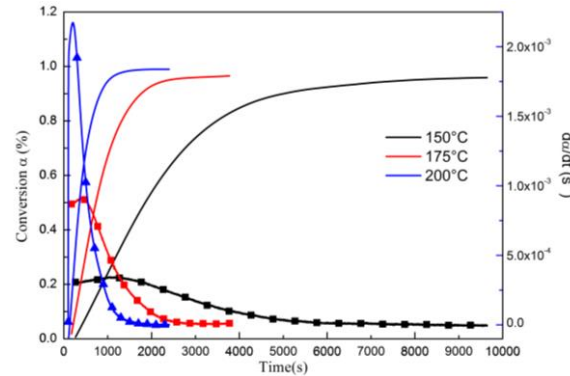


Figure 3. Overall conversion and the curing reaction rate vs time of the NCM with 0.1 wt. % MWCNTs. Calculated from DSC data showing variation at different reaction temperatures. (Conversion α : lines without symbols; $d\alpha/dt$: lines with symbols)

MWCNT level (wt. %)	150 °C		175 °C		200 °C	
	t_p (s)	t_c (s)	t_p (s)	t_c (s)	t_p (s)	t_c (s)
0	1664	8615	563.9	2678	234.8	1839
0.025	1650	8239	578.5	3591	223.6	2229
0.05	1639	8791	604.6	5989	230.5	2391
0.1	1635	7043	533.5	6028	205.0	2399
0.25	1625	7764	548.2	6036	203.7	2400
0.5	1518	8192	534.7	6238	195.0	2400

Table 3. Time to maximum reaction rate (t_p) and maximum conversion (t_c) for isothermal cure tests of MWCNT/TGPAP NCM systems at different temperatures

The time at the maximum reaction rate (t_p) and the time to reach maximum conversion (t_c) for NCM systems with different MWCNT loadings are listed in Table 3. The t_p slightly decreases at higher MWCNT level, while the t_c increases at 175°C and 200°C. It is well known that the curing reaction of an epoxy resin can be separated into two stages: chemically-controlled followed by diffusion-controlled [11]. From these data, at the beginning of the curing reaction MWCNT aids reactivity (t_p reduces). However, the existence of MWCNTs also blocks the movement of segments and hinders the curing reaction during the diffusion control stage, which leads to a delay in reaching the maximum conversion (t_c increases).

3.3 Dynamic Thermal Mechanical Properties

The effect of MWCNTs on the mechanical properties of the NCM has been studied using DMTA. In order to exclude the effect of the degree of cure on the T_g , all the samples were cured at 200°C overnight to reach the T_g infinite, which is defined as recording no obvious exothermic reaction through DSC non-isothermal testing on the cured samples. As shown in Table 4, T_g decreased by 8 °C on addition of MWCNTs up to 0.1 wt. %, after which the change in T_g was negligible. The decrease of T_g is possibly caused by two reasons: (1) the strong van der Waals force existing between MWCNTs may cause agglomerations in the crosslink network of NCM systems (as shown in Figure 4.a and 4.b), which may act as defects and provide space for chain segments to move easily [12], (2) the weak interfacial bond between the well dispersed MWCNT (as seen in Figure 4.c) and epoxy resin may cause an increase in chain segmental mobility [13]. The MWCNT level reaches a percolation limit at 0.1 wt. %, above which a further addition of MWCNT does not cause a big change in T_g .

MWCNT level (wt. %)	T_g infinite (°C)	E' (at 100 °C, MPa)	$\tan \delta$ peak	Full width at half maximum of $\tan \delta$ curve (°C)
0	256.2	4088	0.403	21.9
0.025	250.7	4820	0.481	26.7
0.05	250.4	5121	0.489	25.8
0.1	248.8	4931	0.486	23.7
0.25	249.1	5398	0.492	22.9
0.5	248.6	5623	0.511	24.9

Table 4 DMTA results for NCM at different MWCNT levels.

* T_g was obtained from the peak temperature of $\tan \delta$).

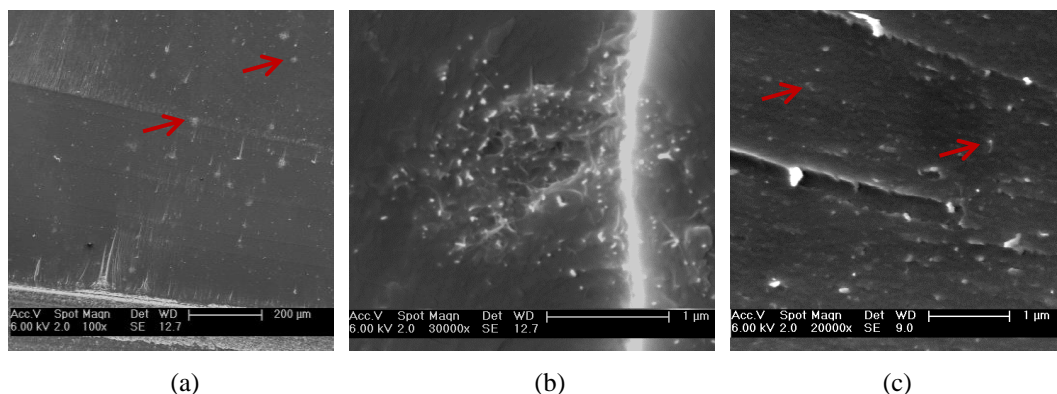


Figure 4. SEM micrographs (from a Philips XL 30) showing the dispersion state of MWCNTs in the 0.1 wt. % NCM. (a), Agglomeration of MWCNT indicated by the red arrows; (b), Close-up of an agglomerate; (c), MWCNTs dispersed in the matrix, red arrows indicate the separated MWCNTs

E' at 100°C, which represents the level of storage modulus before the glass transition region, is listed in Table.4. E' at 100 °C is seen to increase along with at higher MWCNT level. At

the MWCNT level of 0.5 wt. %, E' has increased from 4.09 GPa for the neat TGPAP epoxy resin to 5.62 GPa, an increase of 37%. Figure 5 shows the higher modulus values are maintained until the onset of the glass transition region. E' was improved more obviously in the glassy state than in the rubber state. This implies that the existence of MWCNT has a more significant effect on reducing the mobility of the polymer in the glassy state [14]. The reduced reinforcing effect of MWCNTs in the rubber state can be ascribed to the greater mobility of the epoxy resin segments at very high temperatures ($>T_g$) and the weak bonding between the MWCNTs and the epoxy resin matrix [15].

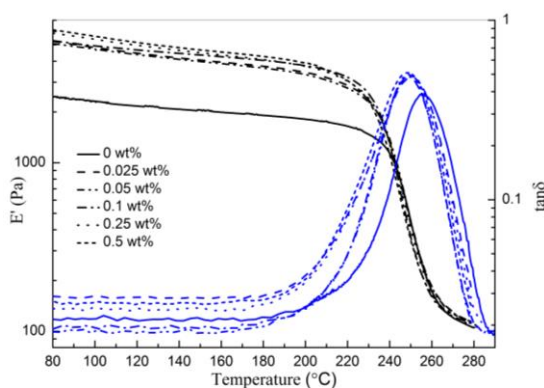


Figure 5. The storage modulus E' and loss factor $\tan \delta$ of NCMs with different MWCNT levels

The addition of MWCNT also increased the loss factor, $\tan \delta$. Similar to E' , the largest $\tan \delta$ was obtained at 0.5 wt. % ($\tan \delta = 0.511$), an increase of 33% compared to the neat resin (Table.2). With the addition of MWCNTs, the curves of $\tan \delta$ as a function of temperature shifted left (Figure 5). The full width at half maximum of $\tan \delta$ is increasing along with higher MWCNT levels (Table 4), which implies that more segments were able to move at a lower temperature. This can be ascribed to (1) the weak bonding between the MWCNTs and the epoxy resin, (2) the increasing amount of agglomerated MWCNTs [15].

4. Conclusion

In conclusion, NCM suitable for the preparation of carbon fibre composites were developed.

- Based on the isothermal DSC results and rheological data, the processing cycle for multi-scale composites was decided as preheating at 80°C for 1h, then go through curing cycle: 130 °C 1h, 150 °C 2h and 200 °C 2h. The degree of cure achieved for all the NCM systems was higher than 95%.
- Much lower resin viscosity below 0.1 wt. % NCM are observed than at ≥ 0.1 wt. % due to the formation of a percolated network. The rheological data show 0.1 wt. % addition of MWCNT to be the rheological percolation for this TGPAP/ MWCNT system.
- DMTA results show that E' was improved by 37% at 0.5 wt. % MWCNT level. T_g decreased along with higher MWCNT levels and reached a percolation limit at 0.1 wt. %. At >0.1 wt. %, the decrease is not obvious.

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