AMINO FUNCTIONALISATION OF CARBON NANOTUBE WEBS FOR ACHIEVING HIGH STRUCTURAL PERFORMANCE OF MULTIFUNCTIONAL NANO-ENHANCED HIERARCHICAL COMPOSITES

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ABSTRACT

Carbon nanotube (CNT) assemblies such as webs (CNTw) are functionalised in gas-phase reaction in order to chemically modify the CNT surface without disturbing its overall structure. It is proposed for the first time to amino functionalise CNT assemblies in gas-phase to promote bonding with epoxy matrices. Two different diamines are selected, aliphatic (ethylenediamine, EDA) and aromatic (1,5-diaminonaphtalene, DAN). The presence of the diamine molecules is confirmed by infrared spectroscopy and the amount incorporated is estimated by thermogravimetric analysis. Its influence on fracture toughness is studied using a Mode I interlaminar fracture toughness. The functionalisation of the CNTw with EDA results in an increase in G_{IC} of 20 % while the same procedure with DAN gives no improvement. This different observed behaviour is due to the different temperature required to activate the diamines to react with the epoxy rings of the epoxy system, as seen by differential scanning calorimetry.

1 INTRODUCTION

Carbon fibre reinforced polymer (CFRP) epoxy composite laminates are increasingly used in aircraft aerostructures because of their superior specific strength and stiffness, and excellent fatigue and corrosion resistance. Nevertheless, their relatively poor through–thickness strength and toughness make them susceptible to delamination under relatively low–energy impact events [1]. In order to improve the interlaminar matrix–dominated properties of structural composites, carbon nanotubes (CNTs) are considered since they can stiffen, strengthen and toughen polymer matrices [2] while providing electrical and/or thermal conductivity [3] for negligible extra weight.

It has been observed that the Mode I interlaminar fracture toughness of CFRPs can be improved by the incorporation of CNT assemblies, such as vertically-aligned CNT 'forests' [4, 5]. The use of aligned CNT webs (CNTw) oriented perpendicular to the crack growth direction in the plane of the crack surface has also been shown to improve the Mode I fracture toughness in glass fibre laminates [6]. In addition, several reports have demonstrated that the functionalisation of CNTs can improve the load transfer between the matrix and the reinforcing phase and, consequently, the mechanical properties of the composite [7, 8]. Functionalisation with amino groups is ideal for epoxy systems since amines can be part of the crosslinking reaction during curing [8].

The aim of the present work was to determine whether interlaminar fracture toughness (ILFT) of CFRP could be significantly improved using functionalized CNTw. Retention, if not significant increase, of the ILFT is essential to allow the CNT materials to be utilized within a CFRP for a variety of purposes such as hierarchical structural reinforcement using conventionally thick, thin, ultrathin and nano-plies; for electro-thermal functions such as anti-icing / de-icing and thermal management; and for structural health monitoring.

The CNT web was directly drawn from a specially grown highly aligned CNT forest and functionalised in a solvent-free gas phase reaction [9] with an aliphatic diamine (ethylenediamine, EDA) or an aromatic diamine (1,5-diaminonaphtalene, DAN) (Fig 1).

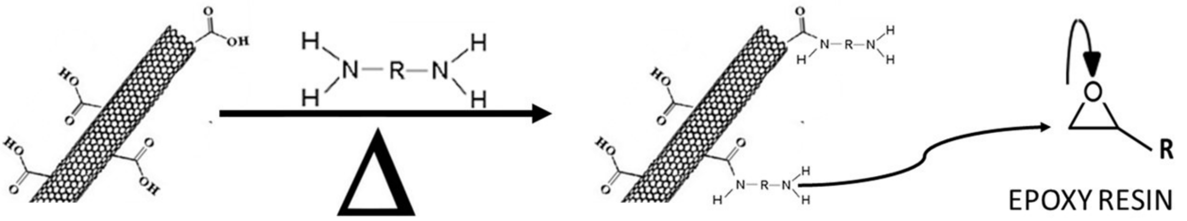

Figure 1: Schematic of the functionalisation process; (left) solvent-free gas phase proposed reaction with CNTs; (right) amino functionalised CNTs react with the epoxy rings of the resin.

The presence of the amines on the surface of the CNTw was demonstrated by infrared spectroscopy while the amount incorporated was estimated by thermogravimetry. The effect of the amino functionalisation on the mechanical properties of a nano-enhanced hierarchical composite was studied by testing the Mode I fracture toughness of a CF/epoxy composite. The fracture surface was studied by scanning electron microscopy and the different observed mechanical behavior was related to the chemistry of the diamines by differential scanning calorimetry.

2 MATERIALS AND METHODS

2.1 Materials

Carbon nanotube webs (CNTw) were directly drawn from highly aligned CNT forests, produced by Chemical Vapour Deposition based on a reported process [10] using silicon wafer bearing 50 nm of thermal oxide and 2.5 nm of e-beam deposited iron. The reaction uses a gas mixture (1 slm for a 42 mm id quartz reactor, 5 slm for a 95 mm id reactor) of acetylene and hydrogen (each 2.5%) in helium at ambient pressure and 690 ºC for 12 minutes. The nanotubes are typically about 300 µm long and 10 nm diameter with an average of 6 walls.

Ethylenediamine (EDA) and 1,5-diaminonaphtalene (DAN) were used as received form Sigma-Aldrich.

A unidirectional carbon fibre/toughened epoxy resin prepreg system (HMC/Gurit SE84LV) was selected to test the performance of the CNTw, both pristine and amino functionalized, under Mode I fracture toughness test conditions [11].

2.2 Sample preparation

A carbon nanotube web of 60 mm width was drawn directly from the substrate supported-forest and wound onto aluminium frames (arranged as four faces around an axis each with 70 mm clear length) to a thickness of 10 layers, with an aerial density of 0.2 $g \cdot m^{-2}$. The CNTw on each frame was secured with polyimide tape and, thus stabilised, used in functionalisation experiments. Neither the aluminium nor the polyimide tape showed degradation after the functionalisation treatment.

The amine functionalisation was carried out by placing 5 mg of an amine into a glass receptacle underneath the CNTw (~ 0.8 mg) in a glass reactor tube within a clamshell furnace. The tube was sealed and evacuated to -100 kPa to maximise the vapour phase concentration of the amines. The reactor was heated to 180 ºC for EDA (bp_{760} 118 ºC) or 200 ºC for DAN (bp_5 200-210 ºC) at a rate of ~ 8 $ºC·min^{-1}$ and held for 2 h. The reactor was purged with pure nitrogen N_2 (~ 94 sccm) and cooled naturally before opening. Unreacted diamine was deposited on the cold ends of the glass reactor, as previously observed by Basiuk et al. [9]. The functionalised CNTw were stored in a desiccator until they were used to prepare samples for the Mode I double cantilever beam (DCB) test. To achieve the required thickness (3-5 mm, ASTM D5528) for the test specimens, 12 plies of unidirectional HMC/Gurit SE84LV (0.297 mm nominal cured ply thickness) were used, with a 13 µm thick PTFE film insert between the 6th and 7th plies to form the pre-crack. The amino functionalised CNTw was then placed contiguous with the PTFE film and aligned at 90º to the CF. The laminates were cured at 120 ºC for 1 h under dynamic vacuum, as recommended by the manufacturer.

2.3 Characterization

The CNTw samples were analysed by means of Fourier transform infrared spectroscopy in total attenuated reflection mode (FTIR-ATR, Spectrum 100 FT-IR Spectrometer, Perkin-Elmer) in the 600-3000 cm^{-1} range, with a resolution of 4 cm^{-1}. For each sample ten scans were used to obtain each spectrum and background was subtracted from all spectra.

Thermogravimetric analysis (TGA, TGA/SDTA851^e, Mettler Toledo) of the CNTw in synthetic air (N_2 + O_2) from ambient to 1000 ºC at 10 $ºC·min^{-1}$ was used to estimate the amount of diamine present on the surface of the CNTw since these organic molecules are decomposed at lower temperature than the CNTs. In order to improve the signal to noise ratio, three CNTw were used for each single run.

For each sample, at least eight DCB specimens were tested using an Instron 5564 Universal Testing Machine in tensile mode at a cross head displacement rate of 1 $mm·min^{-1}$ and the crack length was tracked with a microscope-camera.

Fractography analysis of the fresh fractured surfaces was conducted by means of a Scanning Electron Microscope (SEM, Flex SEM 1000, Hitachi) at a voltage of 5 kV.

The effect of the different diamine molecules on the curing temperature of the Gurit SE84LV system was studied by means of differential scanning calorimetry (DSC, DSC-6, Perkin-Elmer). Two discs, ~ 4 mm diameter, of the HMC/Gurit SE84LV were cut (~ 20 mg) and placed in the DSC pan with ~ 2.5 mg of the corresponding diamine in between. The test was run from 30 °C to 350 °C at a rate of 10 $°C·min^{-1}$.

3 RESULTS AND DISCUSSION

3.1 Amino functionalisation of carbon nanotube web

The FTIR-ATR spectrum of the pristine CNTw (Fig 2) shows only weak bands such as the stretching of the C=O carboxyl bond [12-14] or the C=C bond adjacent to oxygenated groups at around 1740 cm^{-1} and 1580 cm^{-1} respectively [15-17]. In addition, in the 1350-1450 cm^{-1} region other weak absorption bands can be observed. This is the region where CH_2 and CH_3 groups vibrate, indicating the presence of a small amount of adsorbed hydrocarbon or amorphous carbon [18]. The amino functionalized CNTw shows an intense new band at ~1070 cm^{-1} assigned to C–N stretching [19] and a small peak at ~1250 cm^{-1} due to the N–H bending [13]. Overlapped with the frequency at which C=C bonds near oxygenated groups vibrate, a weak new band at ~1534 cm^{-1} assigned to the bending of the N–H bonds is observed. Finally, the stretching of the C=O bond can also be seen as well in the amino functionalised spectra at the frequency where the carboxylic group is assigned [13, 14].

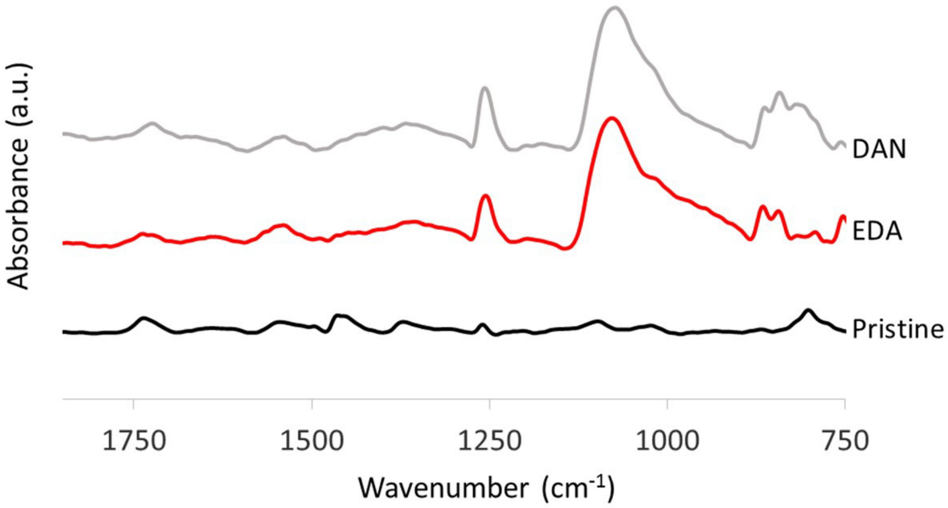

Figure 2: FTIR-ATR of pristine and amino functionalised CNTw.

The reaction of the amino groups with the carboxyl forms an amide group. This reaction causes a shift of the C=O stretching from 1720-1730 cm^{-1} in the carboxyl group to 1620-1650 cm^{-1} in the amide [14]. The absence of this shift indicates that most of the diamine molecules detected by TGA and FTIR-ATR are physisorbed on the CNTw surface rather than attached to the CNTs by a covalent bond.

The TGA of pristine CNTw (Fig 2) shows a slight loss of 2.9 wt. % up to about 300 °C which may be attributed to the loss of adsorbed water or other gases. The CNTw is then stable to about 600 °C. This first weight loss is not observed in the functionalised CNTw as they have undergone heating under vacuum and then desiccator storage. The weight loss observed in the range 300-550 °C was due to the presence of the amine and was used to estimate the mass of amine groups added to the CNTw (Table 1). It is noteworthy that the total mass incorporated is quite similar although this corresponds to a significantly different equivalence of NH_2.

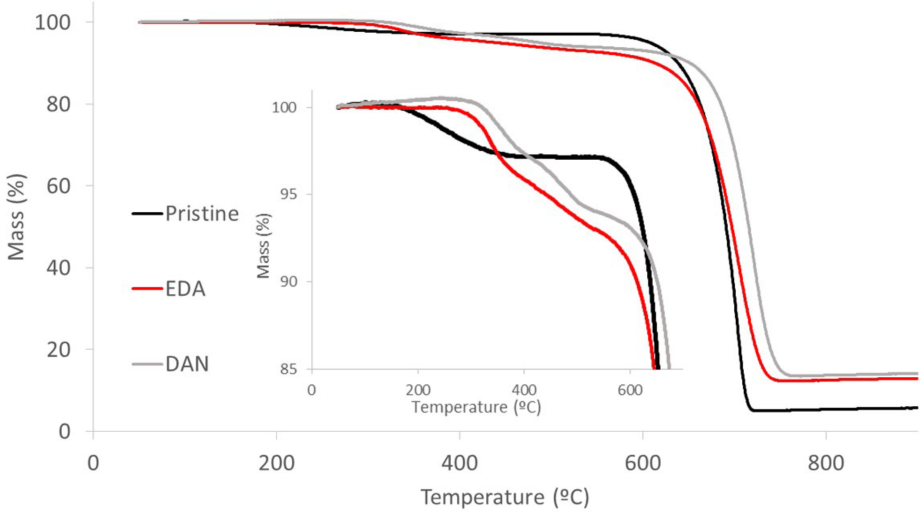

Figure 3: TGA of pristine and amino functionalised CNTw.

CNTw	H_2N-R-NH_2 incorporated	eq. NH_2/g
EDA	7.25 wt. %	$2.4 \cdot 10^{-3}$
DAN	6.54 wt.%	$0.8 \cdot 10^{-3}$

Table 1: Amount of diamine incorporated (wt. %) and the corresponding NH_2 equivalence per gram.

3.2 Mode I fracture toughness of the nano-enhanced hierarchical composites

The Mode I DCB analysis of the CFRP composite modified with pristine CNTw showed a 4% increase in G_{IC} fracture toughness compared with the control, while insertion of the EDA functionalized CNTw gave a 20% improvement (Table 2). In contrast, the use of CNTw functionalized with DAN did not result in a statistically significant improvement. The p-value of all the observations through analysis of variance test (ANOVA) is 0.0008. Hence, the improvement in critical strain energy release rate is very significant.

Composite	G_{IC} prop ($J \cdot m^{-2}$)	% change in average	Number of specimens
Control	348 ± 22	–	8
Pristine	362 ± 29	+ 4	12
EDA	418 ± 41	+ 20	9
DAN	351 ± 50	+ 1	9

Table 2: G_{IC} obtained from Mode I fracture toughness test of HMC/SE84LV DCB specimens with pristine and functionalised CNTw at the crack interface (p-value = 0.0008).

SEM analysis of the fracture surface of the Mode I HMC/Gurit SE84LV control and all CNTw modified samples showed the expected pattern of carbon fibre bridging, breakage and pullout as well as other typical characteristics of delamination in toughened epoxy matrices such as scarps and ribbons (Fig 4a-d, left, centre, right).

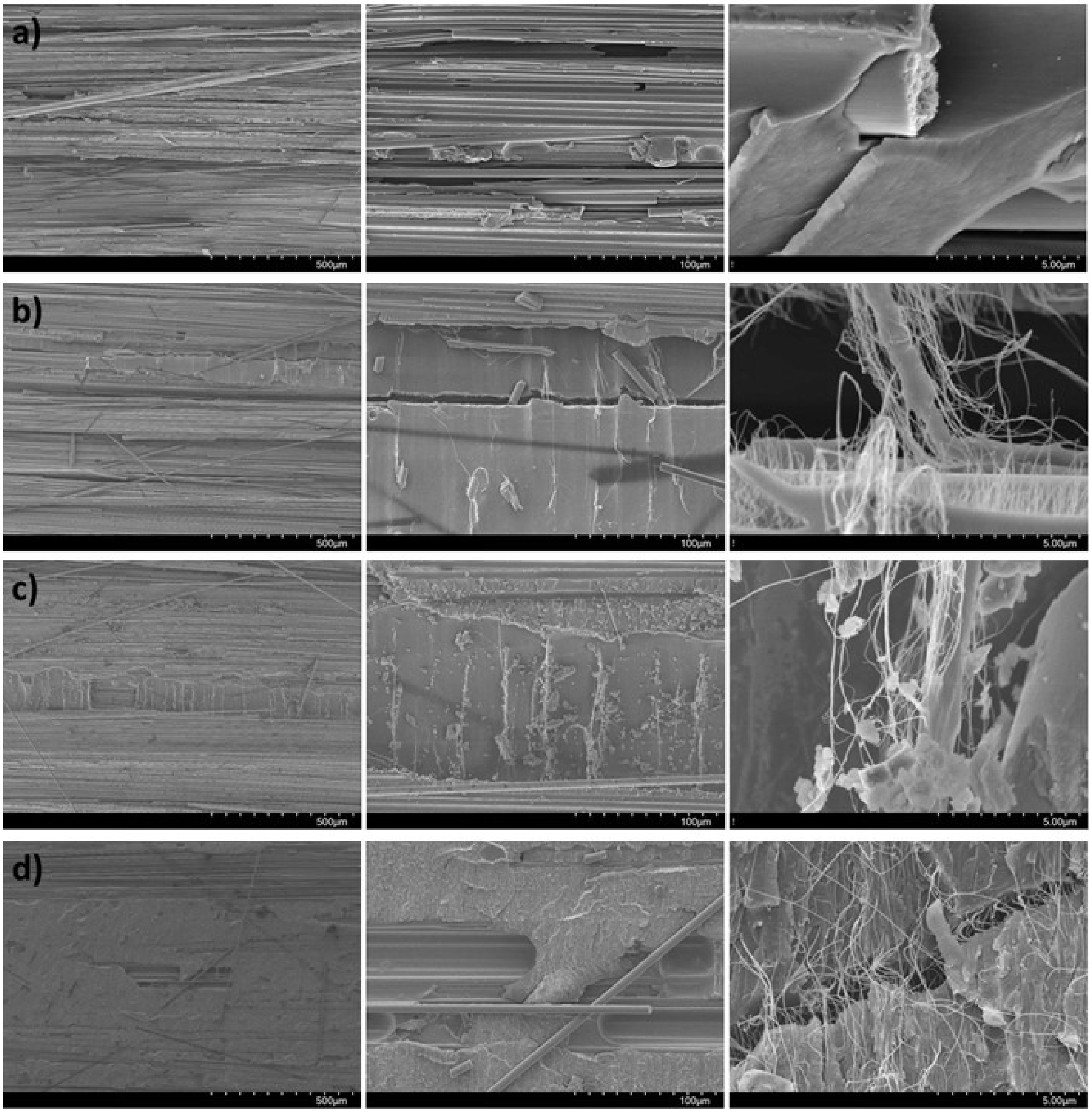

Figure 4: SEM images of the fracture surface of HMC/SE84LV (a), reinforced with pristine CNTw (b) EDA treated CNTw (c) or DAN treated CNTw (d).

When compared with the control samples (Fig 4a, l,c,r) the pristine CNTw-modified sample reveals significant crack diversion away from the CNT- reinforced plane as well as crack bridging by the CNT component, with some involvement of the thermoplastic toughening agent in the resin (Fig 4b, l,c,r)). Functionalization with EDA (Fig 4c) produces a dramatic change, with clear evidence again of crack diversion and crack bridging but also of enhanced resin – CNT interaction (Fig 4c c,r). The CNTs are decorated with numerous resin fragments and there is substantially more resin debris. The diversion and additional fracturing and involvement of the thermoplastic component are all mechanisms to dissipate fracture energy and hence to increase the ILFT of the composite. The CNTw treated with DAN in contrast (Fig 4d l,c,r) shows only some crack diversion but no involvement of the CNTs surrounding the thermoplastic component, indicating that the DAN both fails to contribute to the CNT resin interaction and indeed eliminates the interaction achieved by the pristine CNTw.

The sensitivity of the G_{IC} ILFT to the type of amine used in functionalisation could be due to the difference in the number of amine groups present; to the nature of the binding interaction of those species with the CNT surface and the overlying resin; or to the different reactivity of the aliphatic and aromatic species. At around 7% (Table 1), the mass of amine bound to the CNT surface is approximately the same for both EDA and DAN, however the lower molecular weight of the former means that there are roughly three times as many amine groups present. Given the 20% improvement in G_{IC} for EDA, a proportionate effect would produce an approximately 7% improvement in G_{IC} for DAN rather than the 1% observed (Table 2).

As the CNTs used are approximately six walls in thickness, the outermost and only accessible wall comprises about 20% of the total CNT mass. A 7% addition of amine therefore equates to approximately 35% of the outer wall mass, or close to a molecular monolayer, and clearly very much more than could be covalently bound to it. This and the evidence from TGA and FTIR-ATR support the view that the interaction is one of physisorption. The rigid aromatic DAN is likely to align strongly with the surface of the CNTs to maximize pi-pi interactions and thus make the amine groups less accessible for reaction. This effect may go further in blocking the interaction of the resin with the CNT surface and eliminating any benefit. The alkyl EDA, less strongly bound and also more flexible, would thus be more available to the surrounding epoxide, with some possibly even diffusing locally to create a micro/nano environment.

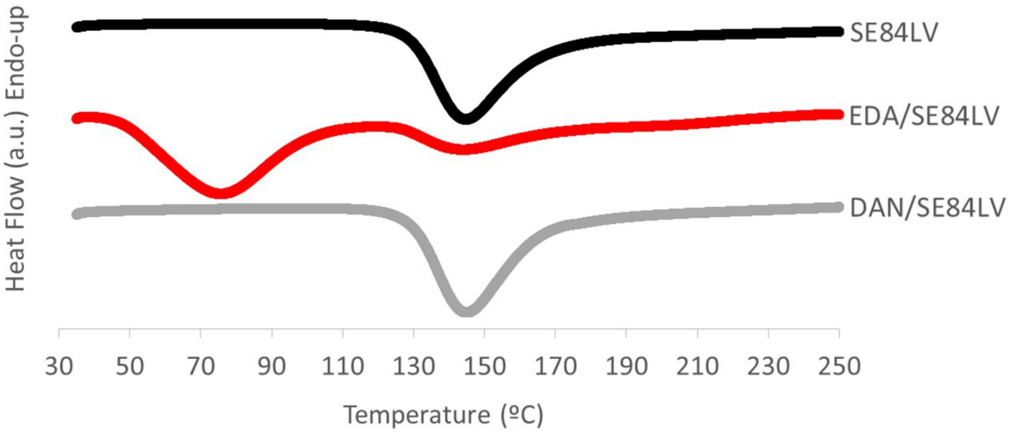

Figure 5: DSC of the pristine HMC/SE84LV system and with EDA and DAN

The different reactivity of alkyl and aryl amines may also be responsible for the different performance of EDA and DAN. A DSC analysis of the HMC/SE84LV system alone shows (Fig 5) a single exotherm starting at 120 °C which is the recommended curing temperature. When the EDA is present, a new exotherm due to its reaction with the epoxide and starting at ~ 40 ºC is observed. The normal curing reaction of the SE84LV system, less pronounced due to the earlier reaction of the EDA is still evident. In contrast, when the SE84LV is in contact with the same amount of DAN, the DSC is essentially unchanged from the control, indicating the DAN is having no effect on the curing. Thus, it can be seen that the DAN requires a temperature above the temperature at which the SE84LV system cures and explains the lack of mechanical reinforcement when DAN functionalised CNTw is used in this epoxy system.

4 CONCLUSIONS

The amino functionalisation of CNTw in gas-phase reaction has been proved as an effective method to increase the chemical interactions between the CNTs surface and the epoxy matrix, without disturbing the orientation of the CNTw. Using such gas-phase functionalisation the average G_{IC} was enhanced by 20%. The type of diamine molecule used has been proved to be a key factor, since the temperature at which it is activated for the epoxy ring opening reaction depends on it. Through DSC it has been demonstrated that the ethylenediamine functionalised CNTw reacted with the SE84LV epoxy system, and the reinforcing mechanism has been observed by fractography. In addition, DSC has been proved as a useful tool to forecast the behavior of an amine with a selected epoxy system. This way, amino functionalisations can be tailored for selected epoxy systems.

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