Tailored SWCNT functionalization optimized for compatibility with epoxy matrices

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Abstract

We have modified single walled carbon nanotubes (SWCNTs) with well defined matrix-based architectures to improve interface interaction in SWCNT/epoxy composites. The hardener and two pre-synthesized oligomers containing epoxy and hardener moieties were covalently attached to the SWCNT walls by in situ diazonium or carboxylic coupling reactions. This way, SWCNTs bearing amine or epoxide terminated fragments of different molecular weights, which resemble the chemical structure of the cured resin, were synthesized. A combination of characterization techniques such as Raman and infrared absorption (FTIR) spectroscopy, elemental analysis and coupled thermogravimetry-FTIR spectroscopy were used to identify both functional groups and degree of functionalization of SWCNTs synthesized by the laser ablation and arc-discharge methods. Depending on the type of reaction employed for the chemical functionalization and the molecular weight of the attached fragment, it was possible to control the degree of functionalization and the electronic properties of the functionalized SWCNTs. Improved dispersion of SWCNTs in the epoxy matrix was achieved by direct integration without
using solvents as observed from optical microscopy and rheology measurements of the SWCNT/epoxy mixtures. Composite materials using these fillers are expected to exhibit improved properties while preserving the thermosetting architecture.

1. Introduction

Carbon nanotubes (CNTs) are currently regarded as promising nanoscale fillers for polymer composite materials. Their low density, high aspect ratio, and extraordinary mechanical, electrical and thermal properties make them a perfect candidate in applications where a weight reduction is crucial, such as in aerospace and automotive composites. As a result, significant effort has been oriented towards investigating new ways of processing CNTs to improve their integration into polymer matrices. This need is spawned by the existing drawbacks of pristine CNTs which hinder their true potential as polymer reinforcement, i.e. poor dispersion/exfoliation and poor interface compatibility with matrices. It is in this context where covalent functionalization comes into play. According to a recent review paper [1], more than three quarters of the latest research papers on polymer-CNT composite materials feature covalent functionalization of CNTs prior to their integration. Covalent bonds between chemical species and CNTs are usually achieved during purification and/or specific functionalization processes, and help improve CNT compatibility with the matrix. In some cases, functionalization drastically improves the filler-matrix adhesion, particularly when CNTs are functionalized with a matrix-reactive moiety [2,3].

Epoxy resins are the most extended thermosetting material and widely used for structural applications, coatings, and adhesives. There is extensive literature reporting on preparation and properties of composite materials based on CNTs and a variety of epoxy systems, which almost all consist of diglycidyl ether of Bisphenol-A (DGEBA). Since the curing reaction between the epoxy monomer and the hardener, usually a diamine, leads to a highly crosslinked material, many authors have reported amine covalent functionalization as a way to improve both CNT integration and epoxy physical properties. In this context, a new concept is emerging with respect to covalently aminated CNTs as fillers for epoxy composites, which is based on the chemical functionalization of CNTs with a hardener. This molecule would be anchored to the CNT surface through one of its amine groups while the rest would be available for further reaction with the epoxy matrix. Within this field of
research, triethylenetetramine (TETA) [4], a classical curing agent for epoxy monomers, has been most extensively used. The aliphatic nature of this alkylamine leads to its reaction by classical amidation of carboxylated CNTs, which are generally created after acid treatments. Yang et al. [5,6] integrated TETA-functionalized multi walled carbon nanotubes (MWCNTs) into a DGEBA-based epoxy system. They observed a better dispersion in organic solvents, which led to a more homogeneous distribution of the filler in the matrix and consequently, to better bending and impact properties, as well as improved thermal behaviour (decomposition and glass transition temperatures) with respect to the neat matrix and the composites with unfunctionalized MWCNTs. Other similar works with MWCNT-TETA [7,8] also demonstrated better impact resistance and thermal properties, again caused by a better integration due to an improved solvent miscibility. With respect to the synthesis of other hardener functionalizations for epoxy composites, similar results have been found for classical curing agents such as ethylenediamine [9-11], 1,6-diamine hexane [10,12], and others [10,13-17].

The cited works mostly deal with MWCNTs and amidation reactions since the used hardeners are predominantly alkylamines and the CNTs are carboxylated during acid purification treatments. In contrast, Wang et al. [13] investigated the grafting reaction of an arylamine-based curing agent to single walled carbon nanotubes (SWCNTs) using the in situ diazonium reaction [18]. Through this grafting route, the SWCNT-hardener covalent functionalization caused an improvement in the elastic modulus of the neat (DGEBA-based) epoxy matrix as well as a reduction of the glass transition temperature. In this case, the integration was also carried out by solvent participation, using the functionalization to improve solvent miscibility. In addition to an increase in the solubility in organic media, the chemical similarity between hardener moieties and the epoxy system should also provide a better direct miscibility of CNTs with the resin, which could reduce or eliminate the use of organic solvents and all their related inconveniences [19,20], potentially resulting in better properties.

In comparison to low molecular weight moieties, the addition of entire molecular chains to the CNTs wall is expected to have a more pronounced influence on the CNTs properties and their affinity to polymer matrices as compared to the addition of low molecular weight functionalities [21]. Although the molecular structure and molecular weight of amines is known to have a noticeable influence on the extent of CNT functionalization [22], these parameters have not been explored yet in the hardener functionalization strategy as all the aforementioned research deals with the bare hardener molecule only. In the present paper we report the covalent functionalization of SWCNTs with different matrix-based chemical species using two common approaches: classical amidation and
in situ
diazotization. SWCNTs produced by different methods have shown different reactivity towards chemical reactions where smaller diameter, more strained SWCNTs react more readily than larger diameter SWCNTs [23,24]. In this study we use SWCNTs with similar diameter distribution produced by two different methods: arc-discharge and laser ablation. Targeting the aerospace-grade multifunctional epoxy resin triglycidyl p-aminophenol (TGAP), the curing agent 4,4’-diaminodiphenyl sulphone (DDS) and two higher molecular weight pre-synthesized oligomers containing epoxy-hardener monomers were covalently attached to the SWCNT sidewalls. This way, SWCNTs bearing amine and/or epoxide containing fragments of different molecular weights and structures resembling the chemical structure of the cured resin are successfully synthesized. Using this functionalization approach the chemical structure of the attached fragment is of the same nature as the epoxy matrix of interest. Hence, the chemical composition at the SWCNT/matrix interface should be almost identical to the target epoxy matrix. This strategy should allow an improved interaction with the matrix of interest without changing the chemical composition which would cause a heterogeneous crosslinking at the SWCNT/epoxy interface [25]. The functionalization processes and the extent of the different reactions were carefully analyzed for both types of SWCNTs. The functionalized SWCNTs were directly incorporated in the epoxy resin without using solvents. The SWCNT resin miscibility was evaluated by monitoring the dispersion with optical microscopy and rheological measurements. This versatile and tuneable functionalization approach may offer new perspectives for the epoxy-based composites field.

2. Experimental

2.1. Materials and reagents

SWCNTs synthesized by the laser ablation method (L-SWCNT) and by the arc-discharge method (A-SWCNT) were used without additional purification. The former ones were synthesised using an improved laser-oven method [26], while the latter ones were produced by the large-scale arc discharge SWCNT production [27] using a Ni/Y catalyst at 4/1 atomic ratio. A detailed characterization of these materials can be found in the supporting information (Table and Figure S1). These two materials have a similar diameter distribution but different length, purity and initial degree of defects. The epoxy resin triglycidyl p-aminophenol (TGAP) with the trade name of Araldite MY0510 and the hardener 4,4’-diaminodiphenyl sulfone (DDS) were supplied by Huntsman.
International (Scheme 1).

Scheme 1. Chemical structures of epoxy precursor and hardener.

All other chemicals were purchased from Sigma-Aldrich and used as received without further treatment. Bath sonication (Branson 3510, 45 kHz) and ultrasonic probe sonication (Hielscher DRH-P400S, 400 W maximum power, 24 kHz maximum frequency at 60 % amplitude and 50 % cycle time) were employed as indicated below. Hydrophilic PTFE membranes (0.1 μm pore size, 47 mm diameter) were used for vacuum filtration.

2.2. Synthesis of the TGAP-DDS amine terminated derivative (AD)

In order to synthesize an oligomer containing free primary amine groups, DDS and TGAP were mixed following a procedure similar to the curing protocol of this epoxy resin but using an excess of DDS. 1 equivalent of epoxide and 5 equivalents of NH were mixed at 100 ºC under magnetic stirring while the temperature was increased to 150 ºC at a rate of 2 ºC/min. After 40 min at 150 ºC the mixture gelled and the transparent dark-yellow solid was ground in an agate mortar. Thin layer chromatography (TLC) of the solid dissolved in N,N-dimethylformamide (DMF) indicated that all the TGAP had been consumed. The presence of free DDS was also detected, which was extracted with methanol through several washing cycles. The final product, a pale-yellow powder, was dried overnight under vacuum at room temperature and then characterized.

2.3. Synthesis of the DDS-TGAP epoxide terminated derivative (ED)

In order to synthesize an oligomer containing free epoxide groups, DDS and TGAP were mixed together in a ratio of 1:1.5 of amine to epoxide. In a typical experiment 5 g of TGAP and 2 g of DDS were mixed with magnetic stirring at 100 ºC until the DDS was completely dissolved and the mixture was kept at 140 ºC for 3
hours. Before cooling to room temperature, 20 mL of DMF was added to the viscous mixture to dissolve the product and avoid gelification. This solution was characterized and used without further purification as a reagent for SWCNT functionalization.

2.4. **SWCNT functionalization with DDS (SW-DDS)**

This functionalization procedure is based on the diazonium reaction developed by Bahr et al. [18] DDS was used as the primary arylamine for the *in situ* generation of the diazonium salt. In a typical experiment, 100 mg of as-grown SWCNTs (8.3 mmol C approximately) was suspended in 75 mL of DMF with the aid of bath sonication for 1 h and ultrasonic probe sonication for 30 min. Separately, 2.4 g of DDS (10 mmol) was slowly dissolved in 25 mL of acetonitrile and degassed with argon for 5 minutes. The SWCNT suspension and the arylamine solution were mixed in a vial under constant magnetic stirring, keeping the temperature at 60 °C. Then, 1 mL of isoamyl nitrite (7.4 mmol) was added to the mixture and the vial was partially sealed, leaving a small slit to prevent overpressure due to nitrogen evolution. The reaction was kept at 60 °C overnight. The product was vacuum filtered and washed with DMF until the liquid filtrate was colorless, and then rinsed with anhydrous diethyl ether to remove DMF.

2.5. **SWCNT functionalization with the AD derivative via diazonium reaction (SW-AD)**

The same procedure used for the synthesis of SW-DDS samples was followed. In this case 500 mg of the arylamine AD dissolved in 25 mL of DMF and 200 μL of isoamyl nitrite were used to functionalize 100 mg of SWCNTs.

2.6. **Synthesis of epoxide functionalized SWCNT (SW-DDS-ED)**

100 mg of SWCNTs functionalized with the DDS hardener (SW-DDS) was suspended in 60 mL of DMF using bath sonication for 30 min and ultrasonic probe sonication for 15 min. Then the previously synthesized epoxide derivate ED derivative dissolved in 20 mL of DMF was added and the mixture refluxed at 130 °C with magnetic stirring. After refluxing for 5 hours the product was precipitated in methanol, vacuum filtered and washed with DMF and anhydrous diethyl ether.
2.7. Acid functionalized SWCNT (SW-GAP)

SWCNTs were derivatized with butyric acid moieties by reaction with glutaric acid acyl peroxide (GAP) using the ported rapid functionalization method reported [28]. In a typical reaction, 100 mg (8.3 mmol C approximately) of SWCNTs was suspended in 100 mL of dry THF using bath sonication for 1 hour and ultrasonic probe sonication for 15 min. Then, 92 mg (4 mmol) of sodium and 513 mg (4 mmol) of naphthalene were added to the suspension, under nitrogen. A green mixture was formed and the suspension was stirred overnight, providing reduced SWCNTs. About 6 mM of the diacylperoxide GAP was added directly to the reduced SWCNTs. The reaction was stirred at room temperature for about 30 minutes and then vacuum filtered. The product was washed with toluene, THF, water and methanol.

2.8. SWCNT functionalization with the AD derivative via coupling reaction (SW-GAP-AD)

100 mg of acid functionalized SWCNTs (SW-GAP) was suspended in 60 mL of DMF using bath sonication for 30 min and ultrasonic probe sonication for 15 min. Then 500 mg of the AD derivative dissolved in 10 mL of DMF was mixed with the SW-GAP suspension. At that point, 34 mg of the coupling agent O-Benzotriazole-\(N,N,N',N'\)-tetramethyl-uronium-hexafluoro-phosphate (HBTU) and 1.25 mL of \(N,N\)-Diisopropylethylamine (DIPEA) were added and the bath sonication continued for 4h. The product was then precipitated in methanol and vacuum filtered, washed with DMF, methanol and anhydrous diethyl ether.

2.9. Characterization

Coupled thermogravimetry (TG) and absorption spectroscopy in the mid infrared region (FTIR) analyses were performed on a Netzsch TG 209 F1 Iris® coupled to a Bruker Tensor 27 Fourier Transform Infrared spectrometer via a TGA A588 TGA-IR module. The system was run with BOC HP argon (grade 5.3) gas and residual oxygen was trapped with a Supelco Big-Supelpure Oxygen/water trap. Transfer lines between the TG instrument and FTIR spectrometer were heated to a temperature of 200 °C. The detailed experimental conditions of the measurement have been reported previously [29].

Raman spectra for the purified and functionalized samples were recorded on a Renishaw inVia micro-Raman
spectrometer. Samples were measured in a dry powder form using a 514 nm laser focused to approximately 1 μm through a 50x objective. Laser power density at the sample was maintained below 3 kW/cm² to avoid laser heating effects.

Elemental analysis was performed using a Thermo Flash 1112 analyzer. For a typical C, H, and N determination, samples are burnt in pure oxygen at 950 °C in the presence of V₂O₅. Combustion products pass through an oxidant bed of CuO at 950 °C to be converted into NOₓ, CO₂, and H₂O. Then, a reactor bed of Cu metal at 500 °C transforms NOₓ into N₂. The gases are separated in a polar chromatographic column, and quantified by thermal conductivity. For oxygen content analysis, samples are heated to 1080 °C, and the pyrolysis products are reduced to CO in a carbon black bed. Due to the experimental setup, data is provided without interference of moisture. Elemental composition is expressed as a weight percent.

Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) analysis was performed on an Alliance 2795-996PDA-ZQ 2000 (Waters-Micromass) liquid chromatograph-mass spectrometer. The liquid chromatograph was equipped with Sunfire C18, 2.1x100 mm, 3.5 μm column. Mobile phase solvents were acetonitrile with 0.1% formic acid (FA) and water with 0.1% FA. Gradient elution was as follows: for AD 30% acetonitrile/water/FA for 5 min then gradient to 50% in 20 min and for ED from 10% acetonitrile/water/FA gradient to 60% in 30 min, followed by 5 min. 95% acetonitrile/water/01.% FA at flow rate 0.2 ml/min. The mass spectrometer was equipped with pneumatically-assisted electrospray ionisation source, operating in positive mode. The source temperature was set at 80 °C, and the electrospray capillary was set at 3.5 kV with a cone voltage set at 20 V. Data were collected in centroid mode between 200-1800 m/z with sweep time 0.5 second.

Ultraviolet-visible-near infrared (UV–Vis–NIR) absorption spectra were measured using a Cary 5000 spectrophotometer. The solid samples were homogenized and dispersed in DMF by use of an ultrasonic bath for 1h. The solution was diluted until a final concentration of 0.025 mg/mL was reached. The samples were sonicated just before the spectral measurement in order to assure high quality dispersion.

Transmission electron microscopy (TEM) micrographs were taken with a JEOL-2000 FXII electron microscope, working at 200 kV and with 0.28 nm point-to-point spatial resolution. Samples were prepared by drop casting several diluted supernatant drops on a carbon-coated copper grid. The equipment was coupled to an Oxford Instruments INCA 200 energy-dispersive X-ray (EDX) spectrometer. EDX spectra were recorded during
TEM observation by focusing the electron beam in spots of ~ 40 nm at multiple places across the sample.

Solid-state FTIR spectroscopy was performed using a Bruker VERTEX 70 spectrometer. Functionalized SWCNTs were pelletized in spectroscopic grade KBr prior to their analysis. The electrical conductivity was measured using a Keithley 4200-SCS equipment working in a two-point probe configuration at 20V.

A Zeiss AXIO optical microscope, coupled to a Canon digital camera, was employed to observe SWCNT/epoxy blends at 50x. A small drop of the epoxy blend was cast on a glass slide and covered with a 0.5 mm thin glass cover prior to the observation.

The rheological characterization of the material was done on an AR2000 rotational rheometer from TA Instruments with parallel plate geometry, using disposable aluminum plates with a diameter of 25 mm, and an oscillation frequency of 1 Hz. All measurements were taken in linear viscoelastic region in which the storage modulus (G’) and loss modulus (G’’) were independent of the strain amplitude, i.e. a 30 % strain was used for samples A-DDS and A-DDS-LD, a 8 % strain for sample A-LM and a 2 % strain for sample A-SWCNT. The gap between the parallel plates was 900 ± 150 μm. Dynamic temperature tests (oscillatory temperature ramp) were performed on the composites from room temperature to 250 °C at a ramp rate of 3 °C/min. The apparent viscosity as a function of shear rate profile was measured with a steady state flow test at 30°C, with the shear rate varying from 0.1 to 100 1/s. The gap between the parallel plates was 1000 μm ± 50 μm.

3. Results and Discussion

3.1. Functionalization Procedure

Different strategies to functionalize SWCNTs are studied in order to improve dispersion and interface interaction in SWCNT/TGAP/DDS epoxy composites. SWCNTs were functionalized with the curing agent DDS and an amine terminated derivative (AD), a higher molecular weight oligomer containing terminal amine groups and with a chemical structure analogous to the cured epoxy resin network of interest. The composition of the amine derivative AD was analyzed by LC-ESI-MS and the results are shown in Figure 1. The main product in the AD derivative is the 1TGAP-3DDS adduct (T= 14.82 min and 16.19 min [M+H]^+ 1022.4), obtained as a mixture of regioisomers (α and β-amino alcohol) from the nucleophilic ring opening of the epoxide by amine groups.
Figure 1. LC-ESI-MS analysis of the TGAP-DDS amine derivative (AD) T= 14.82 min and 16.19 min [M+H]^+ 1022.4 (1TGAP-3DDS). Bottom trace UV detection.

The curing agent DDS and the amine derivative AD were covalently attached to the SWCNTs walls through diazotization reaction, as represented in Scheme 2. Due to their structural similarity, the covalent functionalization of the SWCNTs with the AD derivative should improve the affinity of the SWCNTs with the crosslinking matrix and help maintaining the stability of the dispersion during the curing process. In addition, this higher molecular weight functionality could show improved affinity in comparison to the smaller DDS fragments.

Raman spectroscopy is an important technique for the characterization of SWCNTs, particularly when subjecting them to purification or functionalization procedures [30]. Figure 2 shows the Raman spectra of pristine L-SWCNT and SW-DDS samples obtained using a 514 nm excitation laser. The most characteristic features of the Raman spectrum of SWCNTs [31] are the diameter dependent radial breathing mode (RBM) in the 150-250 cm\(^{-1}\) region, the tangential, Graphitic (sp\(^2\) character) modes or G band, near 1600 cm\(^{-1}\), the dispersive disorder-induced D-band around 1300 cm\(^{-1}\), and the second-order G’-band around 2600 cm\(^{-1}\).
Scheme 2. Representation of the diazotization reaction of SWCNTs with the curing agent DDS and the 1TGAP-3DDS derivative AD.

As can be seen in Figure 2, the diazonium reaction of arc and laser-grown SWCNTs with DDS leads to a substantial increase of the D-band intensity, indicating sidewall covalent functionalization. The D to G band intensity ratio \(I_D/I_G\) of A-SWCNT and L-SWCNT changes from 0.03 to 0.25 and from 0.02 to 0.14 respectively after the diazonium reaction. As a reference, a blank reaction was carried out in identical conditions but in absence of isoamyl nitrite. As expected, the Raman spectrum of this sample (Blank A-SW-DDS) did not show a significant increase of the \(I_D/I_G\). These results are summarized in Table 2.

Figure 2. Raman spectra of A) pristine L-SWCNT, B) A-SW-DDS and C) L-SW-DDS after base line correction and normalized to the intensity of the D-band. Excitation laser 514 nm.
The covalent functionalization is also supported by electrical conductivity measurements. About 100 mg of either pristine A-SWCNT or A-SW-DDS were mixed with ~5 wt% Poly(vinylidene difluoride) (PVDF) and pressed at 3 tons in a 13 mm diameter cylindrical mould. DC pellet conductivities were measured at room temperature. The obtained conductivity values were 10.8 and 4.5·10⁻² S/cm for A-SWCNT and A-SW-DDS respectively. The reduction of about two orders of magnitude is in agreement with the literature, where it has been shown that covalent sidewall functionalization causes a localized electronic state near the SWCNT Fermi level [32]. This electronic disruption lowers the electrical conductivity of metallic SWCNTs. Since diazonium reactions are known to preferentially modify SWCNTs with metallic behaviour [33], the conductivity measurements reassert the successful functionalization by this means with DDS.

Figure 3. Raman spectra of A) pristine A-SWCNT, B) A-SW-AD and C) L-SW-AD after baseline correction and normalized to the intensity of the D-band. Excitation laser: 514 nm.

Figure 3 shows the Raman spectra obtained for pristine A-SWCNT and SW-AD samples. After the diazonium reaction of arc and laser-grown SWCNTs with the synthesized ligand AD the Raman spectra of functionalized samples show a smaller increase on the I_D/I_G value compared to SW-DDS samples (Table 2). These results are suggestive of a lower addition density of the AD derivative to the SWCNT wall, probably because a lower reactivity of the AD derivative compared to DDS. A higher molecular weight amine is known to generate lower functionalization degree, usually ascribed to steric hindrance [22]. A similar observation has been reported when using the “grafting to” approach to functionalize CNTs with polymer chains [34].
Scheme 3. Representation of the coupling reaction between acid functionalized SWCNT (SW-GAP) and the TGAP-DDS derivative AD.

In order to increase the density of this functionality on the SWCNT sidewalls, the AD derivative was also covalently connected to SWCNTs using a different approach that involves coupling of the AD derivative to acid functionalized SWCNTs through amidation reaction. Carboxylic acid-functionalized SWCNTs (SW-GAP) were synthesized using a procedure described previously that allows the controlled attachment of butyric acid moieties to the SWCNT sidewalls by free radicals generated in the redox reaction between reduced SWCNTs and diacyl peroxide derivatives [28]. Contrary to the oxidation reactions, which use concentrated acids, this procedure allows a controlled functionalization of the SWCNT walls. Scheme 3 depicts this functionalization route. As expected, the amidation reaction did not change the $I_D/I_G$ value with respect to SW-GAP samples (Table 2) because it is not creating new defects on the SWCNT sidewalls.

In the case of the SW-DDS, SW-AD and SW-GAP-AD samples presented above, the SWCNTs bear amine-terminated moieties that can participate in the crosslinking reaction during the epoxy system curing stage and create a covalent connection between the matrix and the SWCNTs. On the other hand, the functionalization of SWCNTs with epoxide groups has also shown to be an effective approach to improve interface interaction in SWCNT/epoxy composites [35]. Following a strategy similar to the one described for the synthesis of the AD ligand, another DDS-TGAP derivative (ED) was synthesized in the presence of an excess of TGAP in order to obtain epoxide-terminated oligomers with an alternative chemical structure similar to that of the binary cross-linked network. The functionalization of SWCNTs with epoxide groups should promote their miscibility with the epoxy precursor, when the SWCNTs are dispersed before the addition of the hardener. The composition of the epoxide derivative ED was analyzed by LC-ESI-MS and the results are shown in Figure 4.
As can be observed in Figure 4, the conditions employed for the synthesis of the ED derivative produced a complex mixture of different adducts from the ring opening of the epoxide by amine groups. The major components of this mixture are unreacted TGAP, and different isomers of adducts 1DDS-1TGAP and 1DDS-2TGAP. A solution of this mixture and SW-DDS samples was refluxed in DMF at 120 ºC (see experimental section) in order to create a covalent connection between DDS-functionalized SWCNTs and the epoxide-containing molecules in the ED derivative. This functionalization strategy is shown in Scheme 4, where only the coupling of the 2TGAP-1DDS adduct has been represented for simplicity.
Scheme 4. Representation of the reaction between SW-DDS and the mixture of adducts present in the ED derivative (TGAP; 1TGAP-1DDS and 2TGAP-1DDS). Only the addition of the 2TGAP-1DDS oligomer has been represented.

3.2. Identification of functional groups and estimation of the functionalization degree

Solid-state FTIR spectra (Figure 5) gave knowledge about the different moieties covalently attached to the SWCNT sidewalls. While only a set of A-SWCNT are represented, equivalent results were obtained for the analogous L-SWCNT (data not shown). As-produced A-SWCNT do not show any significant feature, except for a band located at 1559 cm\(^{-1}\) due to the CNT C=C phonon modes [36,37]. The wide band at about 1150 cm\(^{-1}\) corresponds to the C-O stretching modes due to native oxygen functional groups [38], which was corroborated by TGA (vide infra). The other visible bands in A-SWCNT (centered at 750 and 1610 cm\(^{-1}\) could be attributed to moisture contained in the SWCNT sample. When A-SWCNT are functionalized different features arise and can be assigned to the attached functional groups. After the functionalization with DDS the most significant feature of the A-SW-DDS samples is the band at 1650 cm\(^{-1}\) which stands for the N-H deformation in primary amines [39]. In addition, different bands corresponding to aromatic rings are also present. The band at 1590 cm\(^{-1}\) can be assigned to the C=C in-plane deformation of the DDS benzene rings, and the intense 1:4 ring substitution vibration modes are visible at 1098 (in-plane) and 828 (out-of-plane) cm\(^{-1}\) [39]. The sulfone bands can be
identified at 1136 (symmetric SO$_2$ stretching) and 1286 (asymmetric SO$_2$ stretching) cm$^{-1}$ together with a visible knee at 1165 cm$^{-1}$, a typical feature in diphenyl sulfones [40]. In the case of the diazonium functionalization with the AD oligomer (A-SW-AD), the IR spectrum is very similar to that of the A-SW-DDS, but a noticeable difference is revealed as for the band at 1500 cm$^{-1}$ which can be assigned to the N-H deformation in secondary amines [39], contained within the AD molecular structure. The joint presence of the 1650 and 1500 cm$^{-1}$ bands support the successful attachment of the AD ligand with free NH$_2$ groups. The carboxylation of SWCNTs with butyric acid moieties (A-SW-GAP) exhibits a different profile as compared with the previous samples. A band at 1723 cm$^{-1}$ indicates the C=O stretching mode in carboxylic groups, while at 1540 cm$^{-1}$ the presence of some carboxylate ions would also be noticed [39]. At 1620 cm$^{-1}$ the COOH intramolecular bonds could be attributed, and the band at about 1190 cm$^{-1}$ would be characteristic of solid fatty acids [39], compatible with this sample. The band doublet at 2914 / 2843 cm$^{-1}$ standing for CH$_2$ vibration modes is slightly visible.

![Figure 5. Solid-state FTIR spectra for pristine and functionalized arc-discharge SWCNT.](image_url)
The coupling reaction of A-SW-GAP with the AD oligomer (A-SW-GAP-AD) gives rise to some aforementioned features: the primary amine (1650 cm\(^{-1}\)) and the secondary amine bands (1500 cm\(^{-1}\)) are again visible, so as the benzene ring and sulfone vibrations. The higher intensity of the 1650 cm\(^{-1}\) band relative to the rest of bands suggests a higher degree of functionalization. Further TG experiments confirmed this fact (*vide infra*). The carbonyl band downshifts to 1700 cm\(^{-1}\) (amide I band). A band at 1051 cm\(^{-1}\) could be attributed to the C-O stretching vibration of the primary alcohol groups. Finally, for the A-SW-DDS-ED sample, the same profile as the A-SW-DDS sample is present, with the following differences: the primary amine band at 1650 cm\(^{-1}\) is noticeably less intense relative to the 1590 cm\(^{-1}\) C=C in-plane deformation of the DDS benzene rings, which evidences the consumption of primary amines through the coupling reaction. The remaining signal is probably coming from grafted uncoupled DDS and/or coupling of the 1DDS-1TGAP adduct which contains free amine groups. The appearance of a band at 1276 cm\(^{-1}\) together with an association of several weak bands at about 900 cm\(^{-1}\) indicates the presence of epoxide rings [41].

The extent of functionalization was estimated throughout elemental analysis. In Table 1 some of the elemental compositions of the different samples are displayed. In the elemental determination the amount of metals has not been examined, and the oxygen determinations were carried out in separate experiments, which is why the total percentage does not add up to 100%. However, some useful information can be drawn from the elemental characterization. Both laser- and arc-grown SWCNTs contain a small amount of oxygen, in the range of 2-3%, yet another confirmation of the existence of functional groups in the pristine samples. The diazonium reaction with DDS in both kinds of SWCNTs induces an increase in the sulphur content, reaching ~2%. In parallel, there is an increase in the nitrogen content also in the range of 2-3%, The diazonium blank reaction exhibits a minor amount of nitrogen (probably due to remaining DMF traces) and almost no presence of sulphur, which corroborates the successful DDS grafting in SW-DDS samples. Furthermore, the nitrogen content only increased slightly after coupling SW-DDS with the ED derivative while the sulphur content slightly decreased, which would be in agreement with the introduction of grafted molecules present in the ED mixture. However, such a small increase in the nitrogen content could be indicating that mainly the TGAP monomer has been grafted to the SW-DDS samples. The diazonium grafting of the AD ligand gives slightly lower nitrogen content than the SW-DDS samples while the nitrogen/sulfur ratio is higher than that of SW-DDS samples, which is consistent with the
lower $I_D/I_G$ ratio determined from Raman spectroscopy and the structural differences of the attached fragments. The SWCNT carboxylation (SW-GAP samples) raises the oxygen content up to ~10% and the subsequent reaction with the AD ligand yields the product L-SW-GAP-AD with nitrogen and sulphur content as high as 3.6% and 2% respectively, almost twice the values for SW-AD samples.

Table 1. Elemental composition for SWCNT samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>%O</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
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</tr>
<tr>
<td>A-SW-AD</td>
<td>1.9</td>
<td>84.0</td>
<td>1.2</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>A-SW-GAP-AD</td>
<td>2.8</td>
<td>98.1</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>L-SWCNT</td>
<td>0.2</td>
<td>98.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>L-SW-AD</td>
<td>1.2</td>
<td>84.1</td>
<td>1.5</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>L-SW-GAP-AD</td>
<td>3.6</td>
<td>97.0</td>
<td>0.5</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>L-SW-DDS-ED</td>
<td>2.2</td>
<td>98.5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Blank A-SW-DDS</td>
<td>0.1</td>
<td>72.8</td>
<td>0.9</td>
<td>0.1</td>
<td>0.0</td>
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</table>

TG-FTIR under inert desorption conditions was used to identify and quantify functional groups attached to functionalized SWCNTs. As a baseline, measurements were performed on the as-grown SWCNTs samples. TGA results and IR absorption spectra of the species desorbed at the temperature of maximum loss rate for unfunctionalized and functionalized laser SWCNTs are presented in Figure 6. A summary of the results obtained for all the studied samples, with an estimation of the functional groups per nanotube carbon atom based on thermogravimetric analysis weight loss, is given in Table 2. As-grown L-SWCNT and A-SWCNT showed a
weight loss of 3 and 2 % respectively following thermal desorption at 700°C. These low values suggest that there are low levels of functional groups present on the SWCNTs pristine samples. The slightly higher weight loss observed for A-SWCNT is in agreement with our observation by Raman spectroscopy which indicated that the initial level of defects (I_D/I_G ratio) on A-SWCNT samples was higher than in L-SWCNT samples, probably corresponding to the aforementioned native surface covalent groups. The FTIR measurements of the evolved gases show the presence of CO2 and water through most of the temperature range.

Figure 6. A) Thermogravimetric analysis of as-grown L-SWCNT and functionalized L-SW-DDS, L-SW-AD and L-SW-DDS-ED sample under desorption conditions. B) IR spectra of the species desorbed from functionalized SWCNT sample at the temperature of maximum mass loss rate.
Table 2. Raman I_D/I_G ratio and TGA-determined weight loss for SWCNT samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>I_D/I_G Ratio^a</th>
<th>TGA wt loss (%) at 700 ºC^b</th>
<th>Functionalization</th>
<th>Degree^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-SWCNT</td>
<td>0.03 ± 0.01</td>
<td>3</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>A-SW-DDS</td>
<td>0.26 ± 0.03</td>
<td>11</td>
<td>1/164</td>
<td></td>
</tr>
<tr>
<td>A- SW-AD</td>
<td>0.07 ± 0.01</td>
<td>12</td>
<td>1/597</td>
<td></td>
</tr>
<tr>
<td>A- SW-GAP</td>
<td>0.13 ±0.02</td>
<td>19</td>
<td>1/58</td>
<td></td>
</tr>
<tr>
<td>A- SW-GAP-AD</td>
<td>0.25</td>
<td>42</td>
<td>1/ 212</td>
<td></td>
</tr>
<tr>
<td>A- SW-DDS-ED</td>
<td>0.02 ± 0.01</td>
<td>2</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>L-SWCNT</td>
<td>0.14 ± 0.02</td>
<td>12</td>
<td>1/164</td>
<td></td>
</tr>
<tr>
<td>L- SW-AD</td>
<td>0.05 ± 0.02</td>
<td>11</td>
<td>1/758</td>
<td></td>
</tr>
<tr>
<td>L- SW-GAP</td>
<td>0.10 ± 0.01</td>
<td>17</td>
<td>1/98</td>
<td></td>
</tr>
<tr>
<td>L- SW-GAP-AD</td>
<td>0.16 ± 0.02</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank A-SW-DDS</td>
<td>0.045± 0.002</td>
<td>6</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

^aRaman spectra, after base line correction and normalized to the G-band intensity

^bIncluding ~ 2 wt% loss due to DMF solvent in amine functionalized samples

^cTGA results show total mass loss. Total mass loss after subtraction of the solvent was attributed to functional groups covalently attached to the sidewall. With use of the mass loss and the molecular weight of the functional group fragment, the number of moles of functional groups present was calculated. With the moles of functional groups present and SWCNT carbons, the functional group to SWCNT carbon ratio was estimated. The metal content (20 % and 11 % for A-SWCNT and L-SWCNT respectively) was taken into account.

In comparison, the TG and IR desorption data for the functionalized L-SW-DDS sample is given in Figure 6. Thermal desorption data show a total mass loss of 12 % upon heating to 700°C (Figure 6A), markedly higher than that obtained for unfunctionalized SWCNTs or the diazonium blank reaction (see Table 2). The DTG data shows two discrete mass-loss events centered at ~225°C, ~425°C and accounting for ~2 wt% and ~10 wt% respectively. Similar results were obtained for A-SW-DDS samples (Table 2). The IR spectrum associated to the event at lower
temperature can be unambiguously assigned to residual DMF present even after carefully drying the samples (see supporting information, Figure S2). On the other hand, the IR absorption spectrum associated with the higher temperature desorption event (Figure 6B) shows bands that are indicative of the covalent attachment of DDS to the SWCNTs and the presence of free amine groups. The shoulder at 3400 cm\(^{-1}\) (-NH stretching vibration) and the bands at 1620 cm\(^{-1}\) (N-H deformation of primary amine), 1501 cm\(^{-1}\), 1270 cm\(^{-1}\) and 747 cm\(^{-1}\) (mono substituted benzene ring) coincide with the gas phase spectrum of aniline, while the bands at 1375-1340 cm\(^{-1}\) correspond to sulfur dioxide. Both species simultaneously desorbed during the decomposition of the covalently attached moiety on SW-DDS samples. It is worth mentioning that only CH-containing fragments were identified on the IR spectrum of Blank A-SW-DDS samples (see supporting information, Figure S3).

On the other hand, as observed in Figure 6A, L-SW-AD sample shows a total mass loss of 11 % upon heating to 700°C, very similar to the value of L-SW-DDS however, as was observed by Raman spectroscopy their I\(_D\)/I\(_G\) ratios are significantly different (Table 2). This result is compatible with the higher molecular weight of the fragment attached to the SWCNT sidewalls of L-SW-AD samples. The TGA-derived levels of substitution upon functionalization with the AD ligand are consistent with the I\(_D\)/I\(_G\) ratios observed in the Raman spectra (see Figure 3 and Table 2). The DTG data shows a mass-loss event centered at a lower temperature of ~370°C. The IR spectrum associated to this event is very similar to the one observed for L-SW-DDS samples except for some changes in the relative intensity of the signals. Specifically, the intensity of the bands associated to SO\(_2\) is very similar to the intensity of NH deformation band (1620 cm\(^{-1}\)) indicating a lower sulfone/amine ratio of the desorbed moiety, in agreement with the structure of the AD derivative and elemental analysis results. Additionally, new bands can be observed at ~2940 cm\(^{-1}\) which corresponds to the stretching vibration of C-H containing fragments and a small broad band at 1075 cm\(^{-1}\) assigned to CO stretching vibrations, further indication of the attachment of the AD derivative to the SWCNTs sidewalls.

Figure 6 also includes results obtained for L-SW-DDS-ED samples (see Scheme 4). The thermal desorption data show a total mass loss of 23 % upon heating to 700°C, 11% higher than the value obtained for SW-DDS samples indicating the successful attachment of species present in the ED derivative mixture. The IR spectrum of the fragments desorbed at the temperature of maximum decomposition rate (360 °C) is also included in Figure 6B. The IR spectra of L-SW-AD and L-SW-DDS-ED are very similar; however, a clear difference is the higher
intensity of the band at 1501 and 1075 cm$^{-1}$ and a new band at 815 cm$^{-1}$ that can be assigned to 1-4 disubstituted benzene rings. These features indicate a different decomposition pathway for L-SW-DDS-ED. However a precise identification of its structure is still elusive.

Figure 7. A) TGA data of functionalized A-SW-GAP and A-SW-GAP-AD sample under desorption conditions. B) IR spectra of the species desorbed from functionalized SWCNT sample at the temperature of maximum rate of mass loss.

The desorption TG and IR data for A-SW-GAP-AD samples that were synthesized by the amidation reaction of the AD derivative to acid functionalized SWCNTs (Scheme 3) is presented in Figure 7 together with acid functionalized SWCNTs (A-SW-GAP). As previously reported [28,29], the thermal desorption data for acid functionalized samples show a total mass loss of 19 % upon heating to 700°C, and the IR spectrum associated to the mass-loss events confirms the presence of attached butyric acid fragments. Only the event centered at 356°C
corresponds to covalently attached butyric acid fragment with an associated weight loss of 9 %. After the coupling reaction, the thermal desorption data show a total mass loss of 43 % upon heating to 700°C, a 23 % higher than the total weight loss for A-SW-GAP samples. This increase in the percent of mass loss is due to the attachment of the AD derivative through the coupling reaction. This value is two times higher than the weight loss percent observed for A-SW-AD samples (Table 2) that were functionalized through the \textit{in situ} diazonium reaction, pointing to the higher yield of the amidation reaction strategy towards decorating the SWCNTs sidewalls with the AD derivative. The estimated functionalization degree of L-SW-GAP (1/98 carbon atom) and L-SW-GAP-AD (1/457 carbon atom) also indicates that not all the acid groups in L-SW-GAP samples have participated in the coupling reaction. The IR spectrum of the desorbed species at the temperature of maximum decomposition rate (360 °C) is also included in Figure 7B. As expected, the IR spectra of SW-AD and SW-GAP-AD samples are very similar due to the structural similarity of the fragments attached to the SWCNT sidewalls.

According to results in Table 2, except for the case of SW-DDS samples, the estimated functionalization degree is higher for A-SWCNT than for L-SWCNT. These results could indicate a higher reactivity of A-SWCNT towards the above functionalization procedures despite their slightly larger diameter. This result could be due to their slightly higher initial level of defects and lower purity as determined by absorption spectroscopy in the Vis-NIR region (see supporting information Table S1) [42]. Interestingly, both materials show the same functionalization degree (1/164) for the \textit{in situ} diazonium reaction with DDS. Recent experiments have demonstrated that diazonium chemistry and oxidative reactions occur on a SWCNT sidewall at random atomic sites [43,44], while the reductive alkylcarboxylation occurs on SWCNTs exclusively by reaction propagation from existing defects [45]. The room temperature redox reaction between reduced SWCNTs and diacyl peroxides (SW-GAP) takes place through the same pathway as the reductive alkylation [28,46]. Consequently the two chemical approaches employed here will have a significantly different effect on the electronic structure of the functionalized SWCNTs. Figure 8 shows the UV-Vis-NIR absorption spectra of unfunctionalized L-SWCNT, L-SWCNT functionalized by the diazonium reaction (L-SW-DDS and L-SW-AD) and by the redox reaction (L-SW-GAP).
There is clearly a more significant loss of the interband electronic transitions for L-SW-DDS and L-SW-AD than for L-SW-GAP samples, which is in agreement with the random addition to atomic sites and propagation from a point defect model respectively [45]. Raman spectroscopy results are also in accordance with these mechanisms. A smaller increase on the $I_D/I_G$ value was observed for SW-GAP than for SW-DDS samples (Table 2). Our results on Table 2 also indicate that the functionalization degree for the diazonium reaction, which occurs in random sites, is not influenced by the initial level of defects and both types of SWCNTs show identical functionalization degrees (L-SW-DDS and A-SW-DDS). On the other hand, in the case of the redox reaction A-SWCNT with a higher level of initial defects, showed a higher functionalization degree (A-SW-GAP: 1/58) than L-SWCNT (L-SW-GAP: 1/98). The diazonium reaction with the AD ligand, with a lower reactivity than DDS, showed a slightly higher functionalization degree for A-SWCNT but this is significantly lower than the differences observed for SW-GAP samples. From these results we can expect a completely different behaviour in terms of electrical conductivity for epoxy resin composites made with functionalized SWCNTs; not only depending on the functionalization degree but the reaction employed for the chemical functionalization.
Figure 9. TEM characterization of functionalized L-SWCNT; a) L-SW-DDS; b) L-SW-AD; c) magnification of
The characterization of SWCNTs functionalization was supported by TEM observation and EDX spectra. As a representative example, L-SWCNT functionalized with DDS and AD are shown in Figure 9. L-SW-DDS images appear to have a higher degree of coverage on their surfaces than L-SW-AD, as observed from the higher bundle thickness and coating of the former, as compared to the latter. This would be in good agreement with the functionalization degree quantified by coupled TG-FTIR, where L-SW-DDS exhibited a significantly higher extent of functionalization (see Table 2). The appearance of molecular clusters along the SWCNT surface in TEM observations has been proposed as an indicative of successful covalent attachment of chemical species to the SWCNT sidewalls [35]. More specifically, the EDX spectra recorded during the TEM observation provided quantitative information about the degree of functionalization. Figure 9e contains representative EDX spectra for L-SW-DDS and L-SW-AD, respectively. Elements such as Ni, Co, Cu and Si come from impurities of the SWCNT pristine material and also from the grid holding the sample; the carbon signal can be ascribed to the SWCNTs, their carbonaceous impurities and to the grid coating. However, the signal of the elements coming mainly from the attached functional groups (N, O and S) can be evaluated to assess the extent of functionalization of both samples, particularly regarding the S peak. In L-SW-DDS, there is higher amount of N, O and S than in L-SW-AD, as it would correspond to a higher degree of functionalization (Table 2). Considering S as the distinctive element exclusively coming from the functional groups, the ratio between the sulphur content in L-SW-DDS and L-SW-AD is ~2.6, which is nearly coincident with the sulphur ratio between both samples in the elemental analysis (Table 1). The results observed from microscopic techniques are consistent with the bulk characterization of the SWCNT functionalization.

3.3. Dispersibility of functionalized SWCNTs in the TGAP epoxy resin and corresponding rheological behaviour

The aim of our functionalization procedures is to increase chemical affinity of SWCNTs to our target matrix, causing a direct compatibilization hence improving the epoxy performance. A simple test to examine the functionalization effects on the filler-matrix miscibility was carried out by inspection of SWCNT/TGAP blends with an optical microscope. SWCNT/TGAP blends were prepared by directly mixing 1g of TGAP with 8 mg of SWCNTs through 45min of magnetic stirring at 60ºC followed by 15min of mild probe sonication (ending up in a
mixture with 0.8 wt% SWCNTs). The images of as-prepared blends are shown in Figure 10. For the sake of clarity, only the results for A-SWCNT are shown. As expected, our approach provided an improved integration into the epoxy precursor, since the large aggregates contained in the A-SWCNT/TGAP/mixture (Figure 8a) are not present when using functionalized SWCNTs. The highest homogeneity and smaller aggregate size was achieved for the A-DDS sample (Figure 10b) followed by SW-AD (Figure 10c). Even though a fully homogeneous mixture was not achieved, A-SW-DDS-ED presents visibly lower aggregates than A-SWCNT, indicating a positive effect of the functionalization route. However, these results also indicate that, even with a lower functionalization degree, amine-functionalized SWCNTs are more efficient at improving SWCNT dispersion than SWCNTs decorated with free epoxide groups, as observed by direct integration without using solvents. Contrary to the improvement in dispersion of A-SW-AD samples, which present a low functionalization degree (1/597, Table 2), A-SW-GAP-AD samples with a higher density of the AD functionality (1/212, Table 2) were not successfully dispersed in TGAP (images not shown). The higher degree of functionalization probably leads to stronger inter-tube interactions involving amine and unreacted carboxylic groups, providing a highly compacted material unable to be dispersed without the use of organic solvents. A more accurate and optimized integration route would be necessary in order to prepare epoxy composites based on these fillers. In terms of the effect of the molecular weight of the attached moiety these preliminary results show that the higher molecular weight fragment (SW-AD) could be more efficient than the DDS fragment because similar dispersions were obtained for both materials even though the functionalization degree for SW-LD is considerably lower. From these observations we expect that the interfacial interaction between filler and matrix is strengthened when using these functionalized SWCNTs, particularly for the amine-terminated ones. This would help to improve the intrinsically weak interfacial adhesion of SWCNT to epoxy, which has been reported to be generally low particularly for unfunctionalized CNTs [47].
Figure 10. Optical images at 50x of the TGAP/SWCNT blends containing 0.8 wt% of: a) A-SWCNT, b) A-SW-DDS, c) A-SW-AD, and d) A-SW-DDS-ED.

The effect of functionalization on the rheological behaviour was also investigated for these composites. Dynamic temperature tests (oscillatory temperature ramp) were performed after adding the curing agent DDS in order to observe the variations in the viscosity profile of the resin with temperature. Figure 11 compares the results obtained for the neat resin and for composites containing unfunctionalized or functionalized SWCNTs. Close to temperature (30 °C) the viscosity of composites including unfunctionalized SWCNTs (A-SWCNT) is two times higher than the viscosity of the neat resin, while both the neat epoxy and the composites containing functionalized SWCNTs have similar initial levels of viscosity and a consistent decrease in viscosity until 50 °C. The introduction of CNTs into epoxy matrices is known to drastically increase the resin viscosity, due to strong filler-resin interactions and high aspect ratios, which creates processability problems [48,49].
Figure 11. Temperature dependence of viscosity for the neat TGAP/DDS system and the TGAP/DDS/SWCNT blends containing 0.5 wt% unfunctionalized (A-SWCNT) and functionalized arc grown-SWCNT.

The behaviour observed here for functionalized SWCNTs could have positive implication on the processability of such composites, allowing the incorporation of higher CNTs loadings and facilitating degassing processes. The sudden increase in viscosity at 188 ºC indicates the gelation point of this resin. It can be observed that the gelation started at around 6 and 4 ºC higher in the presence of A-SW-DDS and A-SW-DDS-ED respectively, while no effect was observed for unfunctionalized and A-SW-AD samples. In contrast, Hubert et al. have reported that alcooxide-functionalized SWCNTs can increase the viscosity of the neat resin and lower the gelation temperature [50].
Figure 12. Apparent viscosity as a function of shear rate for the neat TGAP/DDS system and the TGAP/DDS/SWCNT blends containing 0.5 wt% unfunctionalized (A-SWCNT) and functionalized arc grown-SWCNT.

In general, the addition of CNTs into a suspending medium has been found to increase the base viscosity of the whole system, with decreasing viscosity increment effect for increasing shear rates [51], a behaviour known as shear thinning. Figure 12 shows steady shear experimental plots of the apparent viscosity, $\eta_a$, as a function of shear rate for functionalized and unfunctionalized SWCNT/epoxy composites containing the curing agent DDS. As previously reported by other authors [52,53], given the same weight percent, composites with unfunctionalized SWCNTs (A-SWCNT) showing optically resolvable aggregate structures (Figure 10a), tended to exhibit a more significant shear-thinning effect than composites containing functionalized SWCNTs showing little optical microstructure (Figure 10 b, c, d). Rahatekar et al. [49] correlated their rheological findings with optical observation and conjectured that for unfunctionalized CNTs the shear thinning behaviour was due to a disentanglement of SWCNT aggregates. For composites containing functionalized A-SW-DDS and A-SW-DDS-ED samples the viscosity exhibits very little shear thinning which could indicate better particle dispersion and poor interactions between them. However, optical images of A-SW-DDS-ED samples also show visible
aggregates. The behaviour of A-SW-AD, with a lower functionalization degree, is very similar to the behaviour of A-SWCNT samples although at low shear rate the apparent viscosity values are lower. On the other hand other authors have reported a more significant shear thinning effect for fluorinated and acid functionalized CNTs compared to unmodified CNTs [54]. These results indicate that the observed rheological behaviour also depends on the specific functionality, degree of functionalization and its interaction with the matrix.

According to the rheological behaviour observed in Figure 11, these functionalization strategies could also have a positive effect on the composite processing by decreasing the viscosity of the epoxy. Considering the results of apparent viscosity as a function of shear rate (Figure 12) no correlation between shear thinning effect and the dispersion assessment by optical microscopy was observed but rather with the degree of substitution. SWCNTs with the same level of substitution (SW-DDS and SW-DDS-ED) but different functionalities show little shear thinning effect compared to SW-AD samples with better dispersion than SW-DDS-ED samples but a significantly lower level of substitution.

4. Conclusions

A tailored functionalization approach has been undertaken in order to increase both dispersibility and interface interaction of SWCNTs with an epoxy resin. The functionalization strategies consisted of the covalent attachment of the DDS hardener molecules onto SWCNT surfaces via diazonium reaction, and also different ways of covalently grafting higher molecular weight pre-synthesized ligands based on the inherent epoxy chemical structure and containing amine or epoxide terminated fragments. The routes proposed herein exhibited different degrees of functionalization (from ~0.2 to ~1.7 % carbon substitution), as determined by TG-FTIR, and the unambiguous presence of free primary amine or epoxide groups attached to SWCNTs. Direct dispersion of functionalized SWCNTs into the epoxy precursor resulted in a markedly higher mixture homogeneity than using unfunctionalized SWCNTs, especially with those amino-functionalized, as observed by optical microscopy. The functionalization with the higher molecular weight amine derivative AD by the diazonium reaction provides similar results to the lower molecular weight DDS functionalization in terms of dispersion but at a significantly lower functionalization degree, hence lower level of defects, which will be important to control the electrical conductivity of SWCNT epoxy composites prepared with these materials. Increasing the density of the AD ligand
by amidation of carboxylic acid groups, which were first introduced by the redox reaction between reduced SWCNTs and GAP, negatively affected the dispersion, producing a highly compacted material unable to be dispersed without the use of organic solvents.

The two approaches used to covalently modify the SWCNT walls (diazonium and redox reaction) have significantly different effects on the electronic structure of functionalized SWCNTs. For the same type of SWCNTs (arc discharge or laser ablation) a less significant loss of the interband electronic transitions and a smaller increase on the I_D/I_G value was observed for SW-GAP than for SW-DDS samples. However, in contrast with these results the functionalization degree calculated from TGA showed a higher density of functional groups for SW-GAP. These results are in agreement with the sp³ defect propagation mechanism for SW-GAP samples and random addition to atomic sites for SW-DDS. As result A-SWCNT with a slightly higher initial level of defects showed a higher functionalization degree than L-SWCNT for the redox reaction (SW-GAP) but the same functionalization degree for the diazonium reaction (SW-DDS) Rheological studies showed that, while unfunctionalized SWCNTs significantly increased the resin viscosity, functionalized SWCNTs modified the initial viscosity and the viscosity–temperature profile only slightly, which should be advantageous with regard to composite processing. It was found that the extent of shear thinning depended on both the type of functionalization and functionalization degree. Unfunctionalized SWCNTs exhibited a more significant shear thinning effect compared to highly functionalized SWCNTs. The approach presented herein offers versatility in the chemical modification of SWCNTs towards epoxy composites by covalently grafting amine or epoxide–containing moieties of an equal chemical structure to the target matrix. The simplicity and reproducibility of this approach allows applying it to many other SWCNT-reinforced epoxy systems. The integration of SWCNTs functionalized with these reactive moieties into the epoxy is expected to deliver a covalent anchoring while preserving the chemical structure of the matrix. At the same time the level of covalent grafting to the epoxy matrix can be controlled by changing the molecular weight of the attached fragment or the chemical reaction used for the covalent functionalization. Thus, manufacturing of as-prepared composites and characterization of their properties are underway.

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References


[34] Li J, He WD, Yang LP, Sun XL, Hua Q. Preparation of multi-walled carbon nanotubes grafted with synthetic poly(L-lysine) through surface-initiated ring-opening polymerization. Polymer 2007;48:352-60.


