SWCNT FUNCTIONALIZATION FOR OPTIMIZED ELECTRICAL CONDUCTIVITY OF EPOXY MATRICES

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1 Introduction
The one-dimensional structure; low density; high aspect ratio; and extraordinary mechanical, electrical, and thermal properties of single-walled carbon nanotubes (SWCNTs) make them particularly attractive as reinforcing fillers in multifunctional composite materials. Because of their high crystallinity, high aromaticity, and strong van der Waals interactions, pristine SWCNTs tend to have smooth defect-free surfaces and exist as ropes or bundles. This leads to poor dispersion and poor interface compatibility with matrices. A great ongoing challenge in the field of SWCNT/polymer composites is the efficient transfer of SWCNT properties into the polymer matrix. Surface functionalization can solve this problem by allowing better dispersion and improved affinity with the matrix.

Covalent functionalization has been shown to be particularly effective at improving the mechanical properties of SWCNT/polymer composites [1]. In conjunction with mechanical reinforcement it is of interest to develop conductive polymer composites for electrostatic dissipation and electromagnetic interference (EMI) shielding among other applications. Covalent functionalization however, disrupts the sp² network conjugation of SWCNTs creating defects on the SWCNT walls. This will have a negative effect on their electrical conductivity, reducing the maximum conductivity of individual SWCNTs.

Carbon nanotubes (CNTs) produced by different methods have shown different reactivity towards covalent functionalization with smaller diameter, more strained CNTs, reacting more readily than larger diameter CNTs. Recent experiments have demonstrated that diazonium chemistry and oxidative reactions occur on a SWCNT sidewall at random atomic sites [2,3], while the reductive alkylcarboxylation occurs on SWCNTs exclusively by reaction propagation from existing defects [4]. The sp³ defect propagation mechanism creates ‘banded’ SWCNTs, with alternating segments of functionalized (sp³ hybridized) and intact regions (which remain sp² hybridized) through reaction propagation that starts at defects initially present in the nanotubes. Consequently, these two chemical functionalization approaches will have a significantly different effect on the electronic structure of the functionalized SWCNTs.

Previous studies have identified different parameters that affect the electrical conductivity of polymer composites containing CNTs. These include the CNT aspect ratio [5], purity [6], surface area and functionalization [7]. In this work SWCNTs with similar diameter distribution produced by two different methods: arc-discharge and laser ablation were covalently functionalized before integration into an aerospace-grade epoxy resin, triglycidyl p-aminophenol (TGAP). The curing agent 4,4’-diaminodiphenyl sulphone (DDS) and a higher molecular weight pre-synthesized oligomer containing epoxy-hardener monomers (AD; 3DDS-TGAP) were covalently bonded to the SWCNT sidewalls by the diazonium reaction. On the other hand, SWCNTs functionalized with carboxylic acid groups were synthesized at room temperature by reductive alkylcarboxylation using reduced SWCNTs and glutaric acid diacyl peroxide (GAP). The electrical conductivity of epoxy resin nanocomposites containing these functionalized nanotubes was determined. The effect of the SWCNT synthesis method, the degree of functionalization and the chemical reaction used for the functionalization of the SWCNTs is evaluated.
2 Experimental

2.1 Materials and chemical functionalization

SWCNTs synthesized by the laser ablation method (laser-SWCNT) and by the arc-discharge method (arc-SWCNT) were used without additional purification. The synthesis of the amine terminated derivative AD and the SWCNT chemical functionalization have been previously reported [8]. The chemical functionalization strategies are shown in Fig. 1. Carboxylic acid groups were attached to the SWCNT wall by reductive alkylcarboxylation (Fig. 1A) while the curing agent DDS (Fig. 1C) and the AD oligomer (Fig. 1B) were covalently bonded to the SWCNT wall by the diazonium reaction.

Functionalized and unfunctionalized SWCNTs were directly incorporated into the epoxy resin by hot stirring and sonication without using organic solvents. The curing agent DDS was then added to the SWCNT/epoxy mixture in a 100:60 weight ratio. Nanocomposites were prepared at 0.1, 0.5 and 1 wt% loading. The curing was performed by casting the neat epoxy or nanocomposite blends in a steel dish mould (2 mm thick) sealed by 3 mm thick Teflon plates, followed by curing at 160 °C for 45 min and 200 °C for 30 min in a Perkin Elmer hydraulic press coupled to a Greaseby Specac controlled heater under 3 tons of pressure. The samples were removed from the mould, transferred to an oven and postcured at 200 °C for 4 h.

Fig. 1. Chemical functionalization strategies used to modify the SWCNTs
2.2 Characterization techniques
Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 F1 Iris® coupled to a Bruker Tensor 27 Fourier Transform Infrared spectrometer (FTIR) via a TGA A588 TGA-IR module. Prior to the measurement the samples were dried overnight in vacuum at 100 °C. The thermal desorption measurements consisted of a heating from room temperature to 900°C at a rate of 10°C/min [9]. 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. Ultraviolet-visible-near infrared (UV–Vis–NIR) absorption spectra were measured using a Cary 5000 spectrophotometer.

Direct current (DC) electrical conductivity was measured with a Keithley 4200-SCS source measurement unit, working at 20 V. The specimen measurements were ~19.5 x 5 x 2 mm³. Composite test samples were placed in a sandwich-like arrangement using two copper sheets (0.2 mm thick). Measurements were carried out in a two-probe configuration, with each probe placed on different ~19.5 x 5 mm² rectangular surfaces of the test sample.

3 Results and discussion
3.1 Characterization of functionalized and unfunctionalized SWCNTs
Different strategies to covalently functionalize SWCNTs are explored here in order to improve dispersion and interface interaction in SWCNT/TGAP/DDS epoxy composites. SWCNTs were functionalized by the diazonium reaction 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 (Fig. 1B). Using this functionalization approach the chemical structure of the attached fragment is of the same nature as the epoxy matrix of interest. This strategy allows an improved interaction with the matrix of interest without changing the chemical composition at the SWCNT/matrix interface [1]. On the other hand, carboxylic acid-functionalized SWCNTs were synthesized by reductive alkylcarboxylation (Fig. 1A). Free radicals generated at room temperature by a redox reaction between reduced SWCNTs and diacyl peroxide derivatives were covalently attached to the SWCNT walls [10]. Contrary to the oxidation reactions, which use concentrated acids, this procedure allows a controlled functionalization of the SWCNT walls.

Fig. 2. Raman spectra of functionalized arc-grown (top) and laser-grown (bottom) SWCNTs. After base line correction and normalized to the intensity of the G-band. Excitation laser: 514 nm.
order G’-band around 2600 cm$^{-1}$. When addends are covalently bonded to the SWCNT sidewalls, the hybridization of the C atoms changes from sp$^2$ to sp$^3$ which yields a commensurate intensity increase in the D-band. Fig. 2 shows the Raman spectra of Arc- and laser-grown SWCNTs functionalized by reductive alkylcarboxylation and diazotization. The D to G band intensity ratios ($I_D/I_G$) of unfunctionalized and functionalized SWCNT are summarized in Table 1 for both types of SWCNTs (arc and laser grown). After the surface modification the $I_D/I_G$ in all cases increases with respect to unfunctionalized SWCNTs. After the diazonium reaction 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 1). The results are suggestive of a lower addition density of the AD derivative to the SWCNT walls. This is expected considering the higher molecular weight and steric hindrance of the AD ligand.

![Image](image_url)

**Fig. 3.** Thermogravimetric analysis of unfunctionalized laser-SWCNT and functionalized L-SW-GAP, L-SW-AD and L-SW-DDS samples under desorption conditions.

TGA under inert desorption conditions was used to quantify functional groups attached to functionalized SWCNTs (Fig. 3). A summary of the results obtained for all of the studied samples with an estimation of the functional groups per nanotube carbon atom (degree of functionalization) is given in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$I_D/I_G$ Ratio</th>
<th>wt loss (%)</th>
<th>Degree of Funct.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc-SWCNT</td>
<td>0.03</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>A-SW-GAP</td>
<td>0.13</td>
<td>11</td>
<td>1/58</td>
</tr>
<tr>
<td>A-SW-AD</td>
<td>0.07</td>
<td>12</td>
<td>1/597</td>
</tr>
<tr>
<td>A-SW-DDS</td>
<td>0.26</td>
<td>19</td>
<td>1/164</td>
</tr>
<tr>
<td>Laser-SWCNT</td>
<td>0.02</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>L-SW-GAP</td>
<td>0.10</td>
<td>12</td>
<td>1/98</td>
</tr>
<tr>
<td>L-SW-AD</td>
<td>0.05</td>
<td>11</td>
<td>1/758</td>
</tr>
<tr>
<td>L-SW-DDS</td>
<td>0.14</td>
<td>17</td>
<td>1/164</td>
</tr>
</tbody>
</table>

$^a$TGA results show total mass loss after subtraction of the residual solvent. $^b$The metal content (20 % and 11 % for A-SWCNT and L-SWCNT respectively) was taken into account.

Table 1. Raman $I_D/I_G$ ratio ($\lambda_{ex} = 514$ nm) and TGA-determined weight loss at 700 °C for SWCNT samples

According to results in Table 1, except for the case of SW-DDS samples, the estimated degree of functionalization is higher for arc-SWCNT than for laser-SWCNT. This could be due to the slightly higher initial level of defects, as determined from TGA and Raman ($I_D/I_G = 0.03$) and to the lower purity observed for arc-SWCNT according to UV–Vis–NIR absorption (not shown). Laser-SWCNT and arc-SWCNT showed a weight loss of 3% and 2%, respectively, following thermal desorption at 700 °C (Table 1). The carbonaceous purity index was determined by UV–Vis–NIR absorption spectroscopy following the method described by Itkis et al [11]. Values of 0.047 and 0.087 were obtained for arc-SWCNT and laser-SWCNT, respectively in DMF.

In accordance with Raman results, for both types of SWCNTs (laser and arc-grown) the degree of functionalization was lower for the higher molecular weight amine derivative AD as compared to the lower molecular weight DDS, both modified by the diazonium reaction. On the other hand, the highest degree of functionalization was obtained for SW-GAP samples synthesized by reductive alkylcarboxylation (1/58 and 1/98 for arc-SWCNT and laser-SWCNT respectively). However, these samples showed a smaller increase on the $I_D/I_G$ than DDS modified SWCNTs functionalized by the diazonium reaction.
Fig. 4. Absorption spectra of unfunctionalized (L-SWCNT) and functionalized laser-SWCNT.

UV-Vis-NIR absorption spectra of unfunctionalized laser-SWCNT, modified by the diazonium reaction (L-SW-DDS and L-SW-AD) and by the redox reaction (L-SW-GAP) are shown in Fig. 4. A more significant loss of the interband electronic transitions can be clearly observed for L-SW-DDS and L-SW-AD samples than for L-SW-GAP samples. These results are in agreement with the $sp^3$ defect propagation mechanism for SW-GAP samples and random addition to atomic sites for SW-DDS. In the former case, a confined propagation from existing defects leaves intact segments with sustained band structure although a higher number of functional groups are covalently bonded to the SWCNT wall. Interestingly, both type of SWCNTs showed the same degree of functionalization (1/164) for the in situ diazonium reaction with DDS. Our results on Table 1 indicate that the degree of functionalization 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 degrees of functionalization (L-SW-DDS and A-SW-DDS). On the other hand, in the case of the redox reaction arc-SWCNT with a slightly higher level of initial defects, showed a higher degree of functionalization (A-SW-GAP: 1/58) than L-SWCNT (L-SW-GAP: 1/98).

The integration of the functionalized SWCNTs into the epoxy resin considerably increased the physical and mechanical properties of the composites [1].

3.2 Electrical conductivity of the SWCNT modified epoxy nanocomposites

Composites containing conducting fillers in insulating polymers become electrically conductive when the filler content exceeds the percolation threshold. The jump observed in the conductivity by many orders of magnitude is attributed to the formation of a three-dimensional conductive network of the fillers within the matrix. This is in contrast with the recognized requirement of homogeneous dispersion and a strong adhesion to the matrix for enhancing the mechanical properties of CNT/epoxy composites.

Electrical conductivities were obtained for epoxy composites containing functionalized and unfunctionalized arc and laser-grown SWCNTs at different loadings. The results are shown in Fig. 5. The highest electrical conductivity values were observed for composites containing unfunctionalized laser-SWCNT, in agreement with their higher purity and lower initial level of defects. After the chemical functionalization the electrical conductivity decreased for both materials. The SWCNT lengths were not determined but the functionalization strategies employed here are not expected to modify the SWCNT aspect ratios.

The lower electrical conductivity observed for functionalized SWCNTs has been attributed to different factors. As mentioned before the covalent functionalization introduces defects on the SWCNT walls and hence creates scattering sites which decrease the overall electrical conductivity of the filler. The functional groups can also improve the interfacial interactions and form a covalent connection to the epoxy matrix. These interactions can lead to more homogeneously dispersed functionalized SWCNTs that could not form a percolated network easily. Additionally, this chemical reaction can form electrically insulating layers that increase the tunnelling energy barrier and limit the intertube charge transfer [7].
Fig. 5. Electrical conductivities obtained for epoxy composites containing unfunctionalized SWCNTs (■) and functionalized SW-GAP (●), SW-AD (▲), SW-DDS (▼).

We used a conductivity of $10^{-6} \text{ S/m}$ as a criterion for the formation of the percolation threshold. As can be seen in Fig. 5, at 0.5 wt% loading all of the samples have reached the percolation threshold, except for A-SW-DDS samples which did not show the transition from insulating to conducting phase even at 1 wt % loading. A comparison of the electrical conductivity of the nanocomposites at 0.5 % loading is represented in Fig. 6. The results indicate that for nanocomposites containing functionalized SWCNT the values of electrical conductivity were affected not only by the total number of defects introduced but also by the type of chemical reaction employed; with the type of chemical reaction playing a more significant role. This could be due to the effect of the chemical functionalization strategy on the defect distribution along the SWCNT wall. This is more clearly observed for arc-SWCNT samples. The electrical conductivity of arc-SWCNT modified by the same chemical reaction (diazonium) is highly affected by the total number of defects introduced. Thus, the electrical conductivity of A-SW-DDS, with a degree of functionalization of 1 in 164 nanotube carbon atoms, is six orders of magnitude lower than the electrical conductivity of A-SW-AD with a functionalization degree of 1 in 450 carbons.

In contrast with these results, A-SW-GAP samples (alkylcarboxylation) with the highest degree of functionalization of 1 in 58 nanotube carbon atoms show conductivity values very close to A-SW-AD samples. This is also evident for laser-SWCNT samples (Fig. 6) Although the differences are less significant, L-SW-GAP sample shows almost the same values of electrical conductivity as L-SW-DDS nanocomposites and, despite its higher degree of functionalization, it can reach slightly higher conductivities than L-SW-AD samples at 1 wt% loading (Fig. 5).
There is a remarkable difference of five orders of magnitude between the electrical conductivity of arc and laser grown SWCNTs functionalized with DDS, even though both have been modified by the diazonium reaction and they have the same functionalization degree. This could be due to the lower purity (lower carbonaceous purity index) of the arc-SWCNT samples and possible shorter length which considerably affect the formation of the percolated network for heavily functionalized SWCNTs. On the other hand, at low degree of functionalization, like in the case of AD samples, there are no significant differences between both types of SWCNTs and the sample purity seems to play a less significant role. At 0.5 % loading the conductivity of L-SW-AD is only slightly higher than A-SW-AD. The same trend shown by SW-AD samples was observed for nanotubes functionalized with carboxylic acid groups by the redox reaction even though they possess the highest degree of functionalization. However, we have to consider that in the case of SW-GAP samples the defects are concentrated in a band structure rather than randomly distributed on the SWCNT walls. Hence, their behaviour is similar to SW-AD samples with a significantly lower number of defects.

4 Conclusions

SWCNTs were functionalized in order to increase both dispersibility and interface interaction with an epoxy resin. Two approaches were used to covalently modify the SWCNT walls: diazonium reaction and reductive alkylcarboxylation. SWCNTs synthesized by both the arc and laser methods were used in this study. Fragments of different molecular weight containing free amine groups were covalently attached by the diazonium reaction (SW-DDS and SW-AD). Carboxylic acid groups were introduced by the redox reaction between reduced SWCNTs and diacyl peroxide derivatives (SW-GAP). The two chemical reactions used to covalently modify the SWCNT walls 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 $I_p/I_C$ value was observed for SW-GAP as for SW-DDS samples. However, in contrast with these results, the functionalization degree calculated from TGA showed a higher number of functional groups for SW-GAP. The results can be explained considering that these functionalization strategies proceed through different mechanisms, an $sp^3$ defect propagation mechanism for SW-GAP samples and random addition to atomic sites for SW-DDS samples.

The results from electrical conductivity measurements of epoxy composites containing the modified SWCNTs showed a direct correlation between the degree of functionalization and the electrical conductivity for the same type of reaction (SW-DDS and SW-AD). However, SW-DDS composites showed lower electrical conductivity than SW-GAP samples despite having a lower degree of functionalization. These results show that the electrical conductivity is not only affected by the number of defects introduced by the chemical functionalization but also by the reaction employed for the chemical functionalization. The type of chemical reaction will determine the distribution of defects on the nanotube walls with the consequent effect in the modification of the electronic band structure of the functionalized SWCNTs.

Through the proper choice of the functionalization reaction, the type of SWCNTs and by controlling the degree of functionalization and defect distribution on the SWCNT walls, it is possible to optimize the electrical conductivities of these SWCNT/epoxy composites. Even if covalent functionalization usually leads to lower conductivity values (and higher percolation thresholds) compared to raw SWCNTs, the need to functionalize this kind of filler with targeted molecules could arise from the aim of improving mechanical or thermal performance of polymer composites. In this context, our studies provide a way of assessing the most suitable functionalization pathway to preserve, as much as possible, the conductive behavior of nanocomposites, or, to induce insulating behavior ad lib, while increasing mechanical and thermal resistance. In this way, a tailored improvement in selected physical properties could also be undertaken while maintaining the desire electrical conductivity properties.
References


