Dispersion and functionalization of single-walled carbon nanotubes (SWCNTs) for nanocomposite applications

A. Yaya\textsuperscript{1,2,a}, Abraham Tekley\textsuperscript{3}, E. Annan\textsuperscript{1}, J.K. Efav\textsuperscript{1}, E. K Tiburu\textsuperscript{4}, B. Onwona-Agyeman\textsuperscript{1} and Lars R. Jensen\textsuperscript{5}

Received 24 August 2016, Accepted 15 February 2017

Abstract – We present an easy and reliable method of functionalizing and dispersing single-walled carbon nanotubes (SWCNTs) for nanocomposite production. This was achieved via a mixture of the concentrated acids HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}, followed by sonication in appropriate solvents (Ethanol, Acetone and/or Dimethylformamide). SWCNTs were functionalized to attach carboxylic moieties on the walls of the nanotubes, which aided in the production of SWCNT suspensions in acetone, ethanol and dimethylformamide in which nanotubes remained dispersed for a period of two (2) weeks. Energy dispersion analysis (EDS), scanning electron microscopy (SEM) and Raman spectroscopy were used to characterize the functionalized SWCNTs.

Key words: SEM / EDS / Raman / Functionalization / SWCNTs

1 Introduction

Surface modification of carbon nanotubes (CNTs) is an important step in understanding the mechanical properties of uniformly dispersed nanotubes. The procedure also ensures effective interfacial bonding between the matrix and nanotubes for load transfer in the polymer nanocomposite [1].

Carbon nanotubes always appear in agglomerate form due to their higher surface area [2]. Hence, better methods of dispersion need to be formulated to improve surface properties of the nanotubes within the matrix material.

Since the side walls of carbon nanotubes are arranged in a seamless hexagonal ring with no dangling bonds, the end caps of CNTs are more reactive than their side walls [3–7]. The commonest method of improving the surface properties of CNTs is by functionalization, which involves either opening the end caps of the tubes to induce defects and enrich its chemistry or attaching functional groups to the side walls of the carbon nanotubes [1]. Cutting CNTs is one of the approaches used for functionalizing nanotubes [8]. As shown in Figure 1, this method removes the caps at the end and also shortens the SWCNTs so that polymer resin molecules will fill the tube to improve the bonding and surface properties between nanotubes and the polymer matrix.

The cutting of CNTs could be carried out by the use of concentrated acids, fluorination, ultra-sonication or simply by mechanical milling or grinding.

Strong acids such as H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3} can be used to cut CNTs [10]. It was reported by Farkas et al. [11] that although it is possible to cut long and tangled CNTs using these acids, it might not be effective to cut nanotubes with smaller diameters in the range (0.7–0.8 nm).

Cutting CNTs by fluorination was achieved by blending SWCNTs with fluorine and then pyrolysing them at high temperature (\textasciitilde 1000 °C) under inert atmosphere. This resulted in the modification and cleavage of nanotube fragments with different lengths [10].

Another method used to cut and modify CNTs is ultra-sonication. This is a common method of dispersing CNTs in a solvent (resin matrix) as well as shortening of SWCNTs [12]. However, there are some limitations in utilizing ultrasonic waves, as they cause defects such as buckling, bending and sometimes holes in the sidewalls.
of CNTs that might compromise the mechanical integrity of the nanotubes [13]. Long-time sonication has also been reported to cause permanent damage to the nanotubes [14–16].

Additionally, mechanical ball milling or grinding is a solid state process which can be used to cut or shorten CNTs. During this process, the formation of kinks in the CNTs results in bond fracture when the local strain exceeds the critical threshold.

Generally, the methods of cutting CNTs outlined above present some challenges in controlling the length of the shortened CNTs and preserving the original side wall structure of the nanotubes.

The covalent modification of CNTs results in the formation of covalent bonds on the surface of nanotubes. This method, however, has some drawbacks; the mechanical and electrical properties of covalently modified CNTs were shown to decrease significantly compared to the original behaviour of the nanotubes. This was attributed to the disruption of the CNT conjugation system during bond formation and breakage as a result of functionalization.

The reactivity on the end caps of nanotubes is driven by strain relief which stems from the pyramidalization and misalignment of pi-orbitals that causes local strain [17]. As the side walls of the nanotubes are inert to most chemicals, they need to be activated prior to surface modification.

Fluorination of CNTs is the earliest method observed to form a surface bond between the carbon of the nanotubes and fluorine at higher temperatures [18]. The C–F bonds established at the surface are reported to be weaker, thus the C–F bonds can serve as a starting point for surface modification through subsequent addition of various chemical moieties. Once the nanotubes is fluorinated, this then form the basis for the attachment of several groups along the sidewalls of the tube; alkyl groups (alkylation) [19] and amino groups [20]. The side wall alkylation of fluorinated SWCNTs were shown to precede the attachment of other functional moieties either by using alkyl lithium species or alkyl magnesium bromide in tetrahydrofuran (Grignard synthesis) as alkylation precursors. Amino groups can also be attached to the side walls of fluorinated SWCNTs, which provides a synthetic route to bind amino acids to the side walls.

Another strategy for surface modification via covalent method is by inducing defects on the walls of CNTs through oxidation. This helps in generating defects and other functional groups through which a chemical species could be linked [1]. Treating CNTs with strong acids like HNO$_3$, K$_2$MnO$_4$/H$_2$SO$_4$, oxygen gas, O$_3$, and K$_2$Cr$_2$O$_7$/H$_2$SO$_4$ causes defects (Stone-Wales defects, vacancies) and terminal Carboxylic groups, as shown in Figure 2.

The carboxyl groups generated by oxidation of CNTs are important sites for linking nanotubes to polymers in the processing of nanocomposites.

The reactivity of terminal carboxyl groups could be further enhanced by reacting with thionyl chloride (SOCl$_2$) to yield an acyl chloride on the surface of the nanotube which can add several groups at the carbonyl position. This is due to the labile nature of the C-Cl bond [17].
Furthermore, the non-covalent method of surface modification is advantageous, thereby maintaining the original properties of the nanotube. In this method, there is no bond formation or breakage, but only dispersion and wrapping of linear long chain molecules, like surfactants and polymers, on the surface of CNTs.

Finally, surface properties of SWCNTs were reported to be modified by using surfactants such as benzalkonium chloride and sodium dodecylsulfate (SDS) in an aqueous phase, causing well dispersed nanotubes [23]. The surface properties were also modified by DNA molecules, enabling efficient dispersion of CNTs due to the chain flexibility and backbone charge of the DNA molecule [24].

In this paper, we present a soft and simple chemical technique for the dispersion and functionalization of single-walled carbon nanotubes with the formation of fewer defects on the nanotube side walls which can be tailored for nanocomposites and other applications.

2 Experimental procedure

2.1 Chemicals

HCl (37% fuming) supplied by Sigma-Aldrich Inc., H$_2$SO$_4$ (97%) and HNO$_3$ (65%) supplied by Merck, absolute Ethanol (99.9%) supplied by Kemetyl, dimethylformamide (DMF) and acetone were the chemicals used for the purification, dispersion and functionalization purposes.

2.2 Single-walled carbon nanotubes

The as-prepared SWCNTs were supplied by Carbolex Inc., and they were manufactured by the Arc method. These tubes are supposed to have a purity of 50–70 vol%, as provided in the supplier information [25]. According to the manufacturer’s information, these carbon nanotubes have an average diameter of 1.4 nm and are found in “ropes” which are typically ~20 nm in diameter. Impurities within the products include approximately 35 w% residual catalyst (Ni, Y) and some amorphous carbon on the outer surfaces of the ropes. The single-walled carbon nanotubes were purified by a method described elsewhere in the text [26].

2.3 Functionalization of purified SWCNTs

For the preparation of functionalized SWCNTs, the oxidizing acid treatment methods were used. Accordingly, 500 mg of purified SWCNTs were immersed in 250 ml of concentrated H$_2$SO$_4$/HNO$_3$ in a ratio of 3:1 v/v % respectively. As reported in the functionalization of CNTs [27,28], an hour’s sonication and short time acid treatments were deemed to be optimal for oxidizing and preserving the aspect ratio of CNTs. Hence, the acid/SWCNT mixtures were sonicated using a horn ultra-sonicator (type UP 200S) for 30 min. The short sonication time was chosen to avoid damage of the SWCNTs due to prolonged sonication, as these nanotubes will further be sonicated for dispersion purposes. The resulting solution was rinsed well with deionised water till $p_H \sim 7$, after leaving the mixture in reaction time for about 5 h. The functionalized nanotubes (SWCNTs-COO$^-$) were then collected after filtration through a 0.45 µm millipore membrane filter. Finally, the collected solutes were dried overnight in an oven at 100 °C to get rid of water.

Raman spectra were obtained from the raw (r-SWCNTs), purified (p-SWCNTs) and functionalized (f-SWCNTs) nanotubes using an argon (Ar$^+$) laser excitation of 785 nm with a resolution of 2 cm$^{-1}$. The procedure for obtaining the purified SWCNT samples has been described in Reference [26].

2.4 Results and discussion

Due to the substantial van der Waals attractions, CNTs often aggregate and form bundles of nanotubes. When employed as reinforcing materials, efficient and effective dispersion plays a significant role in order to achieve high performance in nanocomposites. Therefore, it is desirable to functionalize the sidewalls of CNTs, thereby generating CNTs-derivatives that are compatible with solvent as well as polymeric matrix materials.

The SWCNTs were functionalized by the chemical method of oxidation using H$_2$SO$_4$/HNO$_3$ mixtures. Since chemical functionalization of nanotubes is believed to start at defect sites (heptagon-pentagon pair; a junction at the walls of nanotube where the hexagon pairs are changed to a heptagon and pentagon pairs), the extent of oxidation depends on the amount of defects in the starting materials. Already, the SWCNTs had some defects as a result of the production methods employed. Moreover, additional defects (bends and opening of the end caps) introduced during purification make functionalization easier. Hence, it is expected that carboxylic functional groups and other oxygen bearing groups will exist at the end caps and defect sites, thus decorating the nanotubes with larger numbers of oxygenated functionalities.

Although it is possible to introduce carboxyl functional groups on the surface of single wall carbon nanotubes using HNO$_3$ alone, the oxidizing acid mixture of H$_2$SO$_4$/HNO$_3$ (3:1 by volume) has been reported to attack almost three times more carboxylic acid sites relative to HNO$_3$ [22].

The H$_2$SO$_4$/HNO$_3$ mixture can generate NO$_3^+$ ions which are strong electrophiles with the ability to attack not only the existing defect sites but also the graphene-like structure of nanotubes to generate new defect sites. Contrarily, this mixture can also cut the nanotubes and may cause the nanotubes to be reduced to amorphous carbons [29,30]. This phenomenon was briefly described by Zhang et al. [8]. Furthermore, the oxidation process is accompanied by defect generating and defect consuming steps. In the former step, electrophilic reactions attacks
the graphene structure to create active sites such as –COOH and –C=O. In the latter step (defect consuming), the graphene structure of the tube is destroyed due to further oxidation of the active sites generated by the first step. Thus, as the defect generating steps were found to be faster than the consuming steps, higher carboxylic groups were found on the surface of nanotubes when oxidized in H$_2$SO$_4$/HNO$_3$ mixture.

In Table 1, representative energy dispersive spectroscopy (EDS) values of the SWCNTs before and after functionalization are given. This qualitative data indicates that there is an increase in atomic percentage of oxygen from 3.15% to 18.73%, which could signify the presence of carboxylic functional groups attached to the SWCNTs. The EDS gives the relative concentration of each element in the sample; nevertheless, it does not confirm the presence of carbonyl group (-C=O) on the side walls of nanotubes. In order to confirm the presence of a carboxyl functional groups, Fourier Transform Infra-red spectroscopy would have been the best method, as it can detect the inter-band transition to determine the effect of bonding on the band structure. Moreover, band frequencies around $\sim$1750 cm$^{-1}$ and $\sim$1640 cm$^{-1}$ give a fingerprint for the presence of C=O stretching vibration modes of carboxylic group and the asymmetric stretching vibration of the carboxylate (-COO$^-$) respectively [31–33]. Unfortunately, we were not able to do any FTIR analysis in this work.

As functionalized SWCNTs were expected to carry several carboxylic acid groups, this offers the opportunity to form well dispersed colloids in ethanol. Furthermore, carboxylic functional groups on the functionalized nanotube walls can undergo esterification reactions with other polymers such as epoxy resins to form covalent bonds which could improve the mechanical properties of the composites.

Generally, functionalization of SWCNTs could enhance the efficiency of reinforcement by improving solubility and dispersion and also by forming chemical bonds with the matrix [34].

Raman spectroscopy studies were carried out on the functionalized SWCNTs to ascertain the degree of functionalization in comparison to raw and purified powders of the SWCNTs. This is shown in Figure 3. As can be seen in Figure 3, the increase in intensity and width of the Raman D-band of functionalized SWCNTs (f-SWCNTs) as compared to the purified ones (p-SWCNTs) could be due to the change of the nanotubes to graphitic structure (and amorphous carbon) owing to the exposure of the nanotubes to strong oxidizing agents (HNO$_3$/H$_2$SO$_4$ mixture).

By similar extension, this concept can be applied to our study to investigate whether purification and functionalization affect the length of SWCNTs. Based on the average Raman spectra intensities of the raw, purified and functionalized SWCNTS, the data values of $I_D/I_G$ were plotted against the type (raw, purified and functionalized) of SWCNTs, showing the extent to which the length of nanotubes was shortened during functionalization, as the values relate inversely to nanotubes length ($1/L_{tube}$) as shown in Figure 4. The $I_D/I_G$ ratio increases from raw

### Table 1. EDS Elemental analysis of SWCNTs before and after oxidative functionalization. (This is only qualitative data averaged for 10 samples).

<table>
<thead>
<tr>
<th>Atom (%)</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Ni</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before functionalization</td>
<td>95.03</td>
<td>3.15</td>
<td>–</td>
<td>1.25</td>
<td>0.51</td>
</tr>
<tr>
<td>After functionalization</td>
<td>80.20</td>
<td>18.73</td>
<td>0.25</td>
<td>0.71</td>
<td>0.11</td>
</tr>
</tbody>
</table>

As reported by M.S. Dresselhaus et al. [23], the intensity of the D-band of Raman spectra increases with decreasing length of nanotubes and the ratio $I_D/I_G$ shows an increasing trend with decreasing nanotube length ($L_{tube}$) of nanotubes, showing the dependence as:

$$\frac{I_D}{I_G} \sim \frac{1}{L_{tube}}$$  \hspace{1cm} (1)

Fig. 3. Raman spectra for raw (r-SWCNTs), functionalised (f-SWCNTs) and purified (p-SWCNTs) showing radial breathing mode (RBM), disorder mode (D), 2nd order D-mode, tangential mode (G) and second order tangential mode (G').

Fig. 4. The intensity of $I_D/I_G$ ratio for the raw(r-SWCNTs), purified (p-SWCNTs) and functionalized (f-SWCNTs) single-walled carbon nanotubes.
A. Yaya et al.: Matériaux & Techniques 104, 607 (2016)

Fig. 5. SEM images of SWCNTs; (A) Pristine SWCNTs, (B) Purified SWCNTs.

to purified nanotubes simply because a fraction of amorphous carbon is removed during purification. The ratio increases from purified to functionalized nanotubes, not only because of the shortening, but simply because of the functionalization of the nanotube sidewalls.

However, the increase in $I_D/I_G$ intensity for functionalised SWCNTs results from the shortening of the nanotubes which increased the intensity of the Raman D-band, but this needs to be verified with other electron microscopy techniques like AFM and TEM which was not done in this studies.

Dispersion and interfacial bonding phenomena are the two most important factors that control the efficiency of load transfer between the nanotubes and polymer matrix in polymer nanocomposites. We tackled these problems by dispersing the nanotubes in an appropriate solvent such as ethanol, which was followed by the sonication and functionalization of nanotube surfaces using $\text{H}_2\text{SO}_4$/HNO$_3$ mixtures. The advantage of using ethanol is that it is easier to evaporate during the processing of composites at lower temperature than other solvents without affecting the property of the polymer.

Solvents such as acetone, tetrahydrofuran and chloroform were reported to better disperse SWCNTs [35, 36]; however, they can interact with some polymer networks which can either affect the mechanical property negatively when composites are formed without ensuring that they evaporate from the mixture.

It is true that the functionalization of nanotubes will contribute more towards addressing the dispersion and adhesion needs. The dispersion process of the purified and functionalized nanotubes by sonication in ethanol was however difficult and needed longer sonication time compared to the fluffy raw SWCNTs in our case. This was due to the highly aggregated and solid nature of the SWCNTs obtained after purification and functionalization, see Figure 5.

In order to verify the extent of our functionalization, the functionalised tubes were placed in acetone, dimethyl formamide and ethanol, see Figure 6. The significance of this dispersion test was that, it enabled us to judge whether the surface of nanotubes had been attached with polar functional groups which could create better interaction (miscibility) with the relatively polar solvents (polarity index of Ethanol, DMF and Acetone is 5.2, 6.4 and 5.1 respectively) and for comparison, the polarity index of water (polar), and hexane (non-polar) is also 9 and 0 respectively [37]. After the dispersion by sonication, the functionalized SWCNTs were observed to have better stability than the raw SWCNTs as shown in Figure 6. The stability of the functionalized SWCNTs in the solvent could be because the polar groups attached to the nanotube surface might create better interaction with the polar solvent.

It is not surprising to see that it is difficult to disperse functionalized or purified nanotubes. It is known that nanotubes often aggregate irreversibly after drying. Samples are sometimes freeze-dried so that they can be more easily processed.

3 Conclusion

To benefit from interfacial properties of SWCNTs with polymers, we had functionalized the purified SWCNTs to attach carboxylic functional groups on the walls of the nanotubes, with the view that these functional groups would enhance the interfacial properties between nanotubes when used as a nanocomposite. Thus, we found that, the strong oxidizing agent, $\text{H}_2\text{SO}_4$/HNO$_3$ mixture, enabled us to attach a significant amount of carboxylates to the nanotubes. However, it was necessary to control reaction parameters (temperature, concentration and time of reaction) to reduce the amount of damage on the surface of nanotubes and a shortening of the SWCNTs. Also, although sonication of SWCNTs in solvents improves the dispersion process, the little residual amount of solvents that remains after evaporation might influence the chemical reaction process which may affect their use in applications such as nanocomposites if they are not completely removed.

Finally, the SWCNTs which were functionalized remained dispersed in different solvents for a period lasting two weeks as compared to the pristine and purified tubes.
Acknowledgements. AY acknowledges support from the Carnegie-NGAA for sponsorship on the write-shop which was organised by Prof. Y. Ntiamoah-Badu. We also thank Prof. Helen Yitah of the English Dept. University of Ghana for proof reading the manuscript.

References

[22] J.E. Fischer, Carbon nanotubes: structure and properties, 2006, pp. 41-75