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Purity evaluation and influence of carbon nanotube on carbon nanotube/graphite thermal stability

Aline M. F. Lima · Anthony W. Musumeci ·
Hong-Wei Liu · Eric R. Waclawik ·
Glaura G. Silva

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Abstract High resolution thermogravimetry has been used to evaluate the carbonaceous content in a commercial sample of single-walled carbon nanotube (SWNT). The content of SWNTs in the sample was found to be at least 77 mass% which was supported by images obtained with scanning and transmission electron microscopies (SEM and TEM). Furthermore, the influence of SWNT addition on the thermal stability of graphite in mixtures of SWNT/graphite at different proportions was investigated. The graphite stability decreased with the increased of SWNT content in the overall range of composition. This behavior could be due to the close contact between these carbonaceous species as determined by SEM analysis.

Keywords Graphite · Mixture · Single-walled carbon nanotubes · Thermogravimetry

Introduction

The structure, topology and size of carbon nanotubes are the source of outstanding mechanical properties, amazing electrical properties and are thus considered a highly promising candidate for use in a range of applications [1–3]. They have potential for use in field emitters, nanoelectronic devices, probe tips for SPMs and nanotube based composites [4]. Despite a range of synthetic techniques (i.e., laser vaporization, arc discharge and chemical vapour deposition) being commonly available, none have proven successful in producing 100% pure single-walled nanotubes (SWNT) in large quantities [5]. As the final characteristics of a nanotube-containing composite or device are highly dependent on the quality of the supplied nanotube soot, a fast and efficient protocol for determining the quantitative and qualitative characteristics is required.

Transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) provide useful information about the intimate structure of carbon nanotubes in a sample; however, they give little information about the overall sample. Thermogravimetry (TG) has been used to study the oxidative stability of carbon nanotubes: single-walled nanotubes (SWNT) and multiwalled nanotubes (MWNT)[6]. This technique is less expensive and permits analysis of content that is representative of the sample.

The as-produced carbon nanotube (CNT) material is known to be inhomogeneous, containing a variety of impurities with the following order of reactivity: amorphous coating > amorphous particle > SWNT > graphitic particles [7]. The first reports of the use of thermogravimetric methods for carbon nanotubes in the presence of high contents of carbon nanoparticles are the works of Pang et al. [8] and Ajayan et al. [9]. Pang et al. [8] analysed TG curves obtained at 1 °C min^{-1} that showed that multiwalled nanotubes and nanoparticles were more resistant to oxidation than other forms of carbon, such as diamond, soot, graphite and C_{60} studied under the same conditions. However, the study of stability of such allotropes, as graphite for example, in presence of SWNT through thermogravimetric analysis has not been reported in the literature.

A. M. F. Lima · G. G. Silva (✉)
Departamento de Química, Universidade Federal de Minas Gerais, Pampulha, C.P. 702, Belo Horizonte 31270-901, Minas Gerais, Brazil
e-mail: glaura@qui.ufmg.br

A. W. Musumeci · H.-W. Liu · E. R. Waclawik
Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

Graphite materials are largely used due to a favourable combination of physicochemical properties such as the relatively high heat conduction and thermal stability [10]. However, graphite exhibits very poor oxidation resistance in air at high temperatures. The influence of temperature on graphite oxidation has been reported in the literature [11–15]. The thermal oxidation of graphite leads to the removal of carbon layers from the surface and the formation of patches and circular pits on the exposed plane [11, 16]. Another influence is the metal and metallic salts which are active catalysts for graphite oxidation, the relative activities probably depend on the chemical nature of the catalyst particle, the localized interaction between catalyst particle and graphite [13]. In this scenario, how SWNTs can affect the thermal oxidation of graphite is an interesting issue to be investigated. For this purpose, the composition of CNTs needs to be well characterized.

The oxidative behavior of CNT samples by TG has been reported in the literature [17–24]. Studies by Trigueiro et al. [25] demonstrated that thermogravimetric techniques (conventional and high resolution thermogravimetry) can be exploited to attain the goal of CNT purity control, associating the fractions of carbonaceous materials with certain maxima in the line shape analysis of derivative thermogravimetric curve (DTG). The assignments were based on the line shape analysis performed for fullerene and graphite [25] and also on several literature studies of carbonaceous forms with a range of techniques [6, 17–24]. The line shape analysis of the DTG curve has also been used by Musumeci et al. [7] to attain a better understanding of the exact composition of purified and unpurified SWNT samples by thermogravimetric analysis.

In this study we present the use of high resolution thermogravimetry (HRTG) and propose assignments for different carbonaceous fractions in an as-supplied sample of SWNT with the support of high resolution electron microscopy imaging techniques. The great advantage of the HRTG technique is that a representative amount of sample is studied in comparison to the infinitesimally small amount of sample analyzed with the use of imaging techniques only. Furthermore, this study reports the thermo-oxidation study of SWNT/graphite mixtures in the entire range of composition. This investigation was performed in order to produce systematic data about the influence of carbonaceous oxidation of the lesser stable species upon the more stable one. The commercially available as-prepared carbon nanotubes can present variable contents of different carbonaceous forms as already mentioned and the study of controlled product mixtures of these carbonaceous forms can be very helpful to clarify the behavior of the soots thermo-oxidation.

Experimental details

The SWNTs purchased from Nanocyl Inc., were produced via catalytic carbon vapour deposition process. The nanotubes have a stated carbon purity exceeding 80 mass%, average diameter of ~2 nm and a metal oxide impurity of less than 20% [26]. Elemental analysis of nanotubes was performed. Although instrumental limitations prevented a quantitative analysis of oxygen, carbon was confirmed to be the major elemental component. The graphite sample was a commercial pure grade used for carbon nanotube synthesis purchased from Carbono Lorena-Brazil, and is 99.9 mass% pure as reported by the supplier. Graphite surface area of approximately 22 m^2g^{-1} was obtained by nitrogen adsorption in a Nova 1200 Quantachrome equipment. By changing the mass ratio of SWNT to graphite (G) 1:9, 2:8, 3:7, 5:5, 7:3, 8:2 and 9:1, a series of mixture coded as SWNT/G 1/9, SWNT/G 2/8, SWNT/G 3/7, SWNT/G 5/5, SWNTG 7/3, SWNT/G 8/2 and SWNT/G 9/1 were prepared, by powder milling.

Thermogravimetric measurements

Thermogravimetric measurements were performed with two different instruments: conventional TG at 5 °C min^{-1} with temperature range from room temperature up to 900 °C in dry air flow of 100 cm^3 min^{-1} were carried out with SDT 2960 TA® Instruments equipment. High resolution TG was carried out in a TA® Instruments Inc., high resolution thermogravimetric analyser (series Q500) in a flowing air atmosphere (60 cm^3 min^{-1}), resolution 6 and sensitivity was maintained at index 1 (these equipment indexes correspond to different analysis times as discussed in previous studies [7, 25]). Approximately 5 mg of sample was heated in an open platinum crucible up to 1000 °C at a rate of 5.0 °C min^{-1}. Derivative thermogravimetric (DTG) curves were generated with approximately 2,000 points for the conventional TG measurements. The data was analysed by non-linear least squares fitting with multiple Gaussian curves. Component analysis was undertaken using the Jandel 'Peakfit' software package The minimum number of curves were used to fit each DTG until the Pearson r^2 value was in general higher than 0.99.

Scanning electron microscopy

Purified SWNT samples and the residues obtained from the mixture SWNT/G 5/5 after thermal treatments during the TG experiment up to different temperatures were prepared for SEM by sonication of a dilute chloroform dispersion (0.1 mg/mL) and drop cast onto clean silicon substrates (from silicon wafer). The silicon wafers were attached to an aluminium stub with the aid of double-sided carbon tape. Secondary electron images were obtained using an FEI Quanta 200 environmental SEM. Accelerating voltages of 10–30 kV and spot size settings of 2–3 were used for the dispersed nanotube material. An initial characterization of composition and dimensions of the SWNT sample was accomplished by analyzing samples produced with a very diluted suspension of nanotubes after more than 8 h of sonication at low power bath.

Transmission electron microscopy

TEM measurements were taken on the Philips TECNAI 20 FEG analytical electron microscope. Samples were prepared by dipping holey carbon grids (200 mesh copper grids, GYCu200) into dilute chloroform suspensions (1 mg/mL).

Results and discussion

From the analysis of several scanning electron microscopy (SEM) images of the SWNT sample deposited from a very diluted chloroform dispersion sonicated for a long period of time, a clear tendency of the nanotubes to form bundled ropes exceeding several microns in length was observed (see Fig. 1a). Also evident from the SEM images is the presence of particulate matter in the supplied SWNT material. Such globular features are believed to stem from amorphous and graphitic carbon impurities as well as residual metal catalysts remaining from the synthesis technique that was employed to synthesize the SWNT.

Transmission electron microscopy studies revealed that the average diameter of the SWNT is 2.1 ± 0.4 nm. This average diameter was assessed from an average of 25 tubes in the high resolution TEM images obtained (for example see Fig. 1b, c). This value is in good agreement with the quoted dimensions of 2 nm provided by Nanocyl S.A. [26]. The TEM image in Fig. 1b clearly shows that even after persistent sonication SWNT bundles still exist, although the occasionally isolated SWNT features may be observed. The high resolution image shown in Fig. 1c is of an isolated SWNT that has a thin amorphous carbon coating on the outsides of the SWNT in certain regions. A number of graphitic shells, as observed in Fig. 1d, and residual metal catalyst impurities were also noted in TEM images. Nevertheless, upon visual assessment it appears that the carbon purity of ≥80 mass%, stated by the manufacturers, may hold true; however, a quantitative evaluation was also obtained through thermogravimetric techniques as shown below.

Thermogravimetric (TG) measurements for the SWNT material was performed in duplicate to ensure accuracy in relation to possible inhomogeneities of the sample. The conventional TG and DTG curve measured at 5 °C min^{-1} is shown in Fig. 2a. Figure 2b presents the region of the main mass loss peak and line shape analyses performed to fit the DTG curve.

From Fig. 2a it is evident that the main carbonaceous decomposition occurs at 494 °C and represents a loss of 83.6 mass%. A small mass loss of 2.2 mass% may be observed at 53 °C which is assigned to the loss of a small amount of absorbed water in the SWNT matrix. A residual metal oxide of 11.5 mass% was also found to remain after the TG experiment. This result supports the manufacturer's claim of ≤20 mass% metal oxide impurity in the sample. The elementary composition for the sample was determined as 73% of carbon and 1.7% of hydrogen. Therefore, the carbon purity is inferior to that claimed by the manufacturer. Oxygen atoms due to the imperfect structure and storage conditions might also be present in the material.

Figure 2b presents the best result of the line shape analysis with Gaussian lines for the conventional TG experiment. The line shape analysis was evaluated by visual inspection of the curve and taking into consideration the Pearson number r^2. The major mass loss peak was fitted to four Gaussian lines. The broad peak centered at 487 °C was required to achieve a reasonable fit and demonstrates that is not possible to propose assignments of carbonaceous fractions for this analysis.

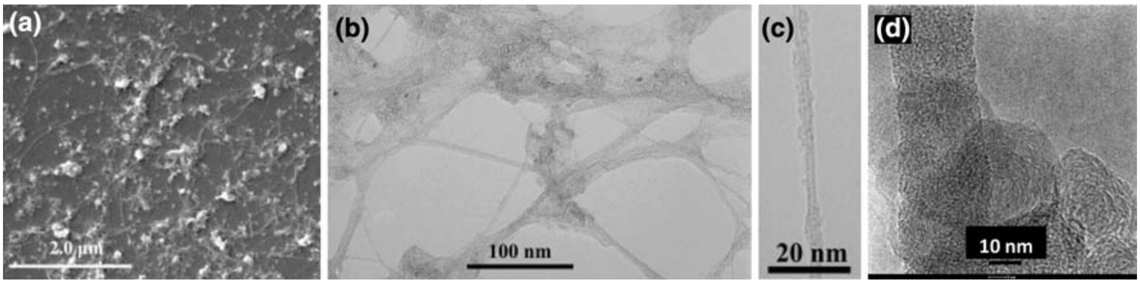

Fig. 1 **a** SEM image of bundled SWNTs of several microns in length; **b–d** high resolution transmission electron microscopy images of the SWNT sample

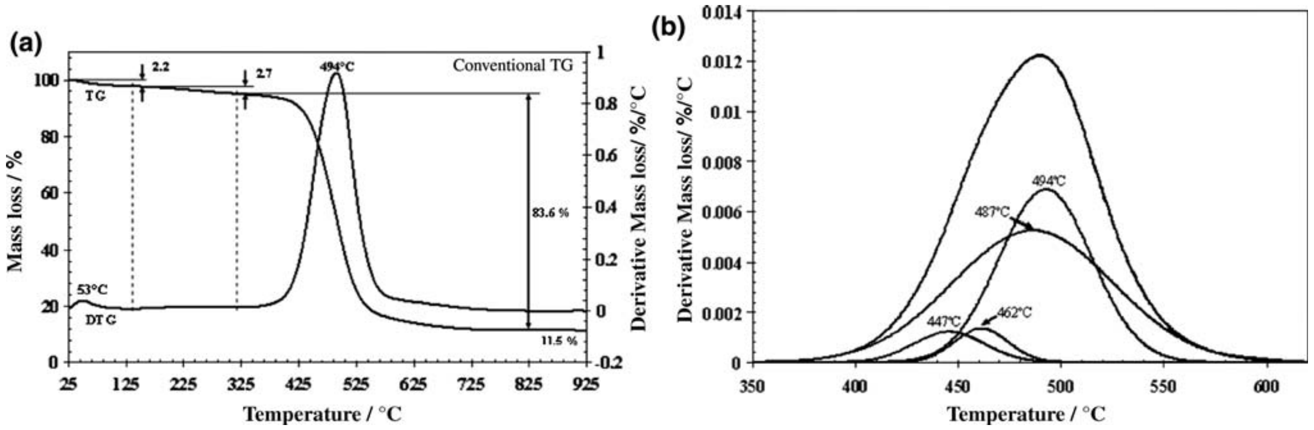

Fig. 2 **a** Conventional TG and DTG curves for SWNT obtained in air at 5 °C min^{-1}, **b** line shape analysis of main mass loss DTG peak

All Gaussian lines in Fig. 2b are overlapped, for instance the lines at 487 and 494 °C correspond to fractions of material oxidizing in the same range of temperature to a large extent. Therefore, this fit could not provide separation of fractions with different reactivities and thus has no physical meaning.

Further studies involving the use of high resolution thermogravimetry were carried out, in order to obtain more detailed information about the thermooxidative behavior of the SWNT sample. The results are shown in Fig. 3a with respect to temperature and the line fit analysis of the DTG curve in Fig. 3b. A small mass loss of 1.4 mass% was observed at low temperature which is due to absorbed water in the SWNT matrix. This value is lower than quoted in the TG experiment probably because the sample was kept longer in the equipment dry atmosphere before run the experiment.

It should be pointed out that the heating rate is not linear in a HRTG experiment as it depends on the reaction rate and is corrected to allow a controlled reaction. Thus, during the decomposition of the major carbonaceous fraction of the SWNT matrix, the experiment enters a quasi-isothermal stage to allow typically overlapped thermo-oxidations (observed during the conventional TG run at 5 °C min^{-1}) to be separated into fractions clearly resolved over time. The Gaussian line profiles related to Fig. 3b have been summarized in Table 1. The assignment of these lines to fractions of carbonaceous material can be achieved based on observations made during SEM and TEM studies and also by taking into account the relative reactivity of different carbonaceous materials investigated separately as discussed in detail previously [7, 25].

It should be emphasized that all assignments mentioned here need to be considered as fractions which are enriched in one or another type of carbonaceous component. The first small line at 218 °C in Fig. 3b corresponds to 0.9 mass% of the sample and is assigned to mainly free amorphous and defective carbon coatings in the sample. The second and third lines at 389 and 393 °C may be assigned to further globular amorphous material that is present in the sample and attached to the SWNT bundles. These Gaussian lines overlap with the main carbon nanotube oxidation and account for 4.3 and 12.8 mass% of the oxidation. The major fractions oxidizing at 397 and 413 °C correspond to 32.2 and 45.4 mass% of the main oxidative peak and may be attributed to two separate carbon nanotube fractions with slightly different reactivity. The final

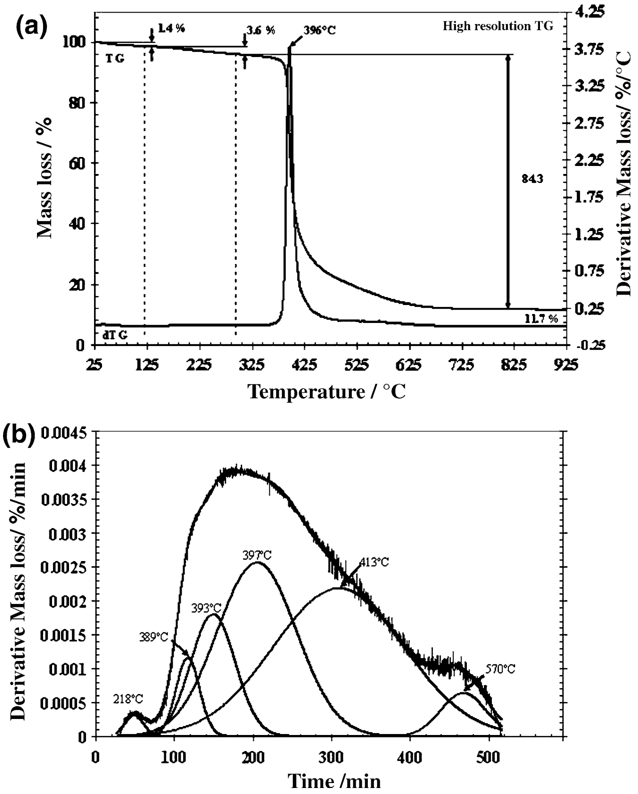

Fig. 3 **a** High resolution TG analysis of SWNT material, **b** DTG curve and line shape analysis

Table 1 Results of Gaussian line profile fitting to HRTG major thermo oxidation peak for SWNT material

Centre (min)	Temperature (°C)	%
48.9	218	0.9
117.1	389	4.3
149.2	393	12.8
205.1	397	32.2
309.1	413	45.2
467.7	570	4.6

small fraction oxidizing at 570 °C corresponds to 4.6 mass% of the sample and may be assigned to the decomposition of a fraction rich in graphitic shells which were observed in several TEM images. Thus, based on these assignments the approximate SWNT content of the as-supplied nanotube soot may be estimated to be at least 77 mass% to possible as high as 85 mass%. It is important to note that, taking into account the elemental analysis, these values should be considered as carbon content added by oxygen content in defects of the tubes.

After having access to an assessment of the carbonaceous content in the carbon nanotube material it is possible to perform further investigations of the reactivity of mixtures SWNT/graphite produced with controlled ratios.

SWNT/graphite mixtures

Figure 4 shows TG and DTG curves obtained at constant heating rate of 5 °C min^{-1} in air for pure and mixture samples. The residue percentage extracted from TG curves (Fig. 4a) for graphite is 2% mass% and increases with the amount of SWNT in the mixture, reaching 11.5 mass% for the SWNT.

Figure 4 shows that the SWNT thermooxidation does not change in the mixtures. On the other hand, an amount of SWNT of 20 mass% in the mixture with graphite (Fig. 4b) leads the temperature of maximum rate of decomposition (T_d) of graphite to decrease from 815 to 795 °C. A pronounced effect was observed in the mixture with 50 mass% of SWNT; in this case the T_d decreases to 658 °C. This behavior can be explained based on the SEM images obtained for the residues of mixture of SWNT/G 5/5 (Fig. 5).

The SEM images of residue obtained after treatment in air in temperature of ~500 °C (during TG experiment) show the closer contact between graphite and SWNT bundles (Fig. 5a). Graphene sheets and carbon nanotube aggregates are observed in Fig. 5b and c, respectively. The SWNT bundles exhibit morphologies which indicate the presence of ropes under an amorphous mass.

It can be proposed that the main reason for the decrease in the graphite stability is the introduction of defects through contact with SWNT undergoing oxidation. The chemical affinity of graphite and nanotube may favour substantial modification of graphite structures during the SWNT thermo-oxidation. It is well-known that the analysis performed in air promotes a large exothermic effect caused by the combustion of carbon forms with similar reactivities present in the sample [6, 20, 25]. Particularly in this study, we suggest that the close contact between graphite and SWNT may promote the oxidation initiated at defects like steps and edges in the graphite (see Fig. 5b). Graphite oxidation studies [11, 13] support this result as they report that the reactivity in the basal plane and at defects like steps (carbon at edges) is different.

We performed the thermogravimetric study for the full range of mixture composition. The values of temperature obtained from the average of the maxima of the two Gaussian lines used to adjust the DTG curve of graphite are

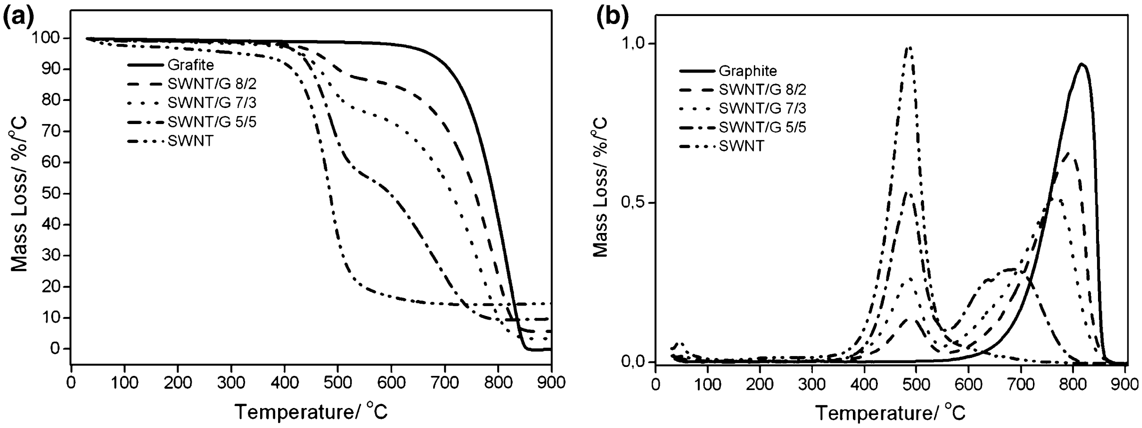

Fig. 4 **a** Conventional TG curve and **b** DTG curve for SWNT/graphite mixtures obtained in air at 5 °C min^{-1}

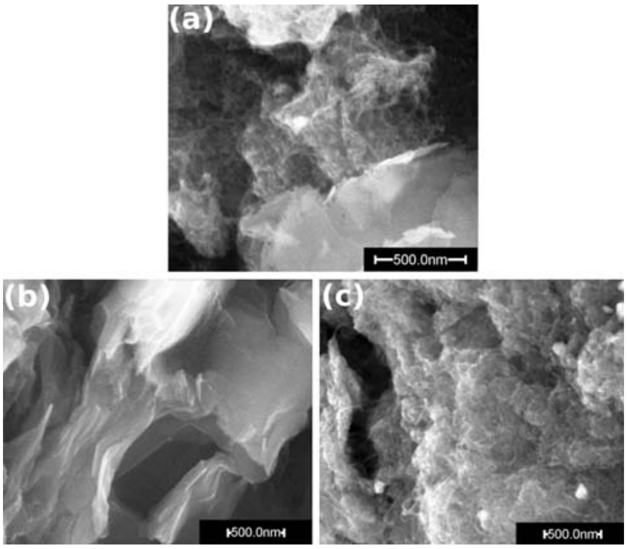

Fig. 5 SEM images of SWNT/graphite 5/5 residues at ~500 °C: **a** SWNT/graphite in contact (80,000×), **b** graphite and **c** SWNT bundles (50,000×)

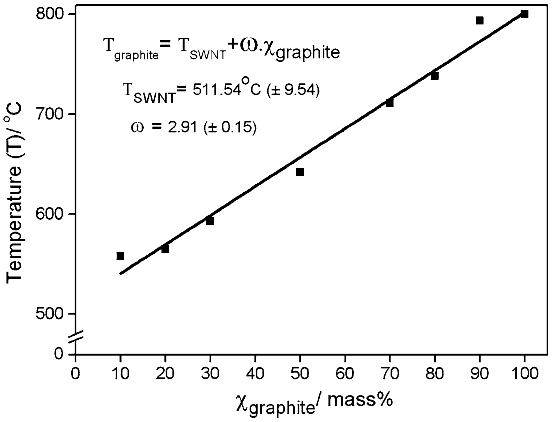

Fig. 6 Average temperature of maximum rate of decomposition for the graphite fraction (temperature of maxima in the Gaussian lines used for the adjustment) of SWNT/graphite mixtures as a function of graphite content

presented in Fig. 6. This experiment revealed a linear dependence on temperature of graphite decomposition maximum as a function of graphite content (χ_{SWNT}).

The linear coefficient of this curve obtained from the fitting is $T_{SWNT} = 511$ °C which is near to the T_d obtained for pure SWNT in this study (T_{dSWNT} 494 °C). Besides, the slope of this curve expresses how the carbon nanotube affects the thermal stability of graphite. On the basis of this result, different carbon nanotubes sample can be compared using a set of values of slope ω, where the higher this factor the greater is the change on graphite stability.

Conclusions

Different types of carbonaceous materials were observed by SEM and TEM in an as-supplied SWNT sample. High resolution thermogravimetry was undertaken and a quantitative evaluation of the carbonaceous fractions was stated. The SWNT content was estimated to be at least 77 mass%. The determination of the SWNT composition was necessary to allow the investigation of mixtures SWNT/graphite proposed in this study with a satisfactory base of information about the carbon nanotube sample.

The effect of SWNT content in mixtures SWNT/graphite was studied and revealed a linear dependence on temperature of decomposition of the graphite fraction as a function of mixture ratio for the full range of composition. The SWNT temperature of maximum rate of thermo-oxidation does not change for all mixtures. It can be proposed that the main reason for the decrease in the graphite stability is the activation of its reactivity by contact with SWNT being oxidized. SEM images indicate that the graphite and the SWNT bundles are in closer contact which promotes the increase of graphene defects when SWNT decomposes.

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