AN INTEGRATED APPROACH FOR MAKING HIGH PERFORMANCE SWNT-BASED MATERIALS

Gervais Soucy*, Keun Su Kim*, Chris Kingston, Jingwen Guan**, Yadienka Martinez-Rubi**, Stéphane Dénommée**, Orson Bourne** and [Benoit Simard]**:**
Benoit.Simard@nrc-cnrc.gc.ca

***Department of Chemical Engineering, Université de Sherbrooke,
Blvd. de l'Université, Sherbrooke, Canada J1K 2R1**

****Steacie Institute for Molecular Sciences, National Research Council of Canada
100 Sussex Drive, Ottawa, ON, K1A 0R6**

Keywords: **Carbon nanotube, SWNT, chemistry, functionalization, epoxy resin, nanocomposite**

Abstract

Single-walled carbon nanotubes exhibit exquisite properties that make them the perfect additives for fabricating high performance multifunctional composites. In order to develop such composites reliably and reproducibly, an integrated approach which affords control over each step of the development cycle must be adopted. The steps include: synthesis, purification, chemistry and integration. Synthesis and purification must yield as much as possible clean and defect-free SWNT. Chemistry must provide a high degree of dispersion and appropriate functional groups for anchoring the SWNT to the matrix in order to achieve proper integration and property transfer. Although these steps are discussed and illustrated herein in the context of fabricating epoxy-based composites, they are applicable and necessary for any other matrices.

1 Introduction

Single-walled carbon nanotubes (SWNT) exhibit the best mechanical, thermal and electrical properties of any known material. Combined with their very high aspect ratios that can reach well over 1000, SWNT are the ultimate material for the fabrication of composites with performance far beyond what is possible today. Unfortunately, despite the wide availability of SWNT and many attempts, all SWNT-based composites reported to date have shown lower than expected performance, often worse than those of the pure matrices [1]. The main reasons for this are:

- highly variable purity and quality of the SWNT samples used
- poor dispersion/exfoliation
- poor interface compatibility with the matrix.

The first reason can be attributed to unreliable and unperfected synthesis and purification methods. The second and third reasons are related to the strong van der Waals interactions among the SWNT, which lead to the formation of large bundles, and to the intrinsic chemical stability of SWNT, which makes binding to matrices rather difficult.

In order to ensure that the full potential of SWNT is exploited, the variables in every step of the overall integration process must be controlled, hence the necessity of an integrated approach. Excellent reproducibility is required in the synthesis, purification, dispersion, functionalization and integration. This paper focuses on each of these steps and shows examples of our unique capabilities towards the development of epoxy based composites.

2 Syntheses and Purification

Reliable and reproducible syntheses methods yielding high purity and high quality SWNT are necessary to the development of high performance materials. Purity relates to the amounts of non-SWNT carbon and catalyst impurities, whereas quality relates to the quantities of sidewall defects on the SWNT. It has been shown by Welch through calculations that defects, even only very few, degrade the mechanical properties of SWNT

substantially [2]. Thus any purification procedures to remove impurities must not introduce (new) defects.

We use two syntheses methods. The first is based upon laser vaporization of a graphite target. The use of lasers to produce SWNT was first reported by Guo et al. [3]. We later improved the method by introducing a second laser whose purpose is to heat the plasma generated by the first laser in order to extend the intervals of SWNT nucleation and growth [4, 5]. This method is able to produce the highest quality SWNT of all available methods. The raw material has a purity estimated to 70-80% using a combination of characterization methods such as transmission and scanning electron microscopies (TEM, SEM), Raman and optical spectroscopy, thermogravimetric analysis (TGA) and porosity measurements. A typical Raman spectrum of the as-produced laser material is shown in Figure 1. The Raman characterization was done with laser power densities sufficiently low as to avoid laser-heating effects. As a result, the Raman spectra provide an accurate assessment of the quality of the SWNT samples.

The raw SWNT are purified to a purity of at least 90% through an in-house process that will be reported in detail elsewhere. The purification does not employ acid treatments commonly used in other published protocols, but only flotation, sedimentation and extraction cycles that leave the SWNT sidewalls intact, as can be seen by their Raman spectra (Fig 1).

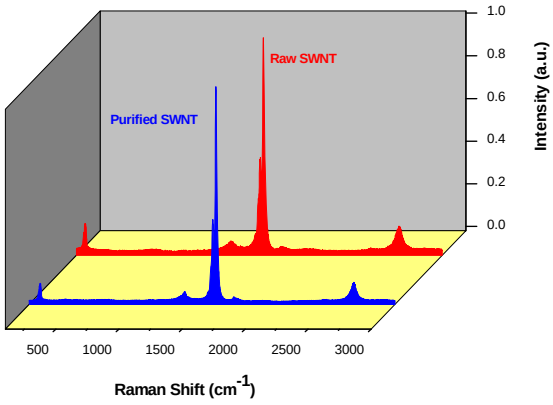

Fig. 1 Raman spectra of raw and purified SWNT. Note that the relative intensity of the D-Band near 1350 cm-1 is smaller for the purified material.

The laser-grown SWNT are used as gold standard to validate further processes and determine what is ultimately possible.

We have emulated the conditions existing in our laser-vaporization method in an industrial RF-thermal plasma reactor. This process is capable of producing SWNT continuously at the rate of 2g/min with a nominal purity of 40%, as determined by a number of characterization methods [6]. This second production method was developed to allow for the fabrication of large SWNT-composite samples that would be otherwise unfeasible due to the high cost and low volumes of commercially available material. As can be seen by the Raman spectra, the quality of the thermal plasma material is similar to that of laser grown materials and superior to those of commercially available SWNT (Fig 2). The purity of the material can be enhanced significantly through simple controlled thermal oxidation cycles.

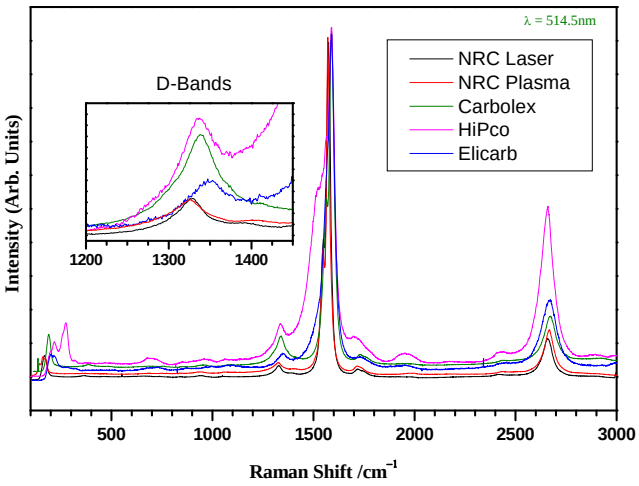

Fig. 2 Raman spectra of some commercially available and NRC-produced SWNT

3 Chemistry of reduced SWNT

It is now widely accepted that chemistry is central to the development of high performance materials based on SWNT. Chemistry can solve the problems associated with bundling and the lack of binding with composite matrices. We favor covalent chemistry because it affords excellent control over the functionalization degrees and minimize the number of "new ingredients" in resin formulations. Strategies for anchoring any practical functionalities to the sidewalls of neutral SWNT have been developed and can be used. But, the

functionalization of neutral SWNT is time consuming and more expensive overall than the cost of production of the SWNT themselves. This is because completion of the reaction at the single-tube level requires a substantial amount of time, typically from several hours to days. We prefer the route of chemical functionalization via reduced SWNT. Reduced SWNT can be prepared in standard solvents by reduction with alkali metals through electron transfer mediated by alkali-naphthalene-THF or alkali-benzophenone-toluene complexes. The SWNT become negatively charged, hence reduced, and naturally exfoliate as a result of electrostatic repulsion. In addition, reduced SWNT possess a higher nucleophilicity thus allowing new chemistry with a variety of electrophilic reagents or radical donor/acceptors. Reduced SWNT, which are obviously good reducing agents, are particularly reactive towards strong oxidizing agents such as peroxides. This patent pending process is depicted in Figure 3. The advantage of this process is that sidewall functionalization at the single-SWNT level occurs at room temperature within minutes, as compared to hours or even days under refluxing conditions for the corresponding reaction with neutral SWNT. Functionalization degrees of 1C % are typically achieved, which is sufficient for enough for effective binding to various matrices.

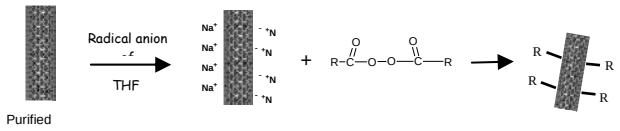

Fig. 3 Rapid functionalization of reduced SWNT with carboxylic functional groups.

Figure 4 shows the Raman spectrum of the functionalized SWNT obtained from the scheme shown in Figure 3 and for which R = -$(CH_2)_3$-COOH (from glutaric acid acyl peroxide (GAP)). The reaction leads to a substantial increase in D-band intensity indicating side-wall functionalization. The identity of the functional group anchored on the side-wall of SWNT can be ascertained by infrared spectroscopy. Figure 5 shows an infrared spectrum of the SWNT material obtained following the reaction shown in Figure 3 in which the reagent was GAP. Features associated with the carboxylic functionality at 1715 cm^{-1} and C-H stretch at 2915 cm^{-1} are clearly observed, indicating that the functional moiety anchored on the SWNT is indeed -$(CH_2)_3$-COOH.

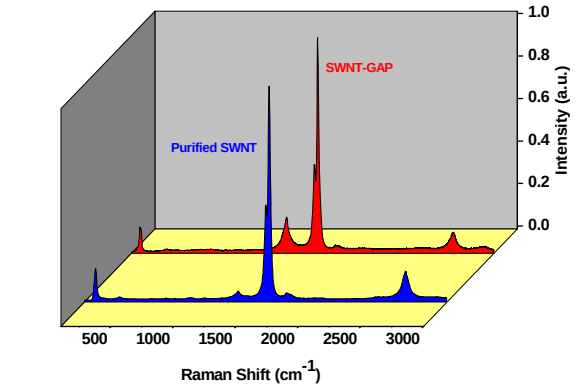

Fig. 4 Raman spectra of pristine SWNT and functionalized SWNT resulting from the reaction with glutaric acid acyl peroxide according to the reaction scheme shown in Fig 3.

A functionalization level of 1C % was determined using ICP-MS by substituting the acidic proton with Na ions, which then served as a probe. This value was confirmed by performing thermal desorption measurements in a TGA thermal analyzer. The –$(CH_2)_3$-COOH moiety desorbs at about 300°C.

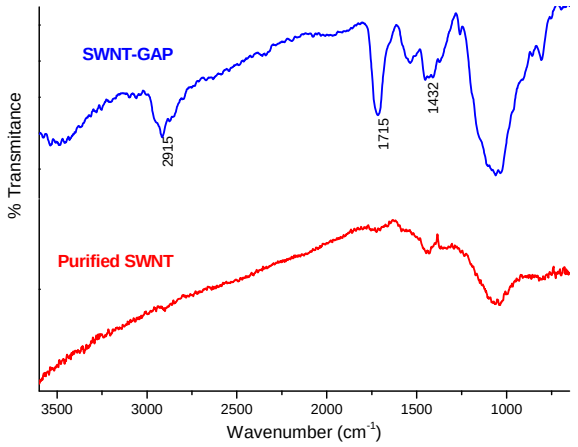

Fig. 5 Infrared spectrum of SWNT–$(CH_2)_3$-COOH from reacting glutaric acid acyl peroxide with reduced SWNT.

Other useful functionalities, such as amine, can be anchored through the same process by preparing the appropriate acyl peroxide derivatives.

4 Integration in epoxy resins

Proper integration in matrices is crucial to obtaining high performance materials. Integration involves achieving dispersion and interface compatibility. Chemical functionalization as we have described satisfies both of these needs. Interface compatibility is achieved by covalent binding between the SWNT and the matrix. We have successfully integrated functionalized SWNT into many thermoset resins and resin formulations of various grades and have obtained excellent dispersions that appear permanently stable. Binding of the SWNT to the matrix backbone can be accomplished in several ways. One efficient method makes use of the chemistry discussed previously to perform esterification of the carboxylic moieties anchored on the SWNT with the epoxide groups of epoxy resins, as illustrated in Figure 6. Although the process is kinetically slow, it is amenable to industrial scale. Figure 7 illustrates qualitatively the

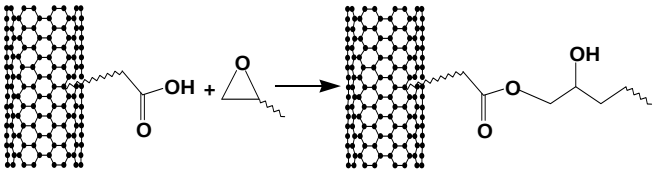

Fig. 6 Esterification reaction of SWNT-COOH with epoxide moieties.

homogeneity of the resulting dispersion as compared to the case where pristine SWNT are mixed into the resin. Despite being processed in an identical fashion the pristine SWNT agglomerate immediately upon mixing into the resin, while the functionalized SWNT show no agglomeration after many months. Confirmation of the esterification reaction can be determined through infrared spectroscopy as shown in Fig 8. The feature at 1735 cm-1 is associated with the ester linkage.

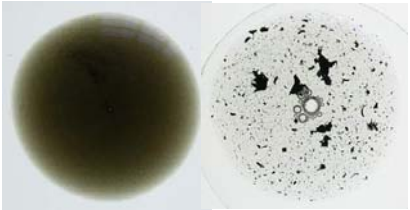

Figure 7 Dispersion of SWNT in epoxy resin. Left- after esterification, right- with no functionalization.

The covalent attachment of SWNT to epoxy resin does not allow for high loadings, as were commonly used in earlier reports of nanotube composites [7]. Viscosity increases significantly with increased loading; for practical purposes only loadings below 1wt% are possible. This is not a major limitation since substantial improvements in mechanical properties can be achieved with such low loading levels.

5 Mechanical Performance

Significant improvements in mechanical properties have been obtained with small loadings

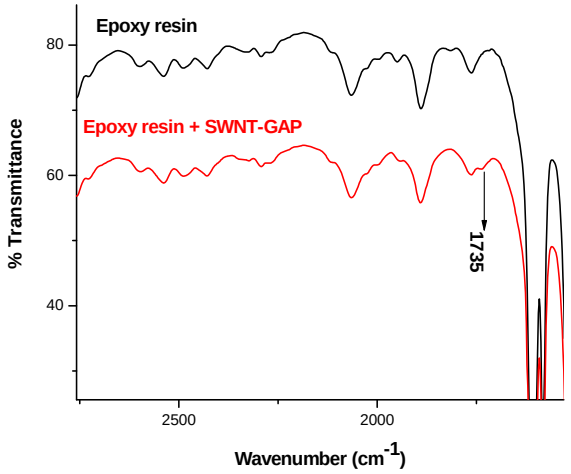

Fig 8: Infrared spectra of neat epoxy resin (top) and epoxy resin functionalized with SWNT-COOH.

of chemically modified SWNT. For example, with the incorporation of as little as 0.2wt% of functionalized SWNT an improvement of 60% in fracture toughness (K_{IC}) has been obtained for an aerospace-grade resin. The modified SWNT formed naturally uniform and stable dispersions within the resin, which were maintained during the reaction and curing processes. No significant changes to the processing of the resin were necessary to achieve the SWNT reinforcement. Recent data suggest that improvement up to 300% should be possible with loading levels below 1wt%.

6 Conclusion

We have demonstrated that the exploitation of the remarkable properties of SWNT for the fabrication of advanced composites is possible when precise control is exerted at every stage of development. Reliable and large-scale synthesis provides a uniform supply of raw material for repeatable production of bulk composite samples.

Efficient purification can remove unwanted synthesis byproducts without deterioration of the SWNT properties. Simple and scalable functionalization protocols give the flexibility to tune the level of dispersion and interface binding for compatibility with any composite matrix. Adjustment of the functionality and SWNT loading levels can then be used to achieve the desired enhancement. When properly executed, significant mechanical improvement can be attained with low SWNT loading and with minimal impact on processing compared to neat materials.

References

[1] J. N. Coleman, U. Khan, Y. K. Gun'ko, "Mechanical Reinforcement of Polymers Using Carbon Nanotubes" Adv. Mat.,, 18, 689-706 (2006).

[2] B. Welch "Effects of molecular defects on CNT Material Properties", Pira Intertech Workshop on Carbon Nanotubes, Brussels, April 2006.

[3] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, "Catalytic Growth of Single-Walled Carbon Nanotubes" Chem. Phys. Lett., 243, 49-54 (1995).

[4] C. T. Kingston, Z. J. Jakubek, S. Denommee, and B. Simard, " Efficient Laser Synthesis of Single-walled carbon nanotubes through laser heating of the condensing vaporization plume "Carbon, 42, 1657-1664 (2004).

[5] C. T. Kingston and B. Simard, "Recent advances in laser synthesis of single-walled carbon nanotubes" J. Nanosci. Nanotech., 6, 3677-3684 (2006)

[6] K. S. Kim, G. Cota-Sanchez, C. T. Kingston, M. Imris, B. Simard, and G. Soucy, "Large-scale production of single-walled carbon nanotubes by induction plasma" J. Phys., D Appl. Phys., 40, 2375-2387 (2007)

[7] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, "Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites" Carbon 44, 1624-1652 (2006).

Acknowledgement

This work was supported by the financial contributions of the National Research Council of Canada and the Natural Science and Engineering Research Council through an Idea-to-Innovation Grant operated by the Université de Sherbrooke.