AN *IN SITU* RAMAN STRESS MEASUREMENT METHOD FOR TENSILE TESTING OF CARBON NANOFIBER/ NANOTUBE COMPOSITES

Bharathi K. Mohan, Gregory Freihofer, Seetha Raghavan
University of Central Florida
4000 Central Florida Blvd
*Orlando, Florida 32816*

ABSTRACT

This research focuses on a novel approach to determine stresses within a carbon nanotube/ nanofiber (CNT/CNF) composite through Raman spectroscopy. Carbon polymorphs are a well-known Raman-active group of materials and hence Raman scattering is an effective technique for their characterization. A conventional visible Raman spectrum of disordered carbon film is dominated by a D peak centered around 1360 cm^{-1} and a G peak around 1580 cm^{-1}. Their peak shifts have been associated with mechanical and thermal stress and also due to variation in the physical parameters and hydrostatic pressure. Our process involves using an optical fiber-based probe to focus and provide laser excitation to the sample under load. Vibrational energy is collected in the form of an emission spectrum and relationships between the mechanical properties and the Raman spectra of Carbon Nanofiber (CNF) are used to establish the stresses within the sample as the load changes. Stress distribution in the sample at discrete force increments is found and the effects on the G band of CNF are observed using this unique setup of a fiber optic probe coupled with an XYZ stage. A deconvolution and fitting process was used to analyze the collected spectral data from CNT/CNF tensile experiments to monitor the independent shifts of peak positions from the G and D bands. Development of this method for non-destructive tensile testing of these materials, will contribute to the improved design of CNT/CNF composites.

1. INTRODUCTION

Addition of Carbon nanofibers in composites have shown improvement in mechanical properties because of their mechanical and physical properties [1].CNF offers chemically facile sites that can be functionalized with additives thereby resulting in a strong interfacial bond with the matrix. Thermoplastics such as polypropylene, polyester, polycarbonate, nylon, poly (ether sulfone), poly (phenylene sulfide), acrylonitrile-butadiene-styrene, thermosets such as epoxy as well as thermoplastic elastomers such as butadiene-styrene diblock copolymer have been reinforced with carbon nanofibers. Nanocomposites prepared by mixing polymer resins with carbon nanotubes or carbon nanofibers exhibit improved mechanical properties such as strength, modulus and fracture toughness. Carbon nanofibers however have received less research and attention compared to CNTs because of the latter's better mechanical properties. However because of their availability and relatively low price, CNFs are an excellent alternative for CNTs and the knowledge obtained through these materials could be transferred to CNTs [2].

1.1 Raman Spectroscopy

Raman spectroscopy, which is one of the most sensitive methods for studying carbon materials, provides very important information on the microstructure and crystalline ordering of carbon materials. Carbon materials exhibit mainly two Raman bands at about 1580 and 1335 cm^{-1}, respectively, the former corresponding to the graphite mode (G-band) and the latter to the defect-induced Raman band called the defect mode (D-band). Fig 1 shows the Raman D and G bands of CNF. For sp2 nanocarbons such as graphene and carbon nanotubes, Raman spectroscopy can give information about crystallite size, clustering of the sp^2 phase, the presence of sp^2-sp^3 hybridization, introduction of chemical impurities, strain, nanotube diameter, chirality, curvature, the metallic versus semiconducting behavior and several other properties. [3]. Laser Raman spectroscopy is a powerful non-destructive technique for monitoring the local stress variations near the surface of materials [4].

Figure 1. Raman Spectra of CNF sample
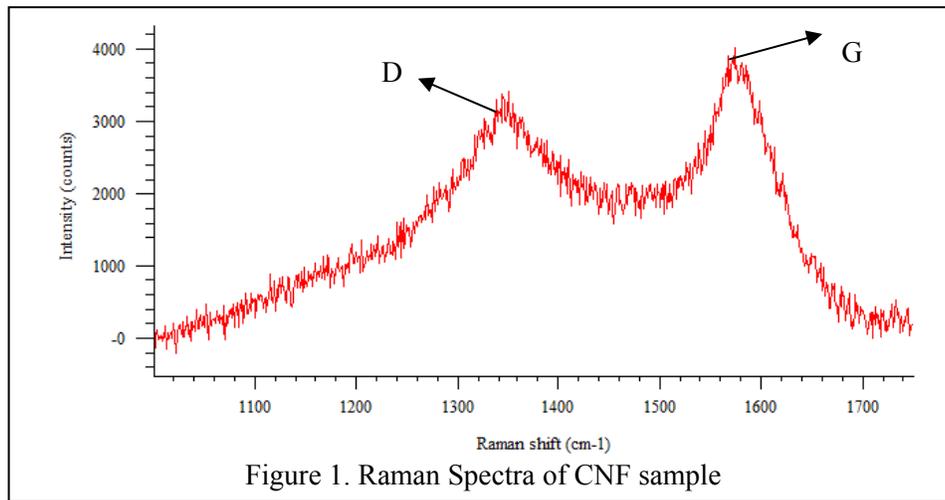
CNT/CNF composites show potential for advancement through studies of Raman spectra with stress. These composites have unique physical and optical properties and their optical properties, while complex, are comprehensive in evaluating stress transfer between the CNT and matrix interface [5]. The use of Raman spectroscopy to characterize composite interfaces relies on the phenomenon that when high-performance fibers are deformed, some of the bands in their Raman spectra shift in a well-defined way. In some conventional fiber-reinforced polymer composites, e.g., carbon fiber-based composites, the distribution of stress/strain fibers carried could be monitored through the shifts of the Raman bands. In this work, after dispersing a very minor amount of CNT/CNFs inside a polymer matrix the stress/strain distributions of the matrix could be detected indirectly through the shifts of the CNT/CNF Raman band [6].

1.1.1 The G band and their shift with stress

The tangential shear mode of most carbon materials, namely the G band at 1500–1605 cm^{-1}, is related to the tangential vibrations of the carbon atoms. The stretching of the C-C bond in graphitic materials gives rise to this Raman feature which is common to all sp^2 carbon systems. This spectral feature is similar for graphene and nanotubes but yet has properties capable of distinguishing one carbon nanostructure from another. When the bond lengths and angles of graphene are modified by strain, due to interaction with a substrate or with other graphene layers or due to external perturbations, the hexagonal symmetry of graphene is broken [3].

Experimental results have also shown that the Raman G band of carbon based composites shifted upwards with the decrease of temperature. The G-band is, therefore, highly sensitive to strain and temperature effects in sp^2 nanocarbons and can be used to probe any modification to the structure of carbon materials. When the CNT/CNF composites are under tension, the nanotubes and nanofibers lying along the tensile direction are under tension, but those aligned perpendicular to it are under compression because of the Poisson's effect. Consequently, the Raman signal is averaged over all of the nanotubes in the probed volume. The shift of the Raman bands greatly depends on the deformation modes, and it will shift upwards under a uniaxial compression, and shift downwards under tension [3].

In this work we attempt to show how Raman spectroscopy can be used to describe fully the stress transfer in a CNF reinforced fiberglass composite.

2. EXPERIMENTATION

2.1 SAMPLE PREPARATION

The sample used for the study contains Carbon Nanofiber, fiber glass and polyester resin. Vapor-grown CNF (Pyrograf-III-PR-19 LHT, Applied Sciences Incorporated) with diameter of 100–200 nm and length of 30-100μm were dispersed into unsaturated polyester resin from Eastman Chemical. The fiber glass is a continuous filament mat, model U720 manufactured by Saint-Gobain Vetrotex. The details behind the manufacturing of the sample are presented elsewhere [7]. The sample was machined so as to avoid plastic deformation; the usual tensile dog bone specimen was avoided because for composite laminates, it will result in the formation of matrix cracks parallel to the fibers and will fail there first [8]. A rectangular configuration was preferred with a length to width aspect ratio of 10 [9].

2.2 EXPERIMENTAL PROCEDURE

The specimen was first tested with the Renishaw Raman spectrometer with a green Argon laser excitation source having a wavelength of 532 nm to observe the spectrum of the unstressed specimen. The sample was then placed under the tensile grips of the MTS machine and perpendicular to laser. To obtain the spectral relationships, a unique experimental system consisting of a fiber optic probe attached to the spectrometer is coupled with a xyz stage which automatically collects spectral data from the specimen [5]. The optical probe system allows for non-invasive collection of optical measurements from a sample as it is being loaded. Fig 2 shows the experimental setup

Figure 2. Experimental Setup
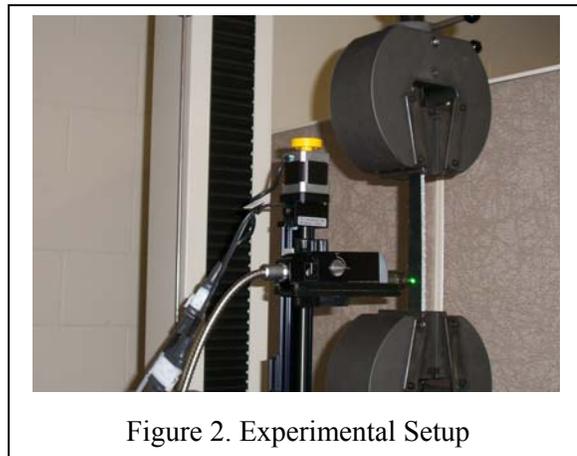
The data is then analyzed by a deconvolution program that characterizes the sample, based on its optical peak's spectral characteristics: FWHM, position, intensity, area, and Gauss ratio. The peak shifts were measured to observe a stress-to Raman shift relationship from it. A long range objective lens of 50x magnification was used to focus the laser beam on the specimen and to collect the scattered radiation. This objective was chosen based on the ideal focal distance for our experimental setup. Specifically, the larger the magnification, the smaller the distance must be to focus the laser dot on the surface. Discrete loads of 5 kN were held by the MTS load frame, during which the spectrometer takes data from the sample via the xyz stage. Extended scans with endpoints from 1100 to 1700 cm^{-1} with exposure times of 100s to observe both the G and D bands were taken and subsequently analyzed. The spectra were averaged over multiple scans to minimize background noise.

The complexity of the CNT/CNF Raman spectra can be managed via genetic algorithm based pseudo-Voigt deconvolution. Developing spectral characteristics for individual peaks will improve with such methods despite the resolvability issues associated with some of the CNT Raman peaks. Deconvolution of these using genetic algorithms has enabled accurate monitoring of spectral characteristics.

3. RESULTS

In this paper, the G band (~1580 cm^{-1}) of the carbon nanofiber's Raman spectra was chosen to monitor the stress transfer in the CNF reinforced fiberglass composite. It has been observed that most carbon materials when loaded in tension result in a negative shift of the Raman frequency [10]. The spectrum of the CNF sample was recorded at every stress increment; the baseline was removed from the entire spectrum as this is crucial for properly interpreting the shoulder of the convoluted G and D bands. Fig 3 compares the G band of the CNF composite in the un-deformed and deformed states.
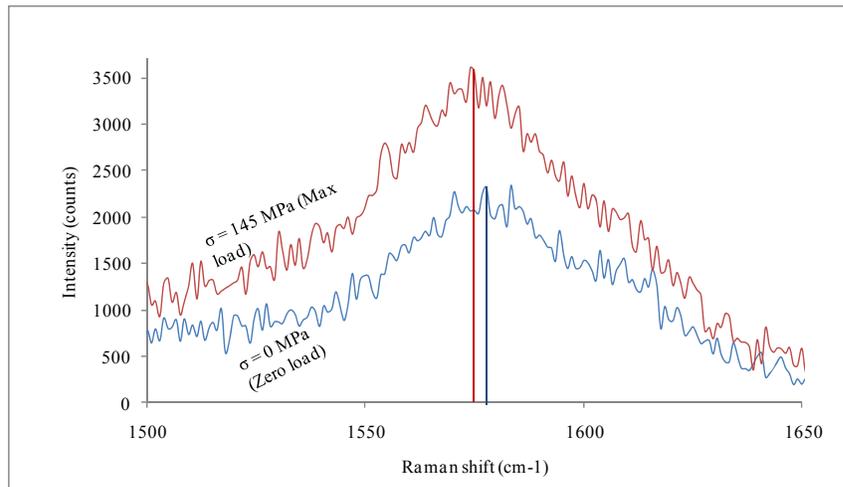

Figure 3. Shift of the G band with the application of tensile load

The optimization for the curve fitting was performed using a genetic-algorithm based code [11]. Peaks were chosen at 1581 and 1369 cm^{-1} corresponding to the G and D bands. 2 other peaks at 1330 and 1498 cm^{-1} were chosen based on previous work conducted on Raman spectra of carbon

materials [12, 13]. The peak at 1330 cm^{-1} has been observed for certain carbon materials at an excitation wavelength of 782 nm [14] and also has been attributed to impurity ions. The peak at 1498 cm^{-1} has been identified as the D" in carbon films [13]. The use of genetic algorithms in the deconvolution process is described elsewhere [15]. After deconvolution, the position of the G peak at each load was noted and the peak shift calculated using the zero stress as the reference. A linear graph with a negative slope was obtained as expected for carbon materials [16]. A slope of -0.034 cm^{-1} has been obtained and this relatively small shift with tension can be attributed to the nanofibers oriented at a different angle with respect to the strain direction. This is almost comparable to the slope obtained by multi-walled carbon nanotubes [17] which has been explained due to the poor bonding between the matrix and the outermost nanotube layers and also because of the weak bonding between the nanotube layers [18]. Since the carbon nanofibers are comparable to multi-walled nanotubes in size and structure, this could be a possibility for the small shifts in stress in the CNF sample. Further tests will be conducted to empirically establish stress-spectral relationships which can be used in future for design, analysis and non-destructive structural stress testing.

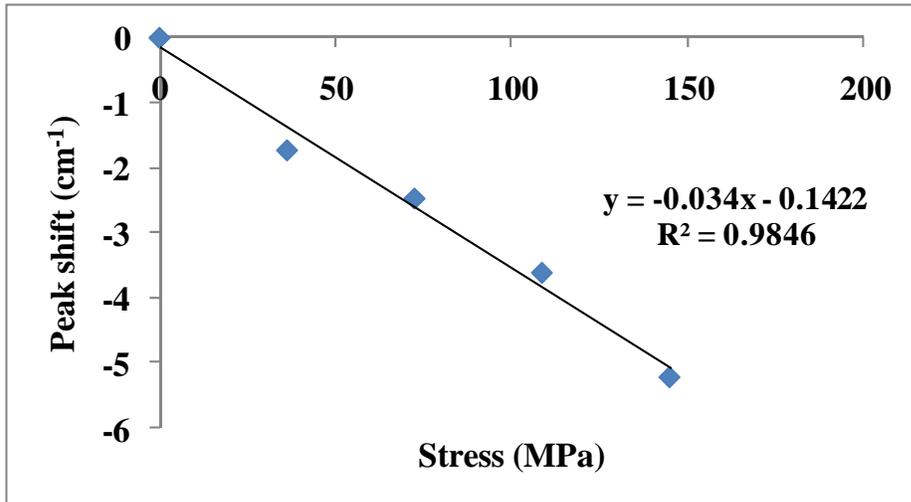| Force (kN)	Stress (MPa)	G peak position (cm^{-1})	Peak shift (cm^{-1})
0	0	1581.865	0
5	36.317	1580.133	-1.732
10	72.634	1579.391	-2.474
15	108.95	1578.247	-3.618
20	145.27	1576.639	-5.226

$y = -0.034x - 0.1422$
$R^2 = 0.9846$

Figure 4. Stress versus G peak shift

4. CONCLUSIONS

An *in situ* method of measuring stress using optical spectroscopy for carbon nanofiber composites has been discussed here. An optical fiber-based probe has been used to focus and provide laser excitation to the sample under load. Stress distribution in the sample at discrete force intervals has been found and the effect on the G band was observed. The stress versus G peak Raman shift for CNF materials has been found to exhibit a linear relation with negative slope as expected for most carbon materials. This indicates that with an application of a tensile load, the band moves towards lower wave numbers and that the macroscopic stress applied to the composite deformed the nanofibers. The slope obtained was very small which might be an indication of the CNF being oriented at a different angle with respect to the strain direction. This behavior resembles multi-walled nanotubes as expected from literature. Future work would involve studying the D peak and observing the shift if any in other spectral characteristics like Full Width at Half Maximum (FWHM), intensity and Gauss ratio.

5. REFERENCES

1. E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder, P. Potschke, 'Carbon nanofibers for composite applications', Carbon 42 (2004) 1153–1158

2. Mohammed H. Al-Saleh and Uttandaraman Sundararaj, 'A review of vapor grown carbon nanofiber/polymer /conductive composites', Carbon 47(2009)2-22

3. Mildred S. Dresselhaus, Ado Jorio, Mario Hofmann, Gene Dresselhaus, and Riichiro Saito, 'Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy', *Nano Lett.* **2010, 10**, 751–758

4. H. Sakata, G. Dresselhaus, M. S. Dresselhaus, and M. Enda, 'Effect of uniaxial stress on the Raman spectra of graphite fibers', J. Appl. Phys. 63 (8), 1988

5. G Freihofer, L Poliah, K Walker, A Medina and S Raghavan, 'Optical stress probe: *in-situ* stress mapping with Raman and Photo-stimulated luminescence spectroscopy', *JINST* **5** P12003

6. GAO Yun, LI LingYun, TAN PingHeng, LIU LuQi and ZHANG Zhong, 'Application of Raman Spectroscopy in CNT based polymer composites', Physical Chemistry, Vol.55 No.35: 3978–3988, 2010

7. Jan Gou, 'Effects of carbon nanofibers on mechanical properties of glass fiber reinforced polyester resin composite laminates', Under preparation

8. George H Staab, Laminar composites, Butterworth-Heinemann,1999

9. ASTM Standard D3039_D3039M-00E02, 2002, "Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials," ASTM International, West Conshohocken, PA, 2003, DOI: 10.1520/C0033-03, www.astm.orgGeorge H Staab, Laminar composites, Butterworth-Heinemann,1999

10. N. Melanitis, P.L. Tetlow, C.Galiotis and S. B. Smith, 'Compressional behavior of carbon fibers', Journal of Materials Science 29 (1994) 786-799

11. Greg Freihofer, Seetha Raghavan and David Gosztola, 'Investigation of the Pseudo-Voight function for the Spectral Analysis of Carbon Nanotube Raman bands', Physical Review B (In Review), 2010

12. James Birrell, J.E. Gerbi, O. Auciello, J.M. Gibson, J. Johnson and J.A. Carlisle, 'Interpretation of the Raman spectra of ultrananocrystalline diamond', Diamond & Related Materials 14 (2005) 86– 92

13. A Cuesta, P Dhamelincourt, J Laureyns, A Martinez-Alonso and J M D Tascon, 'Raman Microprobe Studies on Carbon Materials', Carbon, Vol. 32, No.8, pp.1523-1532, 1994

14. Yan Wang, Daniel C Alsmeyer and Richard L McCreery, 'Raman Spectroscopy of Carbon Materials', Chem. Mater., Vol. 2, No. 5, 1990

15. S. Raghavan, P. Imbrie, and W. A. Crossley, 'Spectral Analysis of R-lines and Vibronic Sidebands in the Emission Spectrum of Ruby Using Genetic Algorithms', Applied Spectroscopy 62, 759 (2008)

16. L D. Leveque and M.-H. Auvray, 'Study of Carbon-Fibre Strain in Model Composites by Raman Spectroscopy', Composites Science and Technology 56 (1996) 749-754

17. Shilun Ruan, Ping Gao and T.X. Yu 'Ultra-strong gel-spun UHMWPE fibers reinforced using multiwalled carbon nanotubes', Polymer, Vol 47, Issue 5, 2006, Pg 1604-1611

18. L. S. Schadler, S. C. Giannaris, and P. M. Ajayan, 'Load transfer in carbon nanotube epoxy composites', Applied Physics Letters, Vol 73, Number 26, 1998