

Raman Scattering Test of Mechanical and Sensor Properties of Advanced Nanocomposites

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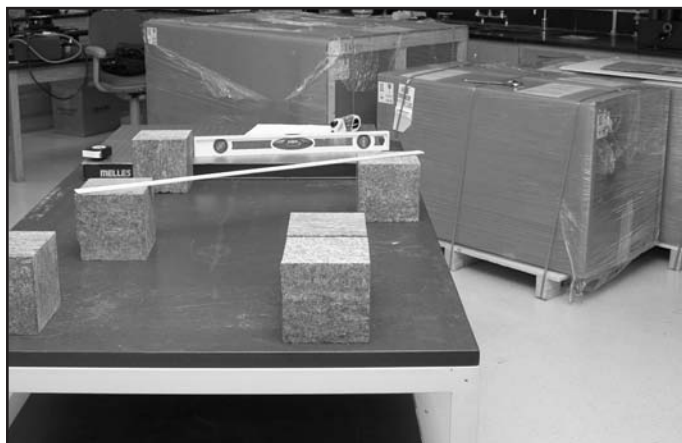
ABSTRACT—In this report on the project completed in 2004, we briefly demonstrated that single wall carbon nanotubes (SWNT) embedded in polymer matrix can be used as distributed, nano-scale, strain gauges measured remotely by Raman spectroscopy.

IN THE COURSE OF THE PROJECT, WE MEASURED LOAD TRANSFER in various SWNT nanocomposites^{1,2} using the Raman scattering micromechanical test.³ As a result, it has been well documented that the *G*-mode frequency at 1590 cm⁻¹ varies linearly with nanotube's axial strain ϵ_{axial} . Specifically, the fractional *G*-mode frequency change is proportional to the axial strain

$$\Delta\omega_G / \omega_G = -A\epsilon_{axial} ,$$

where $A \sim 1$ follows from an empirical model for chiral SWNT,³ and $A \sim 1-2$ is found using the Local Density Approximation (LDA) calculations.⁴ In a nanocomposite containing SWNTs, any external load is transferred to the nanotubes through the interfaces between the matrix and nanotubes. This process can also be described as a strain transfer $S \leq 1$ given by

$$\Delta\omega_G / \omega_G = -A\epsilon_{axial} = -A S \epsilon_m , \epsilon_m \text{ is the matrix strain.}$$



BEFORE—TCSUH, the Texas Center for Superconductivity at UH, with discoveries that require more advanced measuring devices, updates its lab equipment in a periodic reinvestment program.

The strain transfer is deduced from the Raman scattering test in which we simultaneously measure the changes in both the *G*-mode frequency and the surface strain $\epsilon_s \approx \epsilon_m$ (for low SWNT concentration nanocomposites), close to the laser spot, with varying external load.

We measured a nanocomposite sample containing 0.001% SWNTs dispersed in Epon 682 and cured with W-agent in the presence of ~ 16 T magnetic field. Typically, nanocomposites of SWNTs prepared in a strong magnetic field contained well oriented nanotubes along the field direction.

To quantitatively assess the degree of the orientation of SWNTs, we measured a series of Raman spectra for incident laser polarization directions at various angles, $0 \leq \Psi \leq 180^\circ$, with respect to the director (direction of the magnetic field). It is well known that

the *G*-mode intensity of a SWNT varies with the angle Ψ between the incident laser polarization and the nanotube axes as $\cos^4\Psi$. If all nanotubes in the nanocomposite sample are perfectly aligned in one direction, the resulting *G*-mode intensity should follow $\cos^4\Psi$ as well.

Figures 1 and 2 show that the *G*-mode intensity change with Ψ in the sample under study resembles that of $\cos^4\Psi$. These data, however, allow more quantitative treatment, and we find the average degree of nanotube misalignment θ from the fit to the dependence given in Fig. 2 with the expression⁵

$$I_G(\Psi) = A \left[\left(\cos^4 \Psi - \frac{6}{7} \cos^2 \Psi + \frac{3}{35} \right) \langle P_2(\cos\theta) \rangle + \left(\frac{6}{7} \cos^2 \Psi - \frac{2}{7} \right) \langle P_4(\cos\theta) \rangle + \frac{1}{5} \right],$$

where

$$\langle P_2(\cos\theta) \rangle \text{ and } \langle P_4(\cos\theta) \rangle$$

are the second- and fourth-order orientation parameters. We obtained for the second-order parameter (see following page)



AFTER—Shipping cases (*l. photo*) were emptied of a new Raman microscope, which was reconstructed in the lab to perform precise chemical mapping and Raman imaging.

$$\langle P_2(\cos\theta) \rangle = 1/2(3\langle \cos^2\theta \rangle - 1) = 0.69 ,$$

which corresponds to misalignment of the nanotubes of no more than 25 degrees.

In Fig. 3 we present the change in the *G*-mode Raman spectra under external compressive load along the director. The load created a matrix strain $\epsilon \approx -0.004$ measured by a strain gauge placed close to the laser spot. Given the measured fractional frequency change,

$$\Delta\omega_G / \omega_G = 0.0035 ,$$

one obtains very good strain transfer $S \approx 0.88$ in a 0.001 percent SWNT/epoxy sample. This value of *S* is characteristic for well dispersed nanotubes and for those that adhere to the matrix. In addition to the frequency shift, the *G*-mode Raman line in the sample under load becomes inhomogeneous broadened. This effect comes in part from the contribution of those nanotubes that are misaligned and therefore subjected to a reduced load. On the other hand, the nanocomposite contained different diameter nanotubes, which, although having approximately the same *G*-mode frequency, shifted differently under the load due to the different strength of coupling to epoxy. Currently, we are working on a refined approach to resolve these problems of misalignment.

In this study, we demonstrated that in addition to reinforcement, well-dispersed nanotubes and those that adhere to the matrix can serve also as nano-scale strain gauges. Further improvement of the performance of the nano-gauges can be achieved by using nanotubes with narrow diameter distribution.

References

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⁵Liu T. and S. Kumar, "Quantitative Characterization of SWNT Orientation by Polarized Raman Spectroscopy," *Chem. Phys. Lett.* 378.3 (2003): 257.

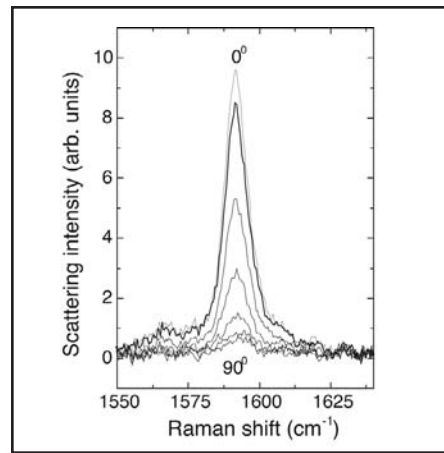


Figure 1. *G*-mode Raman spectra of 0.001% SWNT/epoxy nanocomposite measured at various angles between the laser polarization and the direction of magnetic field applied during the curing process.

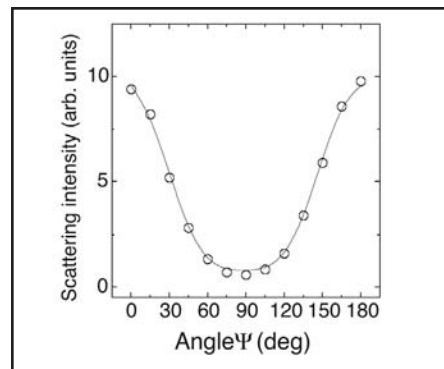


Figure 2. Variation of the *G*-mode intensity with angle (open circles) and the best fit to experimental points (solid line) using the expression 1.

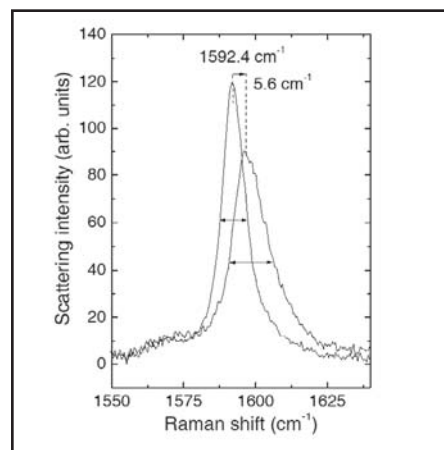


Figure 3. *G*-mode Raman line in 0.001% SWNT/epoxy nanocomposite at zero stress (1592.4 cm⁻¹) and an external load (the line shifted upward by 5.6 cm⁻¹) that creates matrix strain.