Raman Scattering Test of Mechanical and Sensor Properties of Advanced Nanocomposites

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The project, completed in 2004, constituted a study of the interfaces in single-wall carbon nanotube (SWCNT) composites and nanoscale materials suitable for space flight applications. As a part of the project, we also assessed the possibility of reinforcement of cyanoacrylate (CA) adhesives with single wall carbon nanotubes. We report here some of the preliminary results.

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Cyanoacrylate adhesives are based on acrylic resins, which rapidly polymerize in the presence of trace amounts of moisture (hydroxide ions), forming strong chains that join the bonded surfaces. Cyanoacrylates are persistive adhesives particularly suitable for bonding non-porous materials in presence of traces of water. They are biocompatible, very good at bonding body tissue, and largely exploited in sutureless surgery.

Many cyanoacrylate adhesives are known under the commercial name "Superglue," and such a product was used in our experiment. The Superglue used contained 99.5 percent ethylcyanoacrylate ($C_6H_7NO_2$). Nanocomposite samples were prepared by mixing SWCNTs, as grown HiPCO material containing both semiconducting and metallic nanotubes, and cyanoacrylate resin (~0.02 wt % of SWCNT in CA). The mixing was performed in a dry box and the uncured nanocomposite sonicated for seven hours. A drop of the nanocomposite adhesive was deposited on a copper slide, left to polymerize in air, and measured under the Raman microscope.

Our approach to assess the strength of bonding of SWNTs to the cyanoacrylate matrix is based on Raman spectroscopic measurements of the nanotubes' strain created either by shrinkage of the CA matrix upon cure or with decreasing temperature below room temperature.[1,2]

The Raman spectra of pure SWCNTs and SWCNT/CA nanocomposites at room temperature are presented in Fig. 1.

The figure shows an increase of ~3.2 cm^{-1} in frequency of the G-peak at 1590 cm^{-1} on-going from pure SWCNTs to those

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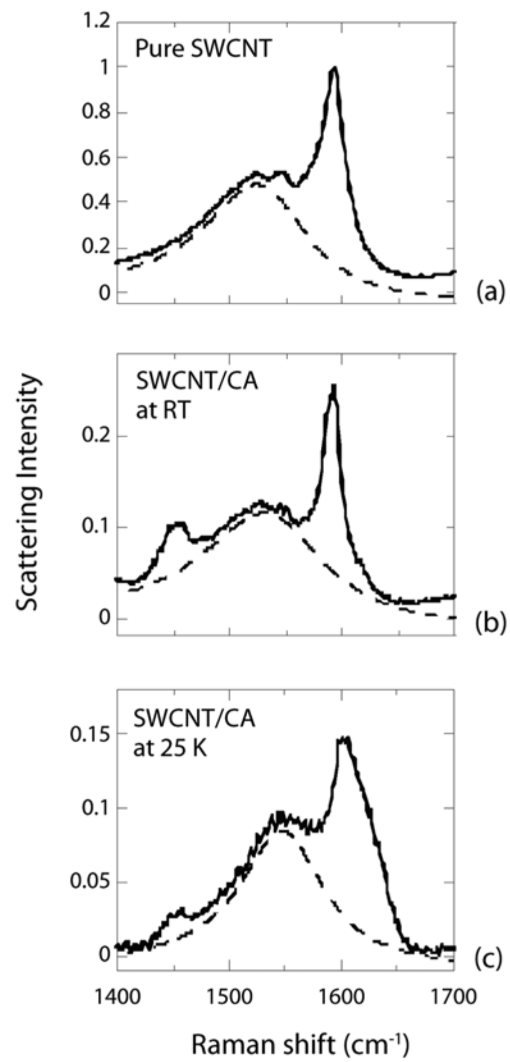

Figure 1. Tangential modes of Raman spectra for pure SWCNTs (a), SWCNT/CA at room temperature (b), and SWCNT/CA at 25 K (c). The sharp peak at 1590 cm^{-1} stems from the semiconducting SWCNT, whereas the broad effect emphasized by the broken line corresponds to the tangential vibrations in the metallic nanotubes in the nanocomposite.

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embedded in the cyanoacrylate matrix. The fractional change of the G-peak position $\Delta\omega_G/\omega_G$ is related to the axial strain ε_z of SWCNTs as $\Delta\omega_G/\omega_G \approx -\gamma(1 - \nu_t)\varepsilon_z$,[1] where γ is the Grüneisen parameter and ν_t is the Poisson's ratio of a SWCNT, with $\gamma = 1.24$[1] and $\nu_t = 0.16$[2]. Thus, estimated strain of SWCNTs due to cyanoacrylate shrinkage upon cure is –0.2%.

Given the strain upon the nanotubes induced by the cyanoacrylate matrix, one can assess the degree of adhesion of SWCNTs to a cyanoacrilate matrix, provided the shrinkage of the matrix upon cure is known. For instance, an indication of good bonding of the nanotubes has the matrix shrinkage close to the resulting nanotube strain. Although the shrinkage upon cure is important as an adhesives application parameter, it is usually not given in the technical specification datasheet for cyanoacrylates. To overcome this problem, we further analyzed the change of the G-peak position in the SWCNT/CA nanocomposite with decreasing temperature.

Figure 1 (c) clearly shows a strong increase of the G-peak frequency upon cooling the SWCNT/CA nanocomposite. The fractional change of the G-peak position upon cooling the nanocomposite from room temperature to 25 K corresponds to 0.6% compressive strain of the SWCNTs. On the other hand, given the coefficient of thermal expansion (CTE) 1.26×10^{-4} of cured cyanoacrylate and Young's modulus 6 GPa, we calculate using the methodology presented in Ref. 2 that the strain on the nanotubes caused by the thermal shrinkage of the CA matrix is 0.63%, provided the nanotubes are firmly bonded to the matrix. The calculated value for the strain is only 5% higher than the one measured, and we conclude that the SWCNTs are very well coupled to the CA matrix. Reviewing the strain caused by the shrinkage upon cure, we believe that it is also close to the contraction of the cyanoacrylate resin during the polymerization.

In summary, we briefly assessed the possibility of making the SWCNTs/cyanoacrylate nanocomposite. We find strong coupling between the nanotubes and the CA matrix which should result in a carbon nanotubes reinforced Superglue, a claim that has yet to be proved also by mechanical tests.

References

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