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Raman Scattering Test of Mechanical and Sensor Properties of Advanced Nanocomposites

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RESearchers focused upon the interfaces in single-wall carbon nanotube (SWCNT) composites and nanoscale materials suitable for space flight applications. Several nanocomposites based on thermoset polymers (epoxy) and thermoplastics (polystyrene [PS] and poly(ϵ -caprolactone) [PCL]) have been investigated by Raman spectroscopy technique and analyzed in detail.

The main finding of this study is the understanding that most of the SWCNT nanocomposites appear to be true structural multifunctional materials in which changes in properties under external forces or variation of temperature can be efficiently monitored by the technique of non-destructive Raman spectroscopy. For instance, we have shown that the Raman microprobe can detect buckling and failure of the nanotubes in SWCNT/epoxy nanocomposites, changes in the reinforcement strength of SWCNT/PS nanocomposites with temperature, and formation of self-assembling SWCNT structures in the SWCNT/PCL thin films. This report cites key results obtained in the course of the project.

Buckling Instabilities of Octadecylamine Functionalized Carbon Nanotubes Embedded in Epoxy

(Research has been achieved in collaboration with groups led by Dr. D. C. Lagoudas at the Texas A&M University, College Station, and Dr. J. M. Tour, Rice University, Houston.)

Synopsis

Octadecylamine (ODA, $H_2N-C_{18}H_{37}$) functionalizes predominantly the semiconducting SWCNTs, thus promoting much desired in the nanocomposite technology exfoliation and separation of the nanotubes. We show that ODA functionalization of SWCNTs provides weak sidewall interaction between the nanotubes and epoxy matrix, which makes axially compressed ODA-SWCNTs susceptible to buckling. The effects of nanotubes buckling and debonding in ODA-SWCNT/epoxy (EP) nanocomposites under mechanical and thermal loads have been uniquely detected by means of Raman spectroscopy and documented by TEM imaging. We have developed a structural mechanics model that reproduces the ODA-SWCNTs buckling in epoxy matrix.

Key Results

In Fig. 1, we present a unique signature of ODA-functionalized SWCNTs buckling embedded in epoxy when loaded under compressive stresses and measured by the non-destructive Raman technique.

The transmission electron microscopy image of a specimen cut from the ODA-SWCNT/EP composite (destructive) confirms (see Fig. 2) a residual buckling state of ODA-SWCNTs in the composite after being thermally cycled between room and low temperatures.

GRADUATE ASSISTANT—Keesu Jean earned his M.S. in chemical engineering at the University of Houston. He currently conducts research under the supervision of Dr. Viktor Hadjiev.

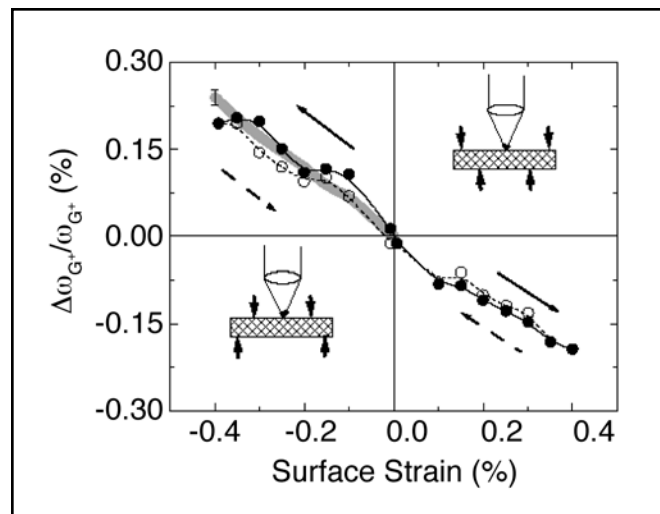


Figure 1. Relative change of $\Delta\omega_{G^+}/\omega_{G^+}$ in ODA-SWCNT/EP composites under increasing (full circles) and decreasing (empty circles) tensile and compressive loads. The grey thick curve presents the compressive loading of non-functionalized SWCNT/EP composite. The thickness of the grey line is equal to the accuracy of the measurements. All the lines that connect experimental points are guided to the eye. The configuration of the sample supports and the microscope objective used for focusing the laser beam are sketched in the figure.

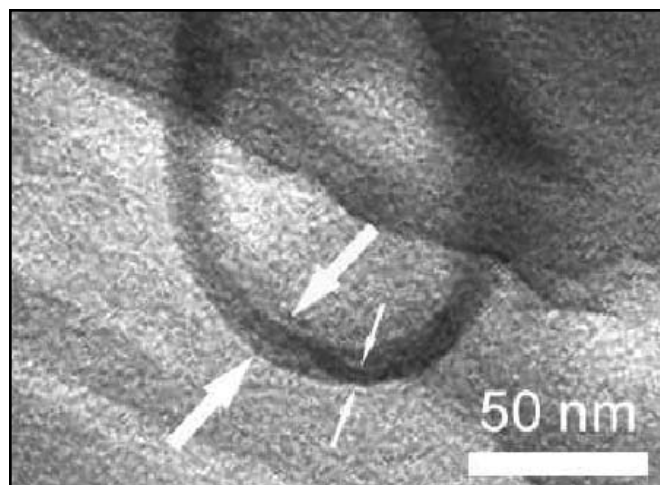


Figure 2. TEM image close-up of a ODA-SWCNT bundle in epoxy matrix. A buckled thin bundle of nanotubes is clearly seen embedded in a channel containing ODA functional moieties.

Impact

We have provided evidence that the observed two plateaus in the strain transfer in ODA-SWCNT/EP under compression are due to buckling of the nanotubes facilitated by the very weak sidewall nanotube-epoxy interactions. Thermal loads created upon cooling the sample below 260 K led to the debonding of the nanotubes, likely initiated by buckling of the nanotube. We

also emphasized the uniqueness of the combined Raman and TEM experiment because the standard mechanical stress measurements hardly could detect this peculiar behavior of tiny amount of ODA-SWCNTs under compression.

Low temperature Self-reinforcement of 4-(10-hydroxy)decyl benzoate (HDB) modified SWCNT/PS nanocomposites

(Work has been achieved in collaboration with the groups led by Dr. R. Krishnamoorti, UH Department of Chemical Engineering, and Dr. J. M. Tour, Rice University, in Houston.)

Synopsis

Thermal strains in 4-(10-hydroxy)decyl benzoate (HDB) modified SWCNT/PS nanocomposites exhibit unusual temperature dependence that suggests strong increase of the nanocomposite reinforcement at low temperatures. The strain transfer from the matrix to nanotubes in these nanocomposites, inferred from the frequency change of the Raman active tangential modes of the nanotubes, is enhanced strongly below 300 K, whereas it is vanishingly small at higher temperatures. On the other hand, the pristine SWCNTs couple weakly to the PS matrix over the entire temperature range of 4.5-410 K. We show that the strain transfer in HDB-SWCNT/PS is determined by the thermo-mechanical properties of the interface region composed of polystyrene plasticized by the tethered alkane-like modifier.

Key Results

The difference between the coefficient of thermal expansion (CTE) of the matrix and nanotubes creates strain mismatch. Usually the CTE of polymers is an order of magnitude higher than those of the nanotubes. The thermal strain mismatch may result in strain transfer from the polymer to the SWCNTs provided the nanotubes are coupled to the matrix. The strain transfer, therefore, serves as a measure for the reinforcement of the matrix.

It is well established that $\Delta\omega_{G'}/\omega_{G'}$ changes with the strain ϵ_z of the nanotube as $\Delta\omega_{G'}/\omega_{G'} = -\gamma(1 - \nu_{nt})\epsilon_z$, $\gamma = 1.24$, and $\nu_{nt} = 0.16$. To better illustrate the processes behind the variation of $\Delta\omega_{G'}/\omega_{G'}$ with temperature displayed in Fig. 3 (a), we plot in Fig. 3 (b) the strain mismatch between HDB-SWCNTs and PS below 300 K calculated from the differences in the coefficients of thermal expansion (CTE) of PS (α_m) and SWCNTs (α_{nt}). We calculate the strain mismatch for the particular case of SWCNT/PS nanocomposites assuming that any of these nanocomposites has 100 percent strain transfer capability. We use two concentric cylinder model assuming long nanotubes embedded in an isotropic matrix. The calculated axial strain ϵ_z^{cal} depends on the difference in CTE, $\Delta\alpha = \alpha_m - \alpha_{nt}$, and a renormalizing $\tilde{E}(T)$ term that accounts for the nanotube's volume fraction and the temperature dependence of the Young's moduli of the matrix and the nanotubes as $\epsilon_z^{cal} = \Delta\alpha\Delta T/\tilde{E}(T)$. The temperature difference ΔT is determined with respect to a given reference temperature T_0 at which the SWCNTs are relaxed. In our calculations we choose $T_0 = 300$ K, the lowest temperature in our experiment for which $\Delta\omega_{G'}/\omega_{G'} \approx 0$. The concentric cylinder model of fibrous com-

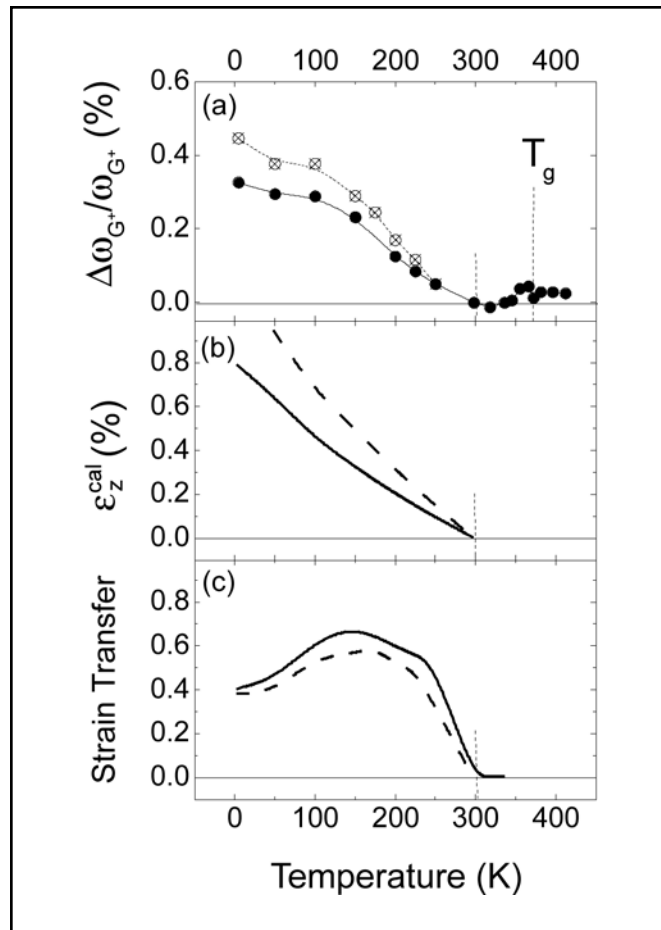


Figure 3. Temperature dependence of (a) $-\Delta\omega_{G'}/\omega_{G'}$, as determined from the Raman spectra (solid circles—1.5% HDB-SWNT/PS, crossed circles—0.75% HDB-SWNT/PS), (b) the calculated strain ϵ_z^{cal} on the nanotubes provided HDB-SWNT/PS coupling allows 100% strain transfer, and (c) the strain transfer $\epsilon_z/\epsilon_z^{cal}$ variation with temperature. Solid and dash lines refer to the 1.5% HDB-SWNT/PS and 0.75% HDB-SWNT/PS samples, correspondingly. The strain of HDB-SWNTs in the nanocomposite was determined from $\epsilon_z \approx -0.96\Delta\omega_{G'}/\omega_{G'}$.

posites predicts that the mismatch stress on a given nanotube should decrease with increasing of the nanotube's volume fraction in the nanocomposite because the product $\Delta\alpha\Delta T$ is distributed over all nanotubes. The dependence $\epsilon_z^{cal}(T)$ calculated for the 0.75 and 1.5 wt% HDB-SWCNT nanocomposites is presented in Fig. 3(b). Given $\epsilon_z^{cal}(T)$ and $\Delta\omega_{G'}/\omega_{G'} = -1.04\epsilon_z$ we can calculate the strain transfer (ST) in both HDB-SWCNT/PS nanocomposites from $ST = \epsilon_z/\epsilon_z^{cal}$ (shown in Fig. 3(c)). Although ϵ_z^{cal} has been calculated under numerous simplifying assumptions and the dependence $ST(T)$ is more qualitative than quantitative, the latter dependence clearly shows an increase of the strain transfer in both nanocomposites below 300 K that passes over a maximum around 150 K.

Impact

The HDB-SWCNT/PS system is an interesting example of a new class of nanocomposites in which load transfer can be changed towards enhancement of reinforcement by varying temperature within a stable matrix phase. The key element in such nanocomposites is the interface region between the matrix and functionalized SWCNTs that can be switched from soft (rubber-like) to stiff (glass-like) coupling with temperature.

Influence of Single-Walled Carbon Nanotubes (SWCNT) on Crystallization of Poly(ϵ -caprolactone) (PCL)

(This study was conducted in collaboration with Dr. R. Krishnamoorti's group, Department of Chemical Engineering, University of Houston)

Synopsis

Poly(ϵ -caprolactone) (PCL) is a biodegradable semicrystalline polymer having a crystal unit cell similar to that of the commonly used polyethylene. Polymer chains crystallize in lamellas (anisotropic polymer units), which coupling and mutual orientation are important in many applications. We have studied the crystallization of PCL in the presence of SWCNTs by means of Raman spectroscopy and atomic force microscopy (AFM). We observed peculiar crystallization morphology in the SWCNT/PCL films. The films consist of toroidal (doughnut-shaped) spherulites. We successfully resolve the structure of the spherulites featuring with edge-on lamellae bounded by circularly arranged SWCNTs in the spherulite.

Key Results

SWCNTs strongly affect crystallization morphology. We conducted the Raman spectroscopy measurements to investigate the orientation and concentration distribution of SWCNTs in the spherulites observed in the 0.05wt% SWCNT/PCL film. Figure 4 presents an optical microscopy image for the donut-like spherulite. The Raman microprobe image of the same spherulite created by mapping the SWCNT G-mode intensity at 1590 cm^{-1} is shown in Fig. 5. The Raman image has one micron spatial resolution and provides a unique probe of the SWCNT distribution in the SWCNT/PCL film.

Impact

We suggest an effective tool for revealing the morphology in advanced polymer composites containing SWCNTs.

Publications

Hadjiev, V. G., D. C. Lagoudas, E-S. Oh, P. Thakre, D. Davis, B. S. Files, L. Yowell, S. Arepalli, J. L. Bahr, and J. M. Tour. "Buckling Instabilities of Octadecylamine Functionalized Carbon Nanotubes Embedded in Epoxy," *Composites Science and Technology* (2005) (*in press*).

Hadjiev, V. G., C. A. Mitchell, S. Arepalli, J. L. Bahr, J. M. Tour, and R. Krishnamoorti. "Thermal Mismatch Strains in Sidewall Functionalized Carbon Nanotubes/Polystyrene Nanocomposites," *J. Chem. Phys.* 122.12 (2005): 124708.

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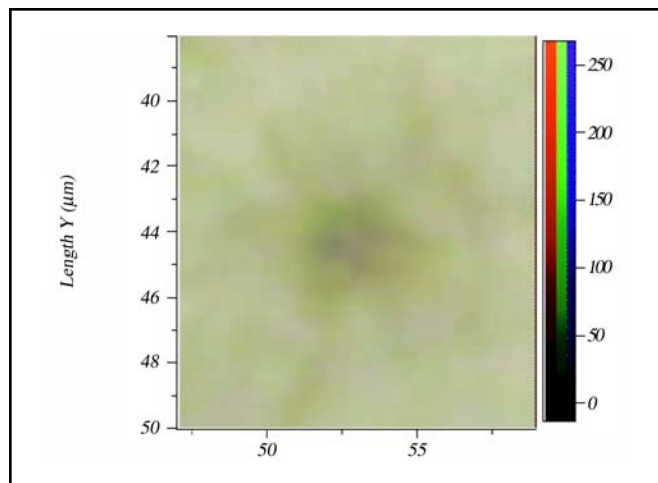


Figure 4. Optical microscopy image of a typical spherulite formed in SWNT/PCL films

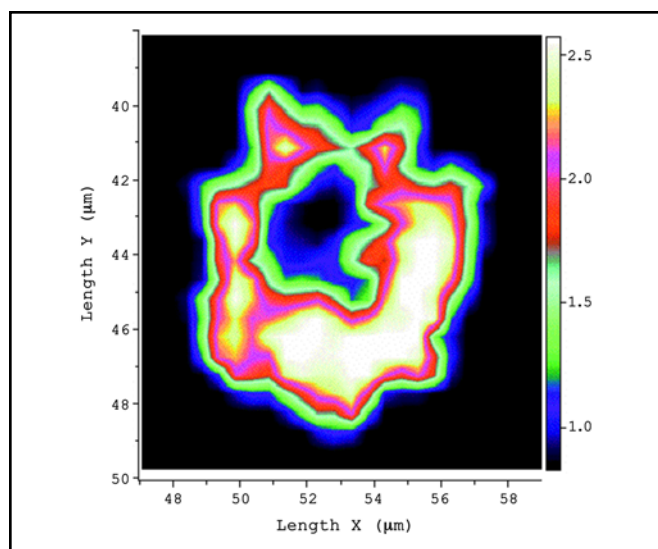


Figure 5. Raman image of the spherulite presented in Fig. 1. The image was created by mapping the SWCNT G-mode intensity at 1590 cm^{-1} .

"Influence of Single-Walled Carbon Nanotubes on Crystallization of Poly(ϵ -caprolactone)," *Nanotechnology* 2005 (*in preparation*).

Presentations

Hadjiev, V., D. Lagoudas, and D. Davis. "A Study of Interfaces/interphases in Functionalized Carbon Nanotube Composites through Strain Transfer Measurements," 2004 ASME International Mechanical Engineering Congress and Exposition (IMECE2004), Anaheim, CA, Nov. 2004.