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Polarized resonance Raman spectroscopy of single-wall carbon nanotubes within a polymer under strain

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The D^* Raman band of single-wall carbon nanotubes aligned by shear flow in a polymer matrix has been measured as a function of tensile strain. The Raman intensity varies with the optical polarization direction, an effect which is used here to assess the degree of tube alignment. The strain dependence of the Raman shift depends strongly on the nanotube orientation and the polarization direction. We show that, using polarized light, unoriented nanotubes can be used as strain sensors so that no tube alignment is necessary and the strain can be measured in all directions in a single sample.

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Embedding carbon nanotubes in a polymer matrix is interesting for two reasons. First, the high aspect ratio and high strength[1–3] of the tubes make them ideal candidates as a reinforcing fiber and, secondly, the tubes are strongly Raman active[4–6] so that structural changes in the tubes, for example, as a function of strain in the matrix, may be observed. This enables study of the mechanical properties of the matrix as well as the nanotubes themselves. Using a Raman microprobe, the Raman spectrum from a region as small as 1 cubic micron can be measured, for small scale mapping of these properties. In this paper we are concerned with the dispersion of nanotube orientations, its detection by Raman spectroscopy and its consequences when nanotubes are used as strain sensors.

When single-wall nanotubes (SWNTs) are embedded in a polymer they are hydrostatically compressed and this shifts the wave number of the disorder induced D^* band upwards from 2610 cm^{-1} in air to around 2628 cm^{-1}, depending on the polymer used.[7] Uniaxial strain applied to the polymer causes a further shift of the D^* band. This shift is measured[7] to be linear with applied strain, with the slope depending on the orientation of the nanotubes.[8] This slope is the crucial parameter for strain mapping by Raman and it is affected by the dependence of both the Raman intensity and strain shift on the orientation of a nanotube with respect to the principal strain axis.

Using plane polarized light for Raman measurements, detailed information about the nanotube orientation can be obtained because then the intensity of the D^* band is orientation dependent. Saito *et al.*[9] recently calculated the intensity I_S of the A_{1g} symmetric component of the G band for (10,10) armchair SWNTs and predicted that, with the polarization of the incident and scattered light parallel, the intensity varies as $I_S \propto (\cos^2\theta - 0.5\sin^2\theta)^2$ where θ is the angle between the optical electric vector and the nanotube axis. Measurements by Rao *et al.*[10] and by Jorio *et al.*[11] of well-aligned nanotubes in air are in good agreement with this theory. The same orientation dependence for the intensity of the (also A_{1g} symmetric) D band was observed,[10] and may be expected for both D and its overtone D^* because they appear to be directly related to the G band.[12] We have measured both the D^* and G bands for partially aligned SWNTs using different polarizations and find that their intensities are proportional to each other but we do not present those results here. Gommans *et al.*[13] and Duesberg *et al.*[14] measured an equal polarization dependence for the intensity of Raman modes of *all* symmetries in SWNTs and interpreted this in terms of resonance effects. The calculation of Gommans *et al.* for the Raman intensity-polarization relationship of SWNTs is in good agreement with their measurements of a fibre made up of aligned SWNTs, allowing for some misorientation of tubes in the fiber.

Here we present measurements of the polarized resonance Raman intensity as a function of polarization direction for nanotubes aligned within a polyurethane acrylate (PUA) matrix, and use the results to estimate the orientation distribution of the nanotubes. To do this we use the resonant Raman theory of Gommans *et al.* and the nonresonant theory of Saito *et al.* and show that our data, as well as that of Gommans *et al.* and Rao *et al.*,[10] is most consistent with the nonresonant theory. We then describe polarized Raman experiments on the nanotube composite under uniaxial strain which show that the measured Raman strain shift is strongly dependent on the optical polarization direction, and conclude by showing how this effect allows the use of unoriented nanotubes as strain sensors. This means that mapping of the strain in all directions is possible using a single sample whereas without polarized light, the nanotubes must be oriented so that the strain in only one direction can be measured. Moreover, the technique can be used in samples where the nanotubes cannot be aligned.

The carbon nanotubes used in this study (Dynamic Enterprises, Ltd.) were single walled, with diameters between 1.4 and 2.4 nm as observed by TEM. Polymer films with oriented nanotubes were prepared by dispersing the nanotubes (0.1% wt.) in the PUA oligomer and then shearing the oligomer across a glass plate using a doktor blade. The resulting high elongation in the shearing direction is comparable to extrusion through a pair of slits.[15] Therefore we expect the nanotubes to be strongly oriented into the plane of the film, which was immediately cured under UV light,[8] to preserve the nanotube alignment. Evidence for two-dimensional nanofiber distribution was published recently.[16] The film thickness was typically 150 μm and tensile test specimens were simple beams of width 2 mm and gauge length 20 mm. Polarized Raman measurements were performed at room temperature using a Renishaw Raman microscope with a few

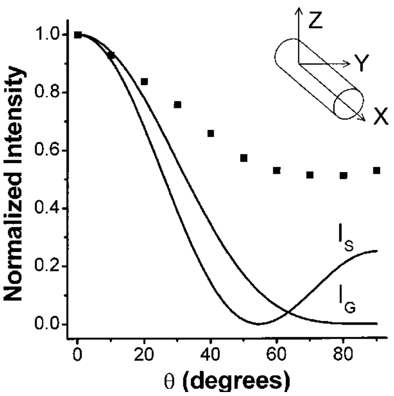

FIG. 1. Raman intensities as a function of the angle between the sample axis and the optical polarization axis. The curves are the theories of Refs. 9 (I_S) and 13 (I_G) for the G band of a single nanotube. The experimental data is for the D^* band of nanotubes oriented in a polymer. X is the nanotube alignment axis (inset).

mW of 632.8 nm laser light focused to a 20 μm diameter spot to avoid excessive sample heating. All Raman measurements were performed in the backscattering geometry $-Z(i,i)Z$ which means that the laser light arrives at the sample in the negative Z direction, and scattered light is collected in the positive Z direction. The indices in parenthesis are the directions of the electric vector for the incident and scattered light. i may be X, which is along the alignment axis (nominally the nanotube axis) or Y which is perpendicular to X and Z as shown by the inset of Fig. 1. For unoriented samples the two perpendicular directions are called 1 and 2 instead of X and Y as there is no alignment axis. We use the notation P_i to describe the polarization conditions. Tensile strain ε is applied in either the X or Y directions and for this we use the index S so that each experiment is denoted by the couple (P_i,ε_S).

Figure 1 shows the measured intensity of the D^* band for nanotubes in unstrained PUA. The polarization direction is rotated from X at $\theta=0°$ to Y at $\theta=90°$ by rotating the sample. There is a marked decrease in intensity with angle, indicating that indeed the tubes are aligned. As expected for nanotubes which are not perfectly oriented, the angular dependence is not of the form predicted by Gommans *et al.*, $I_G \propto \cos^4\theta$ or Saito *et al.*, $I_S \propto (\cos^2\theta - 0.5\sin^2\theta)^2$ which are shown as solid lines in the figure. Assuming in turn each of these theoretical results to be correct for perfectly aligned nanotubes, we now calculate the two-dimensional nanotube distribution in the matrix which is the relative number of nanotubes at an angle ϕ to the alignment axis $N(\phi)$. With the polarization direction at an angle θ to the alignment axis, the contribution to the total Raman intensity $R(\theta)$ from nanotubes at angle ϕ, is $I_G(\theta-\phi)$ or $I_S(\theta-\phi)$ multiplied by $N(\phi)$. We approximate $N(\phi)$ to be split into four angular regions $N_1(\phi_0 \leqslant \phi \leqslant \phi_1)$, $N_2(\phi_1 \leqslant \phi \leqslant \phi_2)$, $N_3(\phi_2 \leqslant \phi \leqslant \phi_3)$, and $N_4(\phi_3 \leqslant \phi \leqslant \phi_4)$, where N_k are constants and where ϕ_k are 0°, 22.5°, 45°, 67.5°, and 90°, respectively, for $k=0,1,2,3,4$, so that

$$R(\theta)=\sum_{k=1}^{4} N_k\left[\int_{-\theta+\phi_{k-1}}^{-\theta+\phi_k} I(\theta-\phi)\,d\phi + \int_{-\theta-\phi_k}^{-\theta-\phi_{k-1}} I(\theta-\phi)\,d\phi\right]. \qquad (1)$$

TABLE I. Nanotube orientation distributions given by fits of Eq. (1) to the data of Fig. 1 and Table II. ϕ is the angle from the alignment axis. G and S indicate where the theory of Gommans *et al.*[13] or Saito *et al.*[9] was used in Eq. (1).

k	ϕ (deg)	Tube distribution $N_k(G)$	$N_k(S)$
Present Work			
1	0–22.5	0.51	0.46
2	22.5–45	0.16	0.26
3	45–67.5	0.06	0.13
4	67.5–90	0.27	0.15
Data from Ref. 13			
1	0–22.5	0.65	0.62
2	22.5–45	0.22	0.32
3	45–67.5	0.00	0.06
4	67.5–90	0.13	0.00

Least squares fits of Eq. (1) to our data and to the data of Gommans *et al.* give the values of N_k listed in Table I. Results using both $I=I_S$ and $I=I_G$ are shown. The nonresonant (I_S) theory gives a more reasonable nanotube distribution for *both* experiments, being roughly Gaussian around the alignment axis in each case, whereas the resonant theory suggests a high proportion of tubes perpendicular to the alignment axis and for a two-dimensional nanotube distribution there is no obvious physical reason for this. Gommans *et al.*[13] assumed their thick bundle of nanotubes to be effectively two-dimensional for Raman measurements due to the small laser-penetration depth. Direct evidence for the two-dimensional distribution in our polymer samples is not available, but measurements on composites containing carbon nanofibrils 500 nm in diameter and 10–20 μm long prepared by an identical method,[17] and fibrils 200 nm in diameter and a few μm long prepared by an infiltration under pressure method,[16] show a strongly two-dimensional distribution. Furthermore, the intensity data of Rao *et al.*[10] for the D and G bands of well-aligned MWNTs exhibits a minimum at $\theta=55°$ which is only consistent with the nonresonant theory. Fitting the nonresonant (Saito) theory to our data, we find that 46% of the nanotubes lie within 22.5° of the alignment axis $N_1(S)=0.46$, compared with 62% for tubes in the fibers of Gommans *et al.* which represents a significant degree of alignment in both cases. Table II shows the two experimental data sets along with the fits of Eq. (1), and the fit of Ref. 13. There is good agreement in each case between theory and experiment. Note that both theories give an *identical* fit to the data, and this implies that the variable N_k (the nanotube distribution function) must exactly compensate for the differences in the theory.

Figure 2 shows the Raman wave number of the D^* band for nanotubes in PUA as a function of tensile strain applied to the matrix. In Fig. 2(a) the tensile strain is applied along the nanotube alignment direction ($S=X$); in Fig. 2(b) it is

TABLE II. Relative Raman intensities. The theories of Gommans *et al.*[13] and Saito *et al.*[9] were used in fits of Eq. (1) to the experimental data. The fit of Ref. 13 is given in parenthesis.

θ (deg)	$R(0)/R(\theta)$ Expt.	$R(0)/R(\theta)$ Eq. (1) fit[a]
	Present work	
10	1.08	1.03
20	1.19	1.14
30	1.32	1.32
40	1.52	1.55
50	1.75	1.77
60	1.89	1.91
70	1.95	1.94
80	1.95	1.92
90	1.89	1.90
	Data from Ref. 13	
23	1.3 (1.2)	1.2
45	2.0 (1.9)	2.1
90	4.9 (4.6)	4.9

[a] Both theories give identical values.

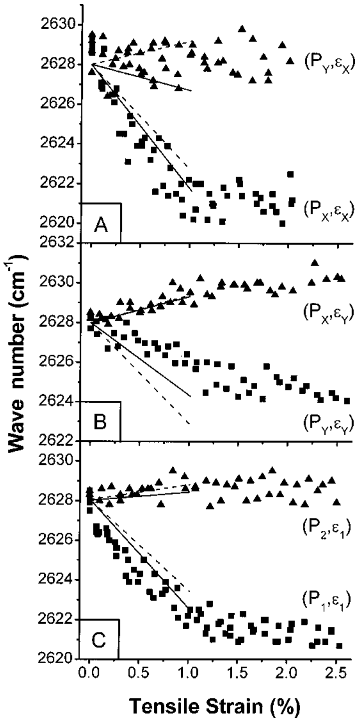

FIG. 2. The D^* peak position for SWNTs embedded in a PUA matrix, as a function of tensile strain. The optical polarization direction P_i and strain direction ε_S are given with respect to the nanotube alignment axis as shown inset in Fig. 1. The solid (broken) line is the result of our theory using the angular-intensity relation I_S (I_G) shown in Fig. 1.

applied perpendicular to the alignment direction ($S=Y$) and in Fig. 2(c), the nanotubes are unoriented. In all cases, the initial wave number strain shift is approximately linear and then after the linear portion, the wave number is constant. This is consistent with the measurements of Wood *et al.*[8] The transition at about 1% strain occurs when the polymer yields, because shear stress can no longer be transferred from the matrix to the nanotubes,[8] as verified using the classical stress-strain curves measured in each experiment. The initial slope of the data clearly varies with the polarization direction and with the orientation of the nanotubes with respect to the strain axis.

Now we give a qualitative explanation of these results and later a quantitative analysis. From the arguments above we assume that the measured Raman intensity from a single nanotube follows the angular orientation dependence calculated by Saito *et al.* and that the tubes lie predominantly around the alignment axis X. For (P_X,ε_X) we therefore measure the most intense Raman from tubes in the strain direction, of which there are a large fraction, and the strain in these tubes is close to the uniaxial strain applied to the matrix. We see a large downward shift of wave number with strain as expected. For (P_X,ε_Y) the signal is largely from tubes perpendicular to the applied strain direction. In this direction the matrix is in compression, via Poisson's contraction, so that we measure an increase in the wave number with strain. For (P_Y,ε_Y) there are few tubes parallel to the polarization direction but the Raman from each tube is intense,[9] whereas there are more tubes along the alignment direction, but the scattering from each is relatively weak. Thus the measured Raman signal has significant contributions from tubes in both tension and compression. The slope of the (P_Y,ε_Y) data is about halfway between the slopes for the (P_X,ε_X) and (P_X,ε_Y) experiments. For (P_Y,ε_X) we see no wave number shift with strain. This is consistent with our assumptions because again we have a combination of (P_X,ε_X)- and (P_X,ε_Y)-like scattering.

The data and theoretical predictions for the unoriented samples [Fig. 2(c)] are similar to those for the oriented case $(P_2,\varepsilon_1)\approx(P_Y,\varepsilon_X)$ and $(P_1,\varepsilon_1)\approx(P_X,\varepsilon_X)$. The slopes are slightly different for the unoriented samples because they have a larger fraction of tubes perpendicular to the polarization axis than the oriented samples. This demonstrates the effectiveness of polarized Raman in selecting out the nanotubes in the polarization direction. Note that for the oriented samples, the (P_X,ε_Y) and (P_Y,ε_X) data are different, as are (P_X,ε_X) and (P_Y,ε_Y), confirming that we do have a significant degree of orientation. Since this paper was submitted, Hadjiev *et al.*[18] have reported experiments in which they applied compressive strain to an unoriented SWNT/epoxy composite, and the results are quantitavely consistent with the data of Fig. 2.

The practical implications of these results are important. If we wish to measure the Raman strain shift from aligned nanotubes as may be used in a real composite—with nanotubes as the reinforcing phase—a more sensitive measurement of the strain, that is a bigger Raman shift with strain, is seen with polarized Raman than without. We measure -7.0 cm^{-1}/% strain here compared with -4.7 cm^{-1}/% strain with[7] only a polarized laser (no analyzer) and presumably the shift measured with completely unpolarized light would be even smaller. When the tubes are only present as strain sensors, the advantage of polarized Raman is that we may now use unoriented nanotubes, since there is still a large strain shift of the D^* band ($-6.3\ \mathrm{cm}^{-1}$/% strain) as seen in Fig. 2(c). Then we have an equally sensitive measurement of the strain in all directions and we can select the direction of interest either by rotating the sample or the polarizing optics. The results also provide a further test of theoretical models such as those of Saito *et al.* and Gommans *et al.*

To apply those theories to the strain experiments, we make the following assumptions. (i) As in conventional highly anisotropic carbon fiber composites, the axial strain in the nanotube and matrix are identical. Therefore the resulting axial stress in the nanotube is proportional to the ratio of tube to matrix moduli and thus is much larger than the matrix stress.[19] (ii) The Raman wave-number-strain relationship for a single nanotube does not depend on nanotube diameter even though the absolute value of the D^* wave number does depend on the nanotube diameter.[20] (iii) The line shape of the D^* Raman peak for a single nanotube does not vary with angle, or with strain. There is experimental evidence for the former for the D band,[10] but not for the latter. We can then treat the Raman line shape as a delta function so that the strain shift $d\omega_R/d\varepsilon_0$ of the center of mass of the total Raman signal ω_R is just the intensity-weighted average strain shift of the signals from the individual tubes:

$$\frac{d\omega_R}{d\varepsilon_0}(\theta)=R(\theta)^{-1}\sum_{k=1}^{4}\left[N_k\int_{\phi_{k-1}}^{\phi_k}[I(\theta-\phi)+I(-\theta-\phi)]\frac{d\omega_{NT}}{d\varepsilon_0}A(\phi)d\phi\right]. \tag{2}$$

$A(\phi)$ is the angular dependence[19] of the axial tensile strain, $\cos^2\phi-\nu\sin^2\phi$, experienced by a nanotube at angle ϕ where ν is the one-dimensional Poisson's ratio of the matrix which is 0.35 for PUA. $d\omega_{NT}/d\varepsilon_0$ is the rate of change of wave number with strain for a single nanotube oriented along the strain direction. This is unknown at present so we assume that it is a constant[8] and perform a least-squares fit of Eq. (2) to all the data for strain less than one percent in Figs. 2(a)–2(c) to obtain the best-fit value of $d\omega_{NT}/d\varepsilon_0=-8.6\ \mathrm{cm}^{-1}$/% strain.

The solid lines in Fig. 2 are the results of the theory.[21] The trend of the change in slope for the different orientations and polarizations is in agreement with the data. We do predict a small slope for (P_Y,ε_X) and (P_2,ε_1) and larger slopes for (P_1,ε_1) and (P_Y,ε_Y) as well as the positive slope for (P_X,ε_Y). For a given nanotube distribution N_k the result of the theory is that, for each case, the change of wave number with strain is a numerical factor times $d\omega_{NT}/d\varepsilon_0$, so that if we increase its value, all the other slopes must be increased in proportion. Therefore this simple theory is unable to predict precisely the initial slopes of all the experimental data. There are several possible reasons for this. First, the component of applied matrix stress in the nanotube-radial direction, although too small in itself to significantly distort the nanotube, may affect the quality of the interface between the two phases and consequently the axial stress transferred to the nanotube from the matrix. A related effect is the difference in Poisson's ratio ν for the matrix and the nanotubes. For the matrix, $\nu=0.35$, whereas for the nanotubes, it may be as low as 0.14 (Ref. 22) and this will affect the radial stress. Finally we need to consider the wave-number-strain relation for the individual nanotubes which may not be linear, and the presence of not only armchair nanotubes, but also zigzag, and chiral tubes, which may[9] have different intensity-angle relationships. Note that again the results obtained using the nonresonant theory $I=I_S$ (solid lines) are a better description of the data than the resonant theory $I=I_G$ (broken lines).

In conclusion, we have estimated the nanotube distribution in a polymer film from the intensity-angle relationship of the polarized Raman spectrum and shown that a nonresonant theory gives the most reasonable orientation distribution for the tubes. This method shows that a good degree of nanotube alignment is obtained by a simple shear flow technique. When the polymer is strained, the Raman strain shift of the nanotubes depends strongly on the optical polarization direction and we have shown that, when using nanotubes as strain sensors for microscale strain mapping, the polarized Raman of unoriented tubes is a simpler and more versatile tool than the unpolarized Raman of oriented tubes.

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