

Fundamental reproducibility of Raman band positions and strain measurements of high-modulus carbon fibre – the effect of laser-induced heating

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We have shown that the E_{2g} , A_{1g} and second-order ($\sim 2700\text{ cm}^{-1}$) Raman band positions of Hercules HMS4 carbon fibres shift as a function of incident laser power. These shifts arise as a result of changes in the local fibre temperature. The sensitivity of band position to varying laser power is different from fibre to fibre within the same tow – thus equally strained fibres subjected to the same laser power can show widely different band positions and so different apparent strains. The same effect can be observed from point to point on individual fibres. If laser power is not carefully controlled (both in magnitude and stability), errors in the accuracy of the measured strain can be greater than the measured strain itself, and have been shown to approach 70% of the breaking strain. These results mean that strain measurements obtained from composite materials containing this fibre must be interpreted with caution unless the laser beam intensity at the fibre is precisely controlled. This effect will also be important with other types of carbon fibre, since in previous work we have observed that laser-induced sample heating occurs with a wide range of materials from cokes to pitch-based fibres.

1. Introduction

It has been demonstrated that Raman microscopy is a powerful tool for following the deformation of high-modulus polymer fibres by measuring the shifts in vibrational frequencies which occur when the fibres are strained [1–3]. More recently it has been shown that strain-induced frequency shifts can also be measured in various types of carbon fibre [4, 5], and such measurements can give a valuable insight into the micromechanics of these systems. The Raman microprobe allows data to be obtained with $\sim 1\text{ }\mu\text{m}$ spatial resolution, so bandshifts can be mapped over single fibres on a composite surface.

These observations have raised the possibility of calibrating the Raman bandshifts as a function of applied strain, using a single carbon fibre under controlled deformation, and then using the resultant calibration curve to relate bandshifts measured from a fibre-reinforced composite to the strains present in the material [5]. While this is an attractive proposition, there are several pitfalls in using this approach which have not been fully appreciated in the literature, but which may invalidate the results obtained. In particular, it has been recently demonstrated in our laboratory that laser-induced heating of carbon fibres can cause bandshifts of magnitude comparable to those induced by sample strain [6]. The need for careful control of laser beam power at the fibre surface is paramount. In addition, we believe that the factors affecting fundamental reproducibility of this technique, particularly with regard to extrapolating results

from single fibres to composite materials, have not been satisfactorily evaluated.

In order to better evaluate the applicability of this technique to real carbon-fibre reinforced materials, we have thoroughly investigated its fundamental precision. In particular, we have studied:

- (a) the reproducibility of Raman band positions obtained from a single HMS4 fibre under constant laser power and zero applied strain,
- (b) the variability of band positions from fibre to fibre (taken from the same tow) under the conditions above,
- (c) the variation in band position as a function of laser power for several fibres from the same batch, and at different positions on individual fibres,
- (d) the effect of laser beam spot size and precision of focusing upon measured band positions.

We have performed these studies not only for the E_{1g} mode (1580 cm^{-1}) but also for the A_{1g} (1350 cm^{-1}) and second-order (2700 cm^{-1}) bands. We have therefore reached what we consider to be reliable conclusions as to the fundamental precision of the method with this particular fibre, and to the general factors which affect this precision.

2. Experimental procedure

2.1. Carbon fibre preparation

For the purposes of this work only one type of material was studied, namely Hercules HMS4 PAN-

based fibre. A tow of fibres was teased apart and loosely taped to a glass microscope slide. The fibres were not mechanically stressed during these experiments.

2.2. Raman spectroscopy

Spectra were recorded with a Dilor XY Laser Raman Spectrometer, using the 514.5 line from a Spectra Physics model 2035 argon ion laser as the excitation source. Spectral resolution was approximately 3 cm^{-1} over the energy range of interest. Raman band positions could be measured from the spectra with an accuracy of about $\pm 1\text{ cm}^{-1}$ (E_{2g} , A_{1g} modes) or $\pm 2\text{ cm}^{-1}$ (second-order mode).

The spectrometer was coupled to an Olympus BH2 microscope, allowing Raman spectra to be obtained from individual ($7\text{ }\mu\text{m}$ diameter) fibres. All Raman measurements were made using $\times 100$ or $\times 50$ microscope objectives, giving approximate laser beam spot sizes of 2 and $4\text{ }\mu\text{m}$ diameter, respectively. Positioning of the focused spot with respect to the carbon fibre was controlled to about $1\text{ }\mu\text{m}$.

The microscope transmission was found to be very sensitive to input laser beam divergence and alignment, particularly when using the $\times 100$ objective. Transmission was therefore checked immediately before each set of measurements was made, and the input power was adjusted to yield the desired laser beam power at the sample. Transmission was also checked after each set of measurements in order to ensure that alignment stayed constant throughout the experiment.

Usable laser powers were limited by the intensity threshold for sample damage. With the $\times 100$ objective, 15 mW laser power at the sample burnt the fibre surface, and so powers below 12 mW were used. With the $\times 50$ objective, higher powers could be safely employed but generally powers were restricted to a maximum of 12 mW .

2.3. Experimental variables

The variability of the Raman band positions was measured under a range of experimental conditions. The A_{1g} ($\sim 1350\text{ cm}^{-1}$), E_{2g} ($\sim 1580\text{ cm}^{-1}$) and second-order ($\sim 2700\text{ cm}^{-1}$) band positions were recorded in each case. Spectra were obtained while

- (a) monitoring one fixed area of a fibre and varying the incident laser power,
- (b) focusing the laser beam on different areas of a fibre, or on different fibres, and varying the laser power,
- (c) keeping a fixed laser power and fibre area, but defocusing the beam at the fibre surface.

Most measurements were made using the $\times 100$ microscope objective, but some were made with the $\times 50$ for comparative purposes. We believe that this data set gives a good indication of the fundamental reproducibility of Raman band position measurements on HMS4 fibre under normal experimental conditions.

3. Results

3.1. Reproducibility between fibres

Two HMS4 fibres from the same tow were subjected to laser powers ranging from 1 to 12 mW , using a $\times 100$ microscope objective. The spectrum obtained from each fibre at 10 mW laser power is given in Fig. 1. The spectra indicate that no gross differences in fibre crystallinity (judged by E_{2g}/A_{1g} intensity ratio) were evident [7].

Fig. 2 shows the A_{1g} and E_{2g} band positions of the fibres as a function of laser beam power, still using the $\times 100$ objective. For the sake of clarity, the overtone band data are not included on this figure. Linear regression analyses of the data yielded gradients of -0.99 ± 0.08 , -1.32 ± 0.12 and $-2.14 \pm 0.31\text{ cm}^{-1}\text{ mW}^{-1}$ for the A_{1g} , E_{2g} and A_{1g} overtone modes, respectively, for fibre 1; and -0.63 ± 0.08 , -0.82 ± 0.03 and $-1.28 \pm 0.15\text{ cm}^{-1}\text{ mW}^{-1}$ for the same modes for fibre 2. The band positions varied with laser power for fibre 1 at about 1.6 times the rate observed for fibre 2 – an unexpected result.

For both fibres, the E_{2g} band position changed with laser beam power at about $\frac{4}{3}$ of the rate of change of the A_{1g} band. The second-order mode position changed about twice as rapidly as that of the A_{1g} fundamental for each fibre. This would be expected if the mode were an overtone of the A_{1g} fundamental. At low powers ($\leq 5\text{ mW}$) both fibres gave very similar band positions. At 12 mW there was about 2 cm^{-1} difference between the A_{1g} band positions of the two fibres, about 4 cm^{-1} difference between the E_{2g} band positions, and about 7 cm^{-1} difference between overtone band positions.

Measurements made on several other fibres, and on several positions along individual fibres, all showed this trend of linearly decreasing vibrational frequencies with increasing laser power, but with a gradient which varied from fibre to fibre or from area to area on individual fibres. The values of the gradients all fell roughly between the values obtained for fibres 1 and 2 noted above. Thus the sensitivity of band position to laser power varies considerably amongst the fibres.

For all fibres which were examined, the range of the A_{1g} and E_{2g} mode positions were roughly bound by the plots in Fig. 2, with a random spread of results between the lines of minimum and maximum slope. Fig. 3 shows this spread of results for the E_{2g} mode in greater detail, obtained from a random selection of fibres and positions on an individual fibre. Only one measurement was taken for any given position on a fibre, with each measurement having an accuracy of about $\pm 1\text{ cm}^{-1}$ (as measured from the spectrum). There is obviously a large spread in measured frequency when too high a laser power is selected. The magnitude of this frequency spread is compared with the strain-induced frequency shifts in section 5.

3.2. Reproducibility for single fibres

In order to investigate the band position variation for individual fibres, spectra were recorded for a few fibres

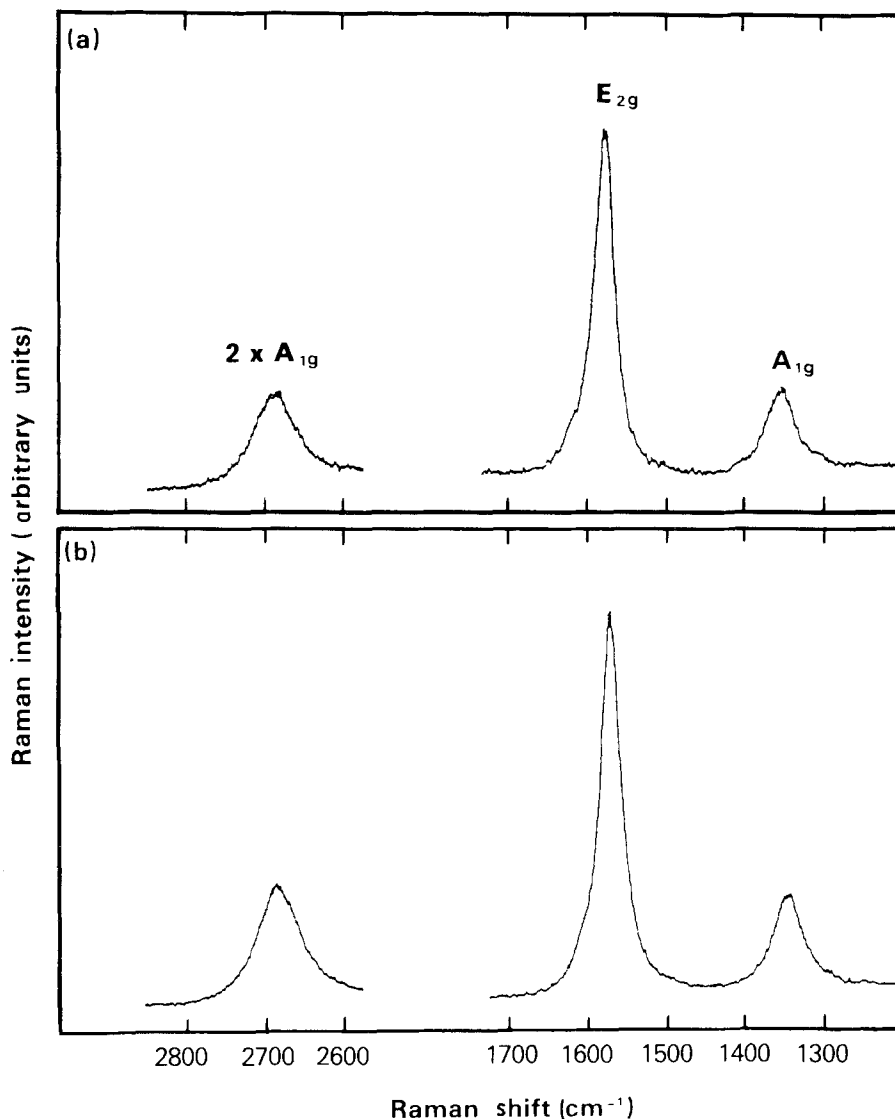


Figure 1 Raman spectra of two fibres separated from same tow, with 10 mW incident laser power. Note that there are no obvious differences in crystallinity (as judged by E_{2g}/A_{1g} intensity ratio) between the two fibres.

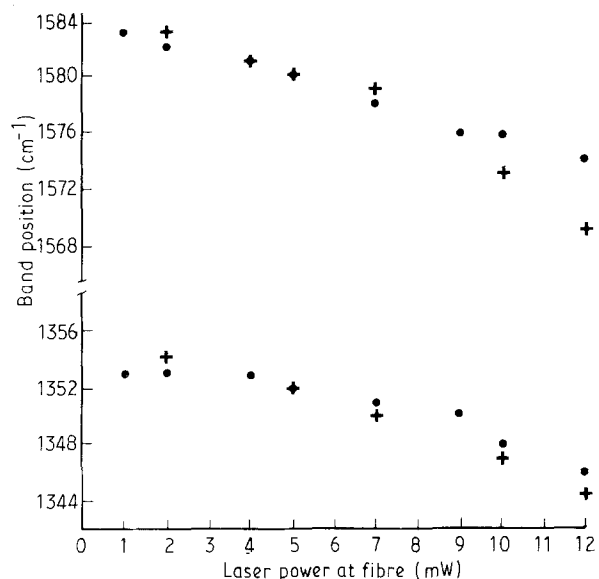


Figure 2 Variation in E_{2g} and A_{1g} band positions as a function of laser power for (+) fibre 1 and (●) fibre 2. Second-order mode positions are excluded from this figure for clarity.

at several positions along their length, with separations of $\sim 100 \mu\text{m}$ between measurements, at constant laser beam power. At these separations, there was a similar degree of scatter of band positions along individual fibres to that observed between separate fibres. It was also found that different regions of the same fibre yielded different gradients in the variation of band position with changing laser power.

Measurements made at varying displacements on the fibre surface perpendicular to the long axis also showed some degree of scatter (e.g. for a fibre measured with 10 mW laser power, $\times 100$ objective, E_{2g} band positions of 1572, 1573 and 1572 cm^{-1} were recorded for the laser beam spot centred at the middle of the fibre and at 1 and 2 μm away from the middle, respectively). The scatter appeared to be random, despite the fact that the laser beam illuminates a different surface area of the fibre surface according to its displacement perpendicular to the fibre long axis; hence the laser intensity (and sample temperature) would be expected to vary.

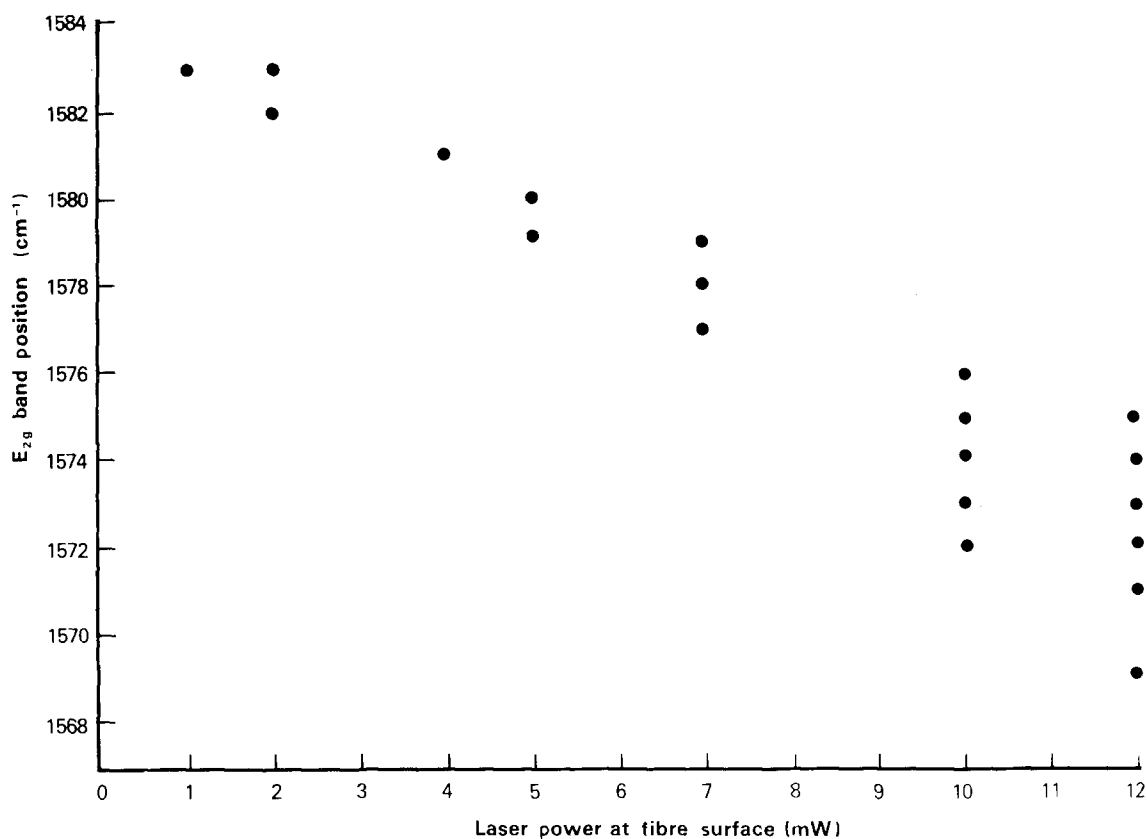


Figure 3 Spread of E_{2g} band positions observed with a range of fibres, and positions on individual fibres, as a function of laser power. Only one measurement was taken at each position – each individual measurement had an accuracy of $\pm 1 \text{ cm}^{-1}$.

Every band position obtained at each laser power has been shown – however, most were observed several times at different fibre positions and this is not indicated on the figure.

Spectra taken from a fixed area of a fibre, firstly with the beam focused, and then defocused to give only half of the original band intensity, gave a shift in E_{2g} band position of only 1 cm^{-1} at 10 mW laser power, showing that small errors in focusing cannot account for the scatter in band positions obtained when different fibres or areas of individual fibres are studied.

Therefore we conclude that bands arising from different areas of individual fibres appear to exhibit different sensitivities to variations in laser power, and that this variation is unlikely to be accounted for by simple changes in experimental conditions such as focusing error or positioning of the laser spot off the fibre long axis. The variation could perhaps arise from differing local thermal conductivity on the fibre surface.

3.3. Effect of changing the microscope objective

All of the previous results were obtained using a $\times 100$ microscope objective. We also recorded spectra using a $\times 50$ long working distance objective, to give a large change in focused beam size on the fibre surface. Fig. 4 shows the band positions for the A_{1g} , E_{2g} and second-order modes at various powers obtained from one area of a single fibre. The rate of change of band positions with power for this fibre were about the same as the shallowest gradients measured using the

$\times 100$ objective ($-0.68 \pm 0.12 \text{ cm}^{-1} \text{ mW}^{-1}$ for A_{1g} , $-0.84 \pm 0.05 \text{ cm}^{-1} \text{ mW}^{-1}$ for E_{2g} and $1.47 \pm 0.20 \text{ cm}^{-1} \text{ mW}^{-1}$ for A_{1g} overtone).

Again different fibres showed a spread in band position at fixed laser power, e.g. at 10 mW laser power, a spread of 3 cm^{-1} was observed for the E_{2g} mode position for several different fibres. However, all deviations from the plot in Fig. 4 were towards higher wave number, and so on average the rate of change of band position with laser beam power was smaller using the $\times 50$ objective than with the 100 objective. This would be expected, since the rate of change of intensity with laser beam power (dI/dP) is given by $1/A$, where A is the laser beam spot area and P is the beam power. Using a larger laser spot size, dI/dP decreases and so laser heating will also decrease relative to that obtained with a smaller spot. Unfortunately, the signal-to-noise of the spectrum also decreases using the larger focused spot.

At low powers ($\leq 5 \text{ mW}$) the band positions for the $\times 50$ and $\times 100$ objectives were very similar, as would be expected, since the heating effect is small in each case.

3.4. Reproducibility of crystallinity measurements

The relative intensity of the E_{2g} and A_{1g} modes and the shape of the second-order band are known to vary with the degree of crystallinity in graphitic materials [7]. This intensity ratio was calculated for several of the spectra which were used to measure band positions. It was found that the random variation in intensity ratios from spectra taken from one fixed

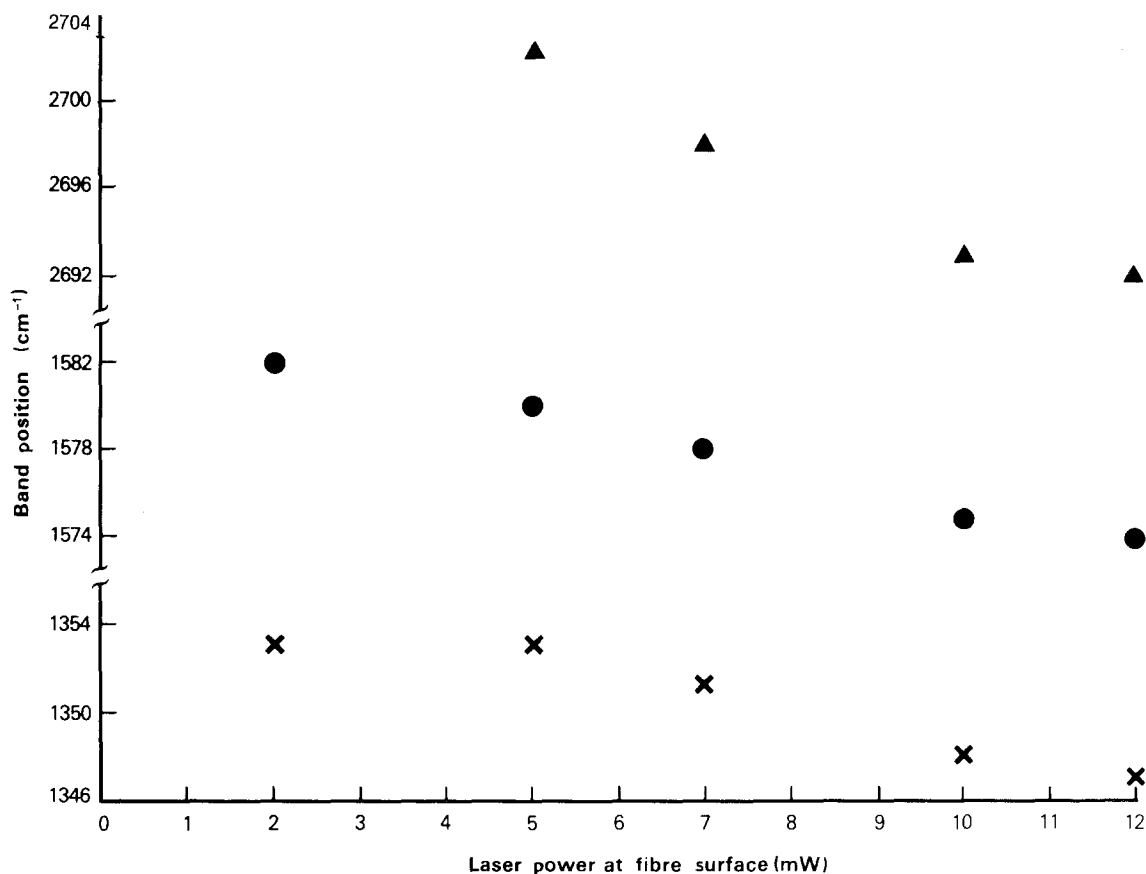


Figure 4 Raman band positions as a function of laser power using $\times 50$ microscope objective ($\sim 4 \mu\text{m}$ spot size). The rate of change of band position with respect to laser power is lower than that obtained for the corresponding mode using $\times 100$ objective, as would be expected. (▲) second-order mode, (●) E_{2g} mode, (×) A_{1g} mode.

point on a fibre at different powers (for which the crystallinity should not change) was as large as the random variation between fibres. Within our experimental error, therefore, there was no obvious difference in crystallinity between fibres, and no correlation of the measured crystallinity with sensitivity of band positions to laser power variations. Therefore, local variations in crystallinity (as measured by the Raman technique) do not apparently account for the observed differing sensitivities to laser power variation.

4. Discussion – implications for strain measurement

The results presented above may be summarized under five main points.

1. Laser power at the sample is important since it affects the vibrational frequencies of the E_{2g} , A_{1g} and second-order modes: variation in laser power will alter mode positions, rendering prior calibrations invalid.

2. The variation in mode position as a function of laser power varies for each mode – the variation of E_{2g} mode is about 4/3 times that of the A_{1g} mode, whereas the overtone mode varies at about twice the rate of the A_{1g} mode, for the HMS4 fibres studied.

3. The rate of change of mode frequency with laser power varies according to laser spot position on the fibre, and also from fibre to fibre. Upper and lower limits of the rate of change have been identified by sampling a range of fibres and positions.

4. Variation in parameters such as precision of focusing, or fibre crystallinity, cannot account for the observed sensitivity variations.

5. Using a lower-magnification objective ($\times 50$) gave a lower sensitivity to laser power variations, as would be expected, for each mode. It also yielded spectra of poorer signal/noise ratio, necessitating longer acquisition times.

These results are important since they show that when working with high laser powers, the scatter in Raman bandshifts on observing several different areas of fibre is not random, since certain areas will always give predominantly “high” or “low” apparent Raman shifts, over and above the errors in measuring band positions from the spectra. This is due to differing sensitivities of Raman band position with respect to laser power. The cause of these differences is not known at present.

The implications of these results for the use of Raman bandshifts for strain measurements are as follows:

(a) The laser power at the fibre surface must be kept fixed if reproducible strain measurements are to be made.

(b) At high laser powers different fibres exhibit different Raman frequencies, even if they are under identical strain – thus at 12 mW with a $\times 100$ objective there was a spread of $\sim 6 \text{ cm}^{-1}$ in the E_{2g} Raman band position, depending upon which fibre was examined. Simply keeping a constant laser power is not

sufficient – a constant, low power is required for precise strain measurement.

(c) For HMS4 fibres the optimum laser power at the fibre surface (minimum scatter in frequency) was ~ 4 mW – at this point the lines of minimum and maximum slope intersect (see Figs 2 and 3), and variations primarily arise from errors in measurement of band positions from spectra.

(d) Translating results obtained from a single fibre in air to those from a fibre embedded in a composite is not straightforward. We must keep the local temperature at the fibre surface equal to that of the fibre used (in air) for calibration purposes. Factors such as beam attenuation on penetrating the resin, and differing thermal conductivities of fibres in air and resin, could influence temperature and hence band-shift in each case. Thus the applicability of calibrations obtained from fibres in air must be carefully considered when results from composites are analysed.

5. Magnitude of error in apparent measured strain

It is instructive to compare the strain error introduced by the local heating effects to the actual strains expected in a real material. Raman band positions (E_{2g} mode) in HMS4 fibres have been determined to vary by -9.2 cm^{-1} per 1% applied strain, with typical compressive strains in HMS4/PEEK composite being reported as $\sim 0.3\%$ [5]. The breaking strain of HMS4 fibres is $\sim 1\%$. From our results, a laser power of 12 mW at the sample gave a scatter of ~ 6 cm^{-1} , or $\sim 0.7\%$ fibre strain – equivalent to about 70% of the breaking strain. A laser power of ~ 5 mW yielded a scatter of ~ 2 cm^{-1} , or 0.2% fibre strain, so even at optimum laser powers, the scatter in measured frequency is still comparable to the shifts in frequency measured by other workers and used to calculate strain. This is exacerbated by failure to control or specify laser power at the sample surface. Thus we believe that the variations in Raman band position, which have been attributed to differing local strains in HMS4/PEEK prepreg material (up to 0.5% [5]) could be simply a manifestation of the effects described in this paper.

6. Future work

We intend to extend this study to other fibres, and also to examine the strain distribution (and errors therein) with real composite materials.

7. Conclusions

We have shown that laser-induced heating of a high-modulus carbon fibre (HMS4) can significantly shift the positions of the Raman-active A_{1g} , E_{2g} and second-order modes. The rate of change of band position with laser power differs not only for each mode, but also from fibre to fibre and with varying position on individual fibres. Thus at high powers (12 mW), the strain measured for several fibres showed a scatter of $\sim 0.7\%$, (equivalent to 70% of the breaking strain!) due to differing laser heating. Laser powers of ~ 5 mW gave a reduced scatter of $\sim 22\%$ of the breaking strain – this was the best accuracy attainable with the present equipment. These results show that even if the laser power is kept constant at the fibre surface, some scatter in band position is inevitable, and can yield errors in strain comparable to the absolute strain being measured. Use of too high a laser power, or failure to maintain constant laser power, exacerbates the problem.

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