Spectroscopic–mechanical analysis of stress distribution in composites

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A Raman spectroscopic–mechanical technique has been used directly to assess the effects of temperature and thermal history on the stress distribution of model composites. The experimental data describing the stress distribution are consistent with previous theoretical studies. However, a quantitative interpretation is still unavailable due to the lack of information regarding the structure and properties of the reinforcement fibres used in the composites.

INTRODUCTION

The incorporation of high modulus/strength fibres in a polymer matrix can significantly improve the overall mechanical properties of the composite. The need to produce three-dimensional reinforced materials of complex geometry, or to incorporate flow moulding processing techniques, has led to a considerable number of studies aimed at developing high performance composites using short fibres as reinforcements. The overall enhancement of the mechanical properties of these composites is based on the efficiency of the stress transfer from the matrix to the fibres so that the major portion of the applied stress is carried by the stronger fibres. Parameters influencing the overall mechanical properties or this stress transfer can be either chemical or physical/geometrical in nature and may be associated with the reinforcement fibres or with the matrix. Understanding the effects of these parameters is essential to the development of high performance materials.

Generally speaking, in a discontinuous fibre reinforced system, the mechanism of load transfer from the matrix to the fibre is interfacial shear stress. However, a quantitative analysis is complicated by the discontinuities at the fibre ends. Therefore, a number of assumptions have been made in order to obtain analytical solutions which describe the load distribution and strain of the fibre or matrix[1,2]. These theories have perhaps oversimplified the effects of fibre geometry and the adhesion properties between the fibre and matrix. In any case, most theoretical predictions have been verified by interpreting the deformation behaviour of the matrix under tensile stress. Recently, advances in computational techniques using finite element analysis have significantly improved this situation[3,4]. However, some uncertainties still exist due to the lack of direct experimental evidence relating the macroscopic deformation caused by tension or compression to the microscopic structural changes occurring within the individual fibres.

Furthermore, in processing of composites, temperature dependence needs to be considered. This factor is important, since the thermal expansion properties of the fibres and the matrix are very different, causing stress to build up in the overall composite. A number of theoretical and experimental studies have been directed at achieving a better understanding of the residual stress of the composites. However, a detailed understanding is lacking in this aspect of the composite study due to the inability directly to obtain stress distributions in both the reinforcement fibre and in the matrix.

Based on a unique experiment carried out by Galiotis and his coworkers[5], we designed a series of spectroscopic–mechanical experiments with high spatial resolution and sensitivity for studying a model composite system in order explicitly to define the stress distribution in the reinforcement fibres, to identify significant parameters associated with composite properties, to test the predictions of the theory of stress transfer from the matrix to the incorporated fibres, and to provide presently unavailable experimental data for further theoretical analysis.

The basis of this technique is to imbed a well defined poly(diacetylene) single crystal in a polymer matrix. Although this poly(diacetylene) crystal cannot be considered as a commercially feasible reinforcement fibre, its geometry and well-defined microstructure make it useful in the study of model composites. Since resonance Raman spectra can be obtained easily from the embedded fibres through a transparent matrix and because the backbone vibrations are extremely sensitive to the strain applied to the chain axis, each of the crystals acts as a strain gauge. By adjusting the back focus of the entrance slit to the monochromator of the Raman spectrometer, it is possible to obtain the frequencies of the vibrations of interest from each location of the fibre, thus providing a well defined stress distribution in the fibre. In this paper we want to demonstrate the applicability of the technique and the caution one needs to exercise in order to interpret the spectroscopic data obtained.

EXPERIMENTAL

In our studies, 'dog bone' shaped specimens are generally used for mechanical testing. To form these samples, one

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half of the mould is first filled with the matrix material and partially cured before a macroscopic polydiacetylene single crystal or crystals is inserted. After the mould is filled, the composite is cured at specified conditions.

The structure of poly(2,4-hexadiyne-1,6-diol bisphenyl-urethane), poly-HDU, is shown in *Figure 1*. It is presently available with a number of side chains (labelled R in *Figure 1*). This polymer has extended π-electron delocalization along the backbone. Our samples have

$$(CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-\langle\!\langle\bigcirc\rangle\!\rangle)$$
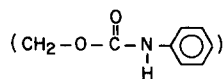
as the side chain, and are generally 1–2 cm long with a diameter of $\sim 30\,\mu m$. These samples have been kindly supplied by Professor G. Wegner of the Max Planck Institute, University of Mainz.

One of the most critical aspects of our model composite study was the determination of the matrix to be used. In order for the laser beam to penetrate the matrix and probe the stress induced structural changes in the reinforcement fibres of the composite, the matrix must be totally transparent. Furthermore, since most of the structural changes are interpreted from the changes observed in the backbone vibrations of resonance enhanced Raman spectra of the fibre, fluorescent background must be minimized, if not totally eliminated. After a number of experiments, Dow's DER 736 and Shell's EPON 825 possessing quite a range of mechanical properties and their mixtures with diethylenetriamine (DTA) as the curing agent were determined to be the most appropriate for our research. Most other resin-curing agent combinations which require accelerators could not satisfy the criteria outlined above.

A mechanical stretcher was built in conjunction with this spectroscopic experiment. Since the stepping motor used to strain the sample is connected to a microcomputer, we are able to control the strain applied to the sample with high precision. In addition, the digitized values of stress can be recorded as a function of time in the computer as well. The entire stretcher can be translated in three directions. This ability to move the sample, along with the availability of 5–6 μm spatial resolution, easily allows the examination of the stress induced microstructural changes as a function of position along the length of the fibre.

The Raman spectrometer used in this experiment is modified from the commercial HG.2S Jobin Yvon instrument. The sample chamber has been enlarged somewhat to accommodate the mechanical stretcher. In our experiment, we were pleasantly surprised that very acceptable resonance enhanced Raman spectra can be obtained even with the red excitation (6328 Å) from a small HeNe laser. In fact, we were generally cautious that no more than 5 mW of laser power was used for excitation. Depending on the slit width used and the
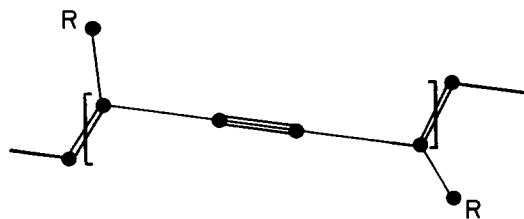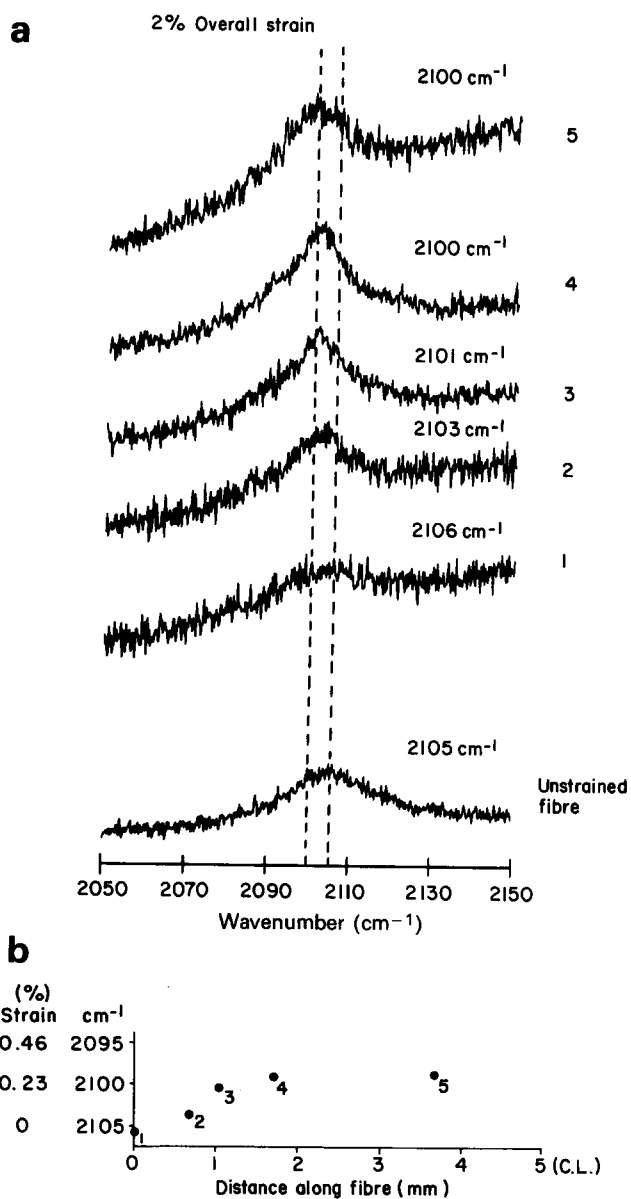

Figure 1 Schematic structure of polydiacetylene

Figure 2 Frequency variation of the $C\equiv C$ stretching vibration observed for the model composite as a function of position away from the fibre end; (a), the various spectra obtained; (b), frequency variation (calculated strain values) as a function of distance from the fibre end; laser excitation: 5145 Å; laser power ~ 5 mW; bandpass $= 1.3$ cm^{-1} at 5100 Å; matrix is EPON 825 cured with DTA at room temperature for seven days

magnification ratio of the illuminated sample volume at the entrance slit, a maximum spatial resolution of 5–6 μm can be achieved. The resonance enhanced Raman spectra of polydiacetylene have been well characterized by Lewis and Batchelder[6]. Usually only the vibrations coupled to the electronic transition associated with the backbone are seen. The most prominent bands which are sensitive to stress are the $C\equiv C$ and the $C=C$ stretching vibrations[7,8]. For a composite incorporating one fibre under stress, a series of Raman spectra obtained at various positions along the fibre direction of the polydiacetylene crystal embedded in an epoxy matrix are shown in *Figure 2*.

The X-ray diffraction study of poly-HDU indicated that one-half of the molecules of dioxane per repeat unit are incorporated in the lattice[9]. This interstitial dioxane can be volatilized readily near 165°C without any chemical degradation of the polymer. However, removal of the dioxane results in a substantially different crystal

structure and consequently different vibrational behaviour. In order to ensure that no substantial irreversible changes in the crystal structure would take place during our thermal experiment, the poly-HDU fibre was annealed at 135°C and 165°C for two hours under vacuum. The room temperature Raman spectra of the fibre before and after annealing at 135°C showed little change, but the changes were considerable after annealing at 165°C. The spectroscopic features found after the removal of dioxane are represented by additional bands found in the double and triple bond stretching regions.

RESULTS AND DISCUSSION

As can be seen in *Figure 2*, the frequency of the C≡C stretching vibration differs significantly along the fibre when the overall sample is mechanically stressed. By using the established linear relationship of $\sim 21\,cm^{-1}/\%$ of strain[8], we can interpret the fibre strain from the vibrational frequency of the C≡C stretching vibration. These data are shown clearly in *Figures 2* and *3*. The data in these Figures show that the frequency difference or the equivalent strain of the fibre is zero or nearly zero at the fibre end, as assumed in many of the earlier analyses[1,2], reaching a plateau as expected near the central region. This type of data does support the hypothesis that the load at the fibre end is zero or nearly zero. Although details differ, the overall stress on the fibre sample is consistent with theoretical expectations, illustrating that this essentially microscopic technique can be used to understand what is actually a macroscopic problem. The ratio of the moduli between the reinforcement fibres and the polymer matrix is a factor of at least 10. The maximum sample strain applied is approximately 4%. The factor which limits the precision in the determination of the fibre strain is associated with the uncertainty involved in measuring the position of the vibrational band. In our case, the uncertainty is approximately $\pm 1\,cm^{-1}$, which translates into an uncertainty of $\pm 0.05\%$ in measuring the fibre strain. It cannot be overemphasized that, unlike most previous studies, this spectroscopic–mechanical technique can provide a stress distribution at the fibre
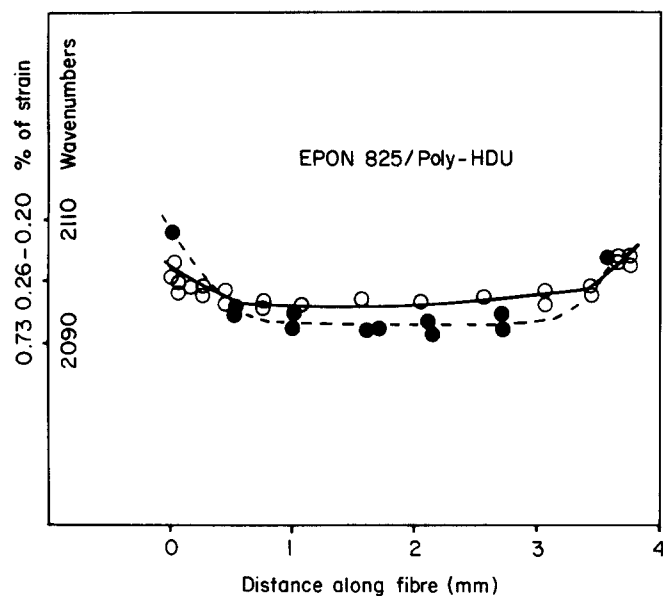
with great spatial resolution and precision, especially for anisotropic fibres.

Galiotis and his coworkers have analysed this type of data in order to interpret the suitability of presently available theories to explain the stress distribution of the fibres embedded in a polymer matrix[5]. From our measurements, we found a number of experimental parameters, such as the moduli ratio, surface treatment of the fibre surface, etc., which can significantly influence the stress distribution and its time dependence after the stress is applied. These will be reported in the near future[10].

As mentioned earlier, one particular aspect of the composite problem is the changing stress distribution as a function of temperature. The stress distribution in an unstressed sample may originate from the disparity in thermal expansion coefficients of the polymer matrix and of the reinforcement fibre when the composite is prepared at high temperatures and then allowed to cool. Or, if composites are required to perform over a wide temperature range, there may be stress build-up as well. It has been speculated that the longitudinal and transverse residual stresses can depend on a number of experimental parameters such as fibre anisotropy, aspect ratio, interfacial thickness, adhesive properties and so on[5,11,12]. Given the demonstrated sensitivity of this spectroscopic–mechanical technique, it is then possible directly to assess the changing stress distribution in the reinforcement fibre as a function of temperature. However, few studies are available to demonstrate the effects of altering these parameters.

The frequency of the $C \equiv C$ stretching vibrational mode for the fibre alone increases by $6\,cm^{-1}$ when the temperature is varied from 20°C to -130°C. This change may be interpreted as being simply due to increasing perfection in the intermolecular interactions. However, when the same fibre is incorporated in the polymer matrix, this change in position of the vibrational frequency shown in *Figures 4* and *5* is much more significant than that for the fibre alone. As can be seen in these Figures, when this fibre is embedded in the epoxy matrix, there are additional changes in band position as a function of temperature. When the temperature is lowered from 20°C to -130°C, the triple bond frequency increases by $\sim 13\,cm^{-1}$; $7\,cm^{-1}$ greater than the increase for the fibre alone. This additional increase in frequency is presumably due to the stress caused by the differences in the thermal expansion coefficient between the fibre and matrix. The associated problem of residual thermal stress is also quite complicated for the composites made with high modulus and strength fibres because of this difference in thermal expansion coefficients.

In order completely to analyse the thermally induced stresses, e.g. type and magnitude, it is important to know both the geometry of the composites and the mechanical and thermal properties of their constituents—fibre and matrix. The theoretical thermoelastic analysis of residual stresses in the unidirectional composites with anisotropic fibres has been carried out[12]. But in general, a complete description of the mechanical and thermal properties of these very small and highly anisotropic fibres used as reinforcements are not available. Therefore, our interpretation of the data obtained is done under various assumptions to estimate the relative magnitude of the thermal stresses that develop in this poly-HDU/epoxy model composite during the temperature change from 20°C to -130°C.

Figure 3 Frequency variation of the C≡C stretching vibration along the fibre for two matrix strain values; (○) 1.0% matrix strain; (●) 2.5% matrix strain; 5145 Å excitation; bandpass = 1.3 cm⁻¹ at 5100 Å

a

−130°C

−68°C

−34°C

0°C

22°C

2050 2070 2090 2110 2130 2150
Wavenumbers (cm⁻¹)

b

−130°C

−68°C

−34°C

0°C

22°C

2050 2070 2090 2110 2130 2150
Wavenumbers (cm⁻¹)

c

(%)
Strain   v⁻¹
−0.820 2118
        2116
−0.620 2114
        2112
−0.420 2110
        2108
−0.220 2106
        2104
−0.020 2102
        2100
0.180   2098
        2096
        2094
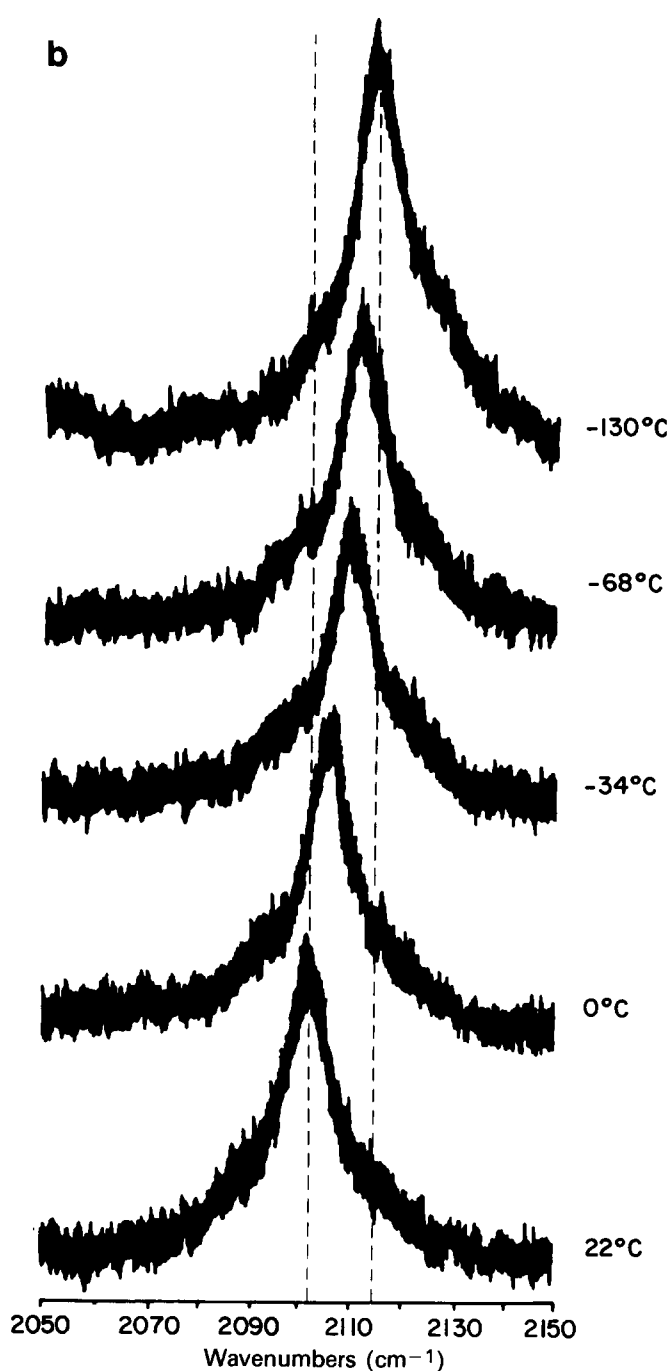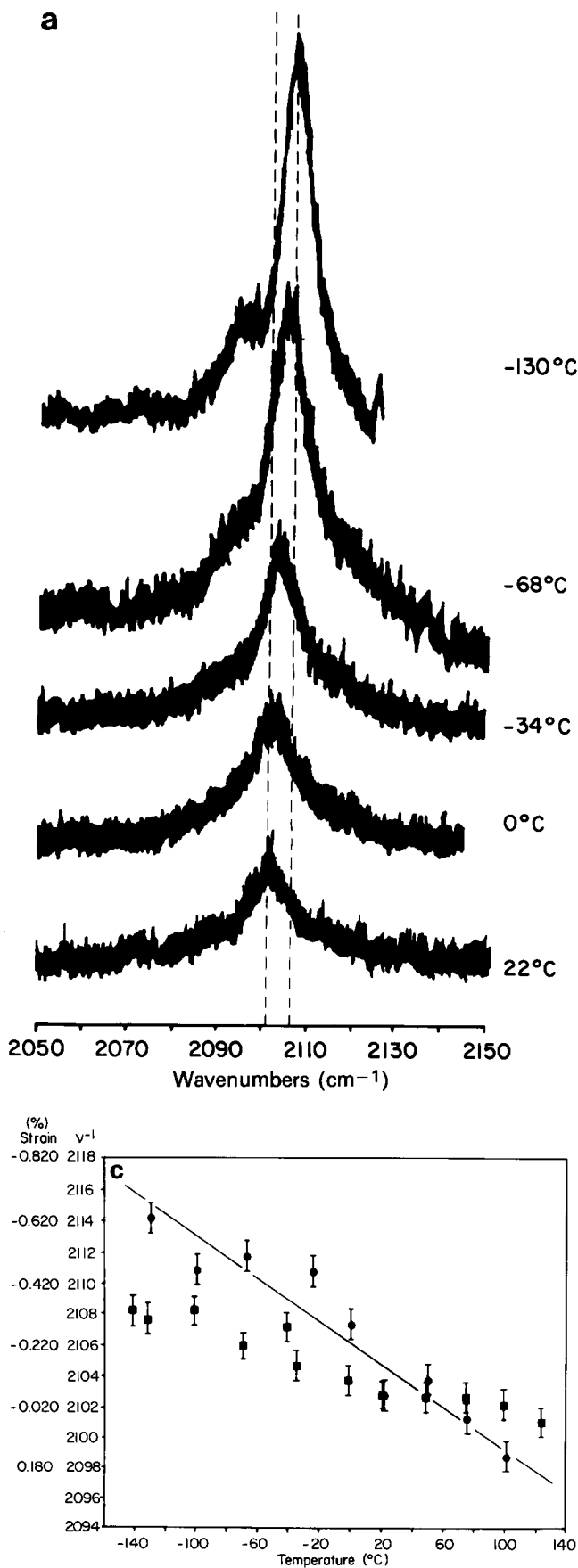   −140 −100 −60 −20 20 60 100 140
              Temperature (°C)

Figure 4   Temperature dependence of the Raman spectra in the triple bond stretching region of poly-HDU; (a) poly-HDU fibre alone, (b) poly-HDU fibre embedded in 60% EPON 825 and 40% DER by weight, cured with DTA at room temperature; (c) plot of the frequency variation observed, (■) for the fibre alone and (●) for poly-HDU embedded in the epoxy matrix

Generally speaking[12], for high performance fibres such as graphite or Kevlar with negative thermal expansion coefficient in the chain direction, the longitudinal thermal stresses in the matrix will be tensile whereas they will be compressive in the fibre as temperature decreases. Radial
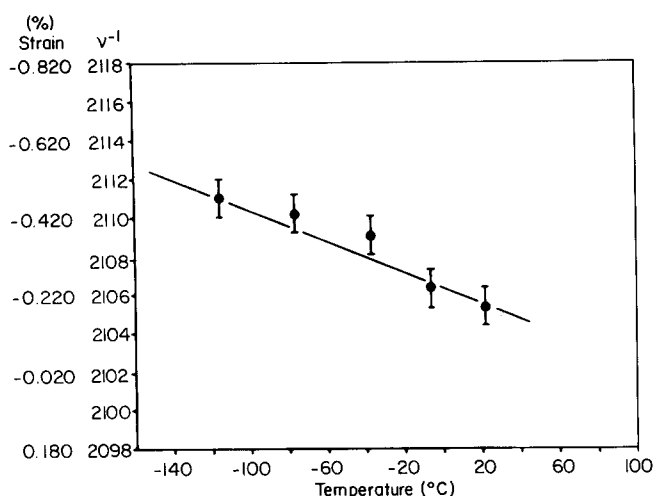
stresses will be compressive in both the fibre and the matrix as temperature decreases, providing that their radial thermal expansion coefficients are both positive. The magnitude of these thermal stresses are strongly dependent on the fibre volume fraction, V_f, in particular at low V_f, because the relative contribution of the fibre to the overall composite modulus increases rapidly at low V_f.

Using Nairn's analysis[12], the upper limit for longitudinal thermal stresses in the matrix is $\Delta\alpha E_m/(1 - v_m)$ and the lower limit is $\Delta\alpha E_m F$, where $F = \dfrac{E_L V_f}{E_m V_m + E_L V_f}$. v_m is the

(%)
Strain v^{-1}

Figure 5 Plot of the triple bond frequency vs. temperature for poly-HDU fibre embedded in the epoxy matrix. The sample is identical to *Figure 4(b)* but post-cured at 120°C for one hour

Poisson's ratio for the matrix, $\Delta\alpha = \alpha_m - \alpha_L$ (the difference in the longitudinal thermal expansion coefficient), V_m is the volume fraction of the matrix, and E_L and E_m are the Young's moduli associated with the fibre and matrix respectively. The upper limit for longitudinal thermal stresses in the matrix is the longitudinal stress expected for a thin matrix shell around an isotropic rigid rod and the lower limit for longitudinal thermal stresses in the matrix is the longitudinal stress expected for one-dimensionally constrained thermal shrinkage[12]. This applies when there is no thermal shrinkage in the transverse direction and the matrix is constrained longitudinally by a rod with modulus E_L.

Using these assumptions the longitudinal stress in the fibre is related to that in the matrix as follows:

$$\sigma_f = \left(1 - \frac{1}{V_f}\right)\sigma_m$$

For the temperature range from 20°C to -130°C change in the fractional length in the longitudinal direction is estimated to be 18×10^{-4} (using Figure 4 of ref. 9) and the average thermal expansion coefficient in this temperature range is then to be approximately $-1.20 \times 10^{-5}\,\text{K}^{-1}$.

Since the tensile modulus of poly-HDU is approximately 45 GPa[13]; and the tensile modulus of this epoxy (60% EPON 825 + 40% DER 736 by weight cured with DTA at 60°C) is 0.42 GPa, then using $v_m = 0.34$, $\alpha_m = 4 \times 10^{-5}$ and $V_f = 0.001$, the changes in the stretching frequency expected for upper and lower limits are listed in *Table 1*. The lower limit of the frequency change due to the thermal stress is greater than the observed $7\,\text{cm}^{-1}$, but the two values are of the same order of magnitude. At very low volume fraction of fibres, the difference in the lower limit of the longitudinal thermal stress and the observed value should be very small since the matrix property dominates the thermal stresses as shown in Figure 3 of ref. 12.

It is extremely interesting to note that the stress on the polydiacetylene fibre, represented by the frequency of the polydiacetylene backbone, can be altered by the curing history. We found the C≡C stretching vibration can be increased by an additional $3\,\text{cm}^{-1}$ for the samples postcured at 120°C as compared to the samples cured at room temperature. This difference shown in *Figures 4* and

5 indicates that additional residual thermal stress buildup associated with the fibre exists. We also found that the change as a function of temperature is much less for this postcured sample, as shown in *Figure 5*. A straight line fit of the two sets of data showed that the slope changes from $-4.6\,\text{cm}^{-1}/100$°C for samples postcured at 120°C to $-6.6\,\text{cm}^{-1}/100$°C for samples that were not postcured. This difference is probably due to changes in the epoxy properties such as glass transition temperature and thermal expansion coefficients associated with the curing procedure[14]. At present, although no satisfactory explanation is available to explain this difference, the utility of this spectroscopic–mechanical technique in detecting sample differences is beyond doubt.

We have shown earlier that when the polydiacetylene fibre is under tensile stress, the backbone vibrations such as the C≡C or C=C stretching modes decrease significantly. However, the converse may not be true, i.e. the increase in the frequency need not directly reflect the contraction along the fibre direction. Similar movements in the positions of the C=C or C≡C stretching vibrations with decreasing temperature have been reported[15]. The polydiacetylene fibre used in that study has a positive thermal expansion coefficient[16]. Therefore, it was not surprising to observe the increasing frequency when the chain repeat shortens at low temperatures. However, the fibre used in the present study has a negative thermal expansion coefficient[9], making the increasing frequency at low temperatures more difficult to explain. Using the expansion coefficient measured earlier, we would expect a total increase of approximately $9\,\text{cm}^{-1}$ in the triple bond frequency going from -140°C to 100°C. Instead, we observed an increase in frequency when the temperature was lowered. This unexpected frequency/temperature relationship demonstrates that the longitudinal stress cannot be the only factor in perturbing the frequency of the polymer backbone vibrations. The effects in the changes in the intermolecular interaction cannot be ignored. A clean separation between these two contributing factors will be difficult to carry out.

It is then extremely interesting to speculate whether the frequency change is due to an effective reduction in the fibre length due to longitudinal compressive stress in a composite, thus raising the frequency, or due to much tighter packing arising from the effective radial stress of epoxy 'squeezing' on the fibre, which would enhance the intermolecular interactions in addition to the temperature effects. Without the Poisson ratio of the fibre, it would be difficult to explain quantitatively the changes observed. Nevertheless, the hypothesis that changes in intermolecular interaction cannot be ignored is supported by two previous observations. It has been found that perfection or delocalization of the electrons along the backbone can depend on the perfection of the chain packing[17]. In addition, the Raman spectra can be

Table 1 Changes in stretching frequency expected for upper and lower limits

	Upper limit	Lower limit
	$\sigma_{Zf} = \left(\dfrac{\Delta\alpha E_m}{1 - v_m}\right)\left(1 - \dfrac{1}{V_f}\right)$	$\sigma_{Zf} = \Delta\alpha E_m \dfrac{V_f E_L}{E_m V_m + E_L V_f}\left(1 - \dfrac{1}{V_f}\right)$
σ_{Zf}:	-4.72 GPa	-0.32 GPa
ε_{Zf}:	-0.105	-0.007
Δv_m:	$210\,\text{cm}^{-1}$	$14\,\text{cm}^{-1}$

altered by hydrostatic pressure[15]. Therefore, the vibrational frequencies measured for polydiacetylene as a function of temperature may not entirely represent the effects induced by external stress.

ACKNOWLEDGEMENT

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