Molecular stress distribution and creep of high-modulus polyethylene fibres*

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Raman spectroscopy has been used to measure the molecular stress distribution in high-modulus, high-strength polyethylene fibres (Allied Spectra 1000 and Spectra 900) at low temperature and as a function of time during creep at room temperature. Increase in band width or change of band shape is interpreted as due to a distribution of stress or strain in molecules in the all-*trans* configuration. Fibres loaded at 77 K show two peaks in the stress distribution, as was found by van Eijk *et al.* at 240 K. About one-sixth of the all-*trans* molecules in a Spectra 1000 fibre as produced carry little load. The rest carry from half to twice the mean load. Spectra 1000 fibres loaded at over 1 GPa for a few minutes at room temperature show two well defined peaks in each of the C–C stretching Raman bands at 1064 and 1130 cm^{-1} and thus a sharp bimodal distribution of stress. At long creep times, the higher stress peak increases in width while keeping the same area. Eventually, the stress distribution has a single peak with a broad tail on the high-stress side. This result unifies the previous two observations, one of which found only a single asymmetric peak and the other only two peaks in the stress distribution. As the tail broadens, the number of very highly strained molecules increases, and a significant number reach strains of 10%. It is not surprising that this leads to fracture of the fibre. After loading for less than a minute at room temperature or for a few minutes at 273 K, there is only a single peak in the stress distribution. The fibre structure is thus undergoing complex changes during creep, and the stress distribution seen at room temperature is not simply related to the original structure.

(Keywords: polyethylene; fibres; high modulus; stress distribution; creep; Raman spectroscopy)

INTRODUCTION

Ultra-high-molecular-weight polyethylene (PE) can be formed into fibres by the process of gel drawing or spinning[1–3]. These fibres have not only a very high Young's modulus of 100–200 GPa but also a very high tensile strength of 2–5 GPa[4,5]. As the density of PE is about 1 g cm^{-3} the mechanical properties are truly exceptional when expressed as a specific modulus or specific strength. For this reason such fibres are now commercially available from a number of sources. The values for fibre modulus and strength are quite close to the theoretical modulus of a PE crystal along the chain direction $E_c = 300$ GPa (refs. 6–8) and the theoretical strength of a molecule, ~35 GPa (refs. 7, 9, 10). The molecules in the fibres are well aligned along the fibre axis and largely extended. Many models exist for the fine structure of the fibres, but it is not clear what mechanisms or defects still keep the properties below their theoretical limits.

An important limitation to the use of these fibres is the creep or stress relaxation that occurs at or above room temperature. It is associated with the crystalline α-relaxation in polyethylene and it means that the high stiffness and strength obtained by impact or rapid testing of the fibres cannot be maintained on static loading[11]. Modifications have been made to the fibre structure, for example by irradiation in an atmosphere of acetylene[12], specifically to try to reduce the creep of the fibres.

I.r. or Raman spectroscopy can be used to study the effects of stress since elastic deformation alters the vibrational modes of a solid[13,14]; Raman spectroscopy is experimentally easier for small fibre samples. In most materials a large elastic extension before yield or fracture is needed as the effect of deformation on the spectrum is small. For polymers, aligned samples are used so that the stress applied to the sample can be related simply to the stress on the molecules. The very high alignment of molecular chains along the fibre axis in high-modulus fibres makes this interpretation straightforward for these materials. Many i.r. and Raman studies have been made on the deformation of oriented polymers[8,15–22]; they show that in tensile stress fields Raman bands usually shift to lower wavenumbers. The amount of shift depends on the sample as a macroscopic applied stress or strain is being compared to a molecular deformation.

The shape of bands under stress has been studied in polypropylene[16,23,24], poly(ethylene terephthalate)[25], polyoxymethylene[26] and polyethylene[8,26–30]. The bands generally increase in width and may become asymmetric or form a doublet; these changes are interpreted as due to a distribution of stress in the samples. The asymmetric bands generally have a long tail extending to lower

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frequencies, corresponding to higher tensile stresses. In polypropylene, poly(ethylene terephthalate) and some PE samples[8,27] an asymmetric tail was assigned to a small fraction of the molecules in the samples being stressed to much higher than average values.

The PE samples were all highly oriented and extended high-modulus fibres or tapes. Wool and Bretzlaff[8] used specimens extruded in the solid state that had high modulus but relatively low strength[31,32]. They were able to use them at stresses up to 0.4 GPa. Asymmetry and broadening of the band shape were seen at higher stresses, and were recognized as being due to non-uniform stresses on the chains. Tashiro *et al.*[26] used drawn gel PE fibres of draw ratio 100 and applied stresses up to 1.2 GPa. The shift of the 1064 cm^{-1} band was -6.0 $(\text{cm GPa})^{-1}$ and of the 1130 cm^{-1} band, -4.5 $(\text{cm GPa})^{-1}$. These authors used a series–parallel Takayanagi model for the fibre structure, as used to interpret X-ray diffraction from stressed PE[33]. They predicted that the bands should split into two peaks under stress because of the two regions in the model under different stresses. The predicted area of the high-stress peak was very small, and no asymmetry was seen.

Using stronger samples, commercial and experimental high-modulus PE fibres from Allied Corp., Prasad and Grubb[27] were able to observe the C–C stretch bands at stresses up to 2.3 GPa. For Spectra 1000 fibres they found smaller shifts, of -4 ± 0.5 $(\text{cm GPa})^{-1}$ for the peak position of the 1064 cm^{-1} band up to 1.2 GPa and -2.5 $(\text{cm GPa})^{-1}$ for the 1130 cm^{-1} band. At higher stresses a long tail extending to lower wavenumbers appeared, and the main peaks stopped moving. Measuring the mean wavenumber of the whole 1064 cm^{-1} band, they found that this continued to move linearly with stress to lower wavenumbers as the tail extended.

As wide angle X-ray diffraction from a similar fibre showed no asymmetry of the (0 0 2) reflection under high stress[34], the highly stressed molecules were identified as taut tie molecules. At high stresses, the stress on this component increased while the fibre load increased but the stress on the crystalline majority did not change. Any structural model where the two components are mechanically in series, as they would be if the tie molecules linked crystal blocks within a fibril, has great difficulty explaining this fact. Therefore the highly stressed disordered material was assigned to interfibrillar regions[27].

Recently Kip and coworkers have studied the 1064 and 1130 cm^{-1} bands in stretched experimental high-modulus fibres from DSM[28–30]. At room temperature and fibre strains of over 1.5% they found that each of the C–C stretch bands split into two peaks. The peak at lower wavenumbers was broad and contained 40% of the area in the band. Above 2.5% strain the higher-wavenumber (lower-stress) peak did not change its position when the strain was increased. Stress relaxation in these fibres was studied by Van Eijk *et al.*[29], who found that the two peaks in the 1130 cm^{-1} band remained in the same position as the stress relaxed. The fraction of highly strained molecules, however, decreased with time at the same rate as the stress. On cooling the fibre to 240 K to reduce (but not remove) the effects of relaxation, they again saw two peaks, with 85% of the molecules highly stressed in a fibre of modulus 196 GPa. At 240 K, both of the peaks in the 1064 cm^{-1} band shifted linearly with fibre strain up to the maximum applied, 4% (ref. 30). The shift factors were -7.4 and -1.8 cm^{-1}/(% fibre strain), in a ratio of 4:1.

Since the experiments described here are stress-controlled, the motion of the Raman bands is given in terms of a shift factor in units of $(\text{cm GPa})^{-1}$. As described above, other authors have used strain control and reported a shift in units of cm^{-1}/(% fibre strain). The fibre strain is not known in these experiments, as the gauge length is poorly defined, but the molecular strain can be estimated from previous wide-angle X-ray diffraction experiments. A crystal strain of 0.49% was found at high stresses in a Spectra 1000 fibre[34] under conditions that gave a shift of -4.5 cm^{-1} in the 1064 cm^{-1} asymmetric stretch band[27]. This band therefore shifts at about -9 cm^{-1} for each 1% of molecular strain. Recently Moonen *et al.*[35] have found a value of -8.7 cm^{-1} for each 1% of molecular strain at 240 K in the symmetric stretch band at 1130 cm^{-1}.

EXPERIMENTAL

Materials

The samples used were two commercial polyethylene fibres (Spectra 1000® and Spectra 900®) obtained from Allied Corporation. To avoid possible confusion with the word 'spectra' in its normal sense of more than one spectrum, these fibre names will be abbreviated to S1000 and S900 from this point on. The manufacturer describes these fibres as having strengths of 3.1 and 2.7 GPa, respectively, and tensile moduli of 180 and 127 GPa at 0.02 s^{-1}. Relaxation at room temperature has a significant effect on the measured modulus, and measurement at a strain rate of 0.003 s^{-1}, strain 0.01, gave moduli of 72 and 45 GPa respectively[27]. The degree of crystallinity was about 0.85 as measured by differential scanning calorimetry; for S1000 fibres the mean misorientation of the crystals in a fibre is only 1.6° (ref. 34).

Spectroscopy

Raman spectra were obtained using a SPEX 1877 Triplemate spectrometer, equipped with a 1800 grooves/mm holographic grating. A 2 W Ar^+ laser (Coherent Nova 90-5) at 514.5 nm was the source and a tunable excitation filter was used to reject spurious lines and background. The laser beam was focused using a Leitz microscope with a 10× objective to a spot ~10 μm in diameter, where the power was about 75 mW. A field stop was used to restrict the area of collection and reduce glare. Scattered light was collected at 180° to the direction of the incident radiation with the same lens. The detection system was a diode array covering 870 cm^{-1}, an EG&G optical multichannel analyser and an IBM XT personal computer. The detection time was normally 180 s, but noisy spectra could be obtained in 30 s.

Spectra were obtained from 800 to 1600 cm^{-1}, a region that contains six strong bands due to all-*trans* PE molecules. These are 1064, 1130, 1295, 1418, 1440 and 1463 cm^{-1} and are assigned to asymmetric C–C stretch, symmetric C–C stretch, CH_2 twisting and the last three to CH_2 bending respectively[36]. For most of the time attention was concentrated on the two stetching modes and particularly on the 1064 cm^{-1} band, which shows the largest effects when stress is applied. When the bands have spread at high stresses, there may be significant overlap between the 1064 and 1130 cm^{-1} bands, so that curve fitting must consider both of them.

Fibre loading

A small strain frame designed to fit on the microscope stage of the Raman equipment and previously used in strain-controlled experiments[27] was modified for use in dead-loaded creep. A single filament is gripped in a capstan insert[37]; it runs horizontally and then passes over a freely rotating smooth glass rod to a second grip. Weights of 2–250 g are hung on the second grip and Raman spectra are obtained from the stressed fibre.

For operation at reduced temperature, the glass rod is raised a few millimetres so that the filament is a few degrees off the horizontal and the frame placed in a coolant bath. The filament passes over the edge of the bath and spectra are taken from a point just above the coolant surface. A plastic bag surrounding the coolant and the objective lens of the microscope prevents condensation from affecting the optics. A slit on the plastic lets the fibre pass through, so that the weights are attached outside the enclosure. This simple arrangement is possible for stress-controlled experiments, where it is not necessary to have all of the fibre at the controlled temperature.

Here '273 K' and '77 K' will be used to describe results obtained with ice/water and liquid nitrogen as coolants, but no attempt was made to measure the fibre temperature accurately. Heating of a few kelvins is to be expected from interaction with the laser beam.

RESULTS AND DISCUSSION

Raman spectra at low stresses

Raman band positions and widths depend on temperature as well as on stress, so it is important to define the spectra obtained at low fibre stresses very carefully. Spectra were obtained at room temperature and in liquid nitrogen from adjacent sections of the same single fibre. The fibres dead-loaded at room temperature show the same effects as previously observed when fixed strain increments were applied to fibres in a staircase manner[27]. The 1064 and 1130 cm^{-1} bands shift linearly to lower wavenumbers as stress increases up to some level, after which a tail appears at the lower wavenumber side and the main peak stops shifting. For S1000 fibres the tail appears at 1.2 GPa and for the 1064 cm^{-1} band the linear shift factor at lower stresses is -4.9 ± 0.3 (cm GPa)$^{-1}$. This is slightly higher than the value previously reported for this material, -4 ± 0.5 (cm GPa)$^{-1}$ (ref. 27). The same maximum stress for linear shift was seen in other bands. Their shift factors and zero-stress peak positions and widths are given in *Table 1*. The accuracy of peak positions is ± 0.3 cm^{-1}.

Table 1 also gives the values obtained at 77 K. Since the fibre has a negative thermal expansion coefficient along its axis, one might expect that cooling and tension would have the same effects at the same strain. The expansion on cooling is 0.2%, so the C–C stretch bands might be expected to shift by 1–2 cm^{-1} to lower wavenumber. Instead the 1064 cm^{-1} asymmetric stretch band moves 1 cm^{-1} and the 1130 cm^{-1} symmetric stretch band 3 cm^{-1}, both to *higher* wavenumber. This must be due to intermolecular interaction, as suggested by Kim *et al.* when similar effects were seen for triple-bond stretching in polydiacetylene crystals[22].

Fibres stressed at 77 K

When S1000 fibres are loaded at 77 K the two C–C stretching bands shift approximately linearly and broaden with stress up to about 1.2 GPa. Above this stress a second peak appears on the high-wavenumber (low-stress) side of each band. *Figure 1* shows this effect in the 1064 cm^{-1} band. Raman spectra in the range 1030–1080 cm^{-1} have had a cubic background subtracted

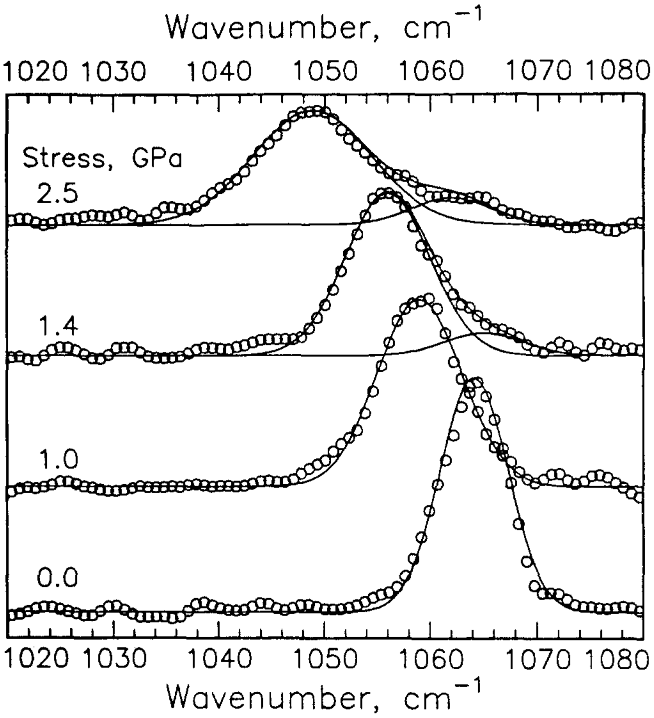

Figure 1 The 1064 cm^{-1} band of the Raman spectrum of an S1000 fibre loaded at liquid-nitrogen temperature: (○) data, (——) fitted Gaussians

Table 1 Peak position, width and shift factors for S1000 fibre loaded at room temperature and in liquid nitrogen. The accuracy of peak position is ± 0.3 cm^{-1} and the accuracy of shift factor is ± 0.3 (cm GPa)$^{-1}$

	Peak oposition (cm^{-1})		Peak width, FWHM (cm^{-1})		Shift factor (cm GPa)$^{-1}$	
	298 K	77 K	298 K	77 K	298 K	77 K
C–C asymmetric stretch (B_{1g})	1063.7	1064.8	7.6	6.8	−4.9	−5.4
C–C symmetric stretch (A_g)	1130.5	1133.5	6.2	4.2	−3.4	−3.9
C–H twisting (B_{1g})	1293.3	1292.2	4.8	4.6	−1.1	−1.3
C–H bending (A_g)	1417.1	1413.2	6.7	4.4	−1.7	−1.4

and have been shifted vertically for clarity. The spectra were fitted with two Gaussian curves and thus six free variables. The computer, like the eye, can fit the data very well with only one Gaussian up to a stress of 1.2 GPa. The full curves in *Figure 1* are the best-fit Gaussian curves and their sum if there are two. The peak positions of the computer fit for this data set are shown in *Figure 2*. When there is only one peak, in the range 0–1.2 GPa, the peak position shifts at $-5.4\ (\mathrm{cm\ GPa})^{-1}$. Above this stress the main peak shifts at an increased rate, $-6.8\ (\mathrm{cm\ GPa})^{-1}$. The small low-stress peak is at approximately $1065\ \mathrm{cm}^{-1}$, and for this trial the best-fit line for this peak has a slope of about $-3\ (\mathrm{cm\ GPa})^{-1}$.

The fitted peak widths are shown in *Figure 3*; the major peak width follows a smooth increase with stress from 8 to $14\ \mathrm{cm}^{-1}$. The line through the widths of the main peak is the best fit of the form FWHM $= [a^2 + (b\sigma)^2]^{1/2}$. The choice of this function is based on the assumption that the peak width is the sum of a natural fixed width and a width proportional to the applied stress. As the major peak is accurately fitted by a Gaussian at all stresses, it is assumed that both the natural zero stress width and the stress distribution are Gaussian. The convolution of two Gaussians of width a and c is another with width $(a^2 + c^2)^{1/2}$.

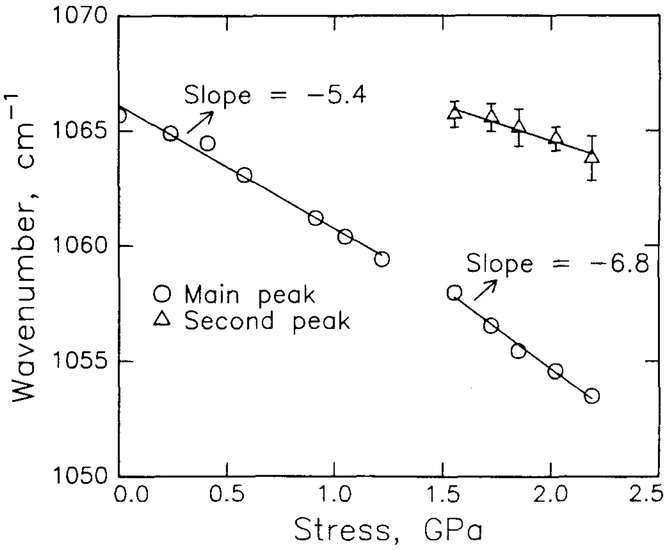

Figure 2 Fitted peak positions of the $1064\ \mathrm{cm}^{-1}$ band of the Raman spectrum of an S1000 fibre loaded at liquid-nitrogen temperature

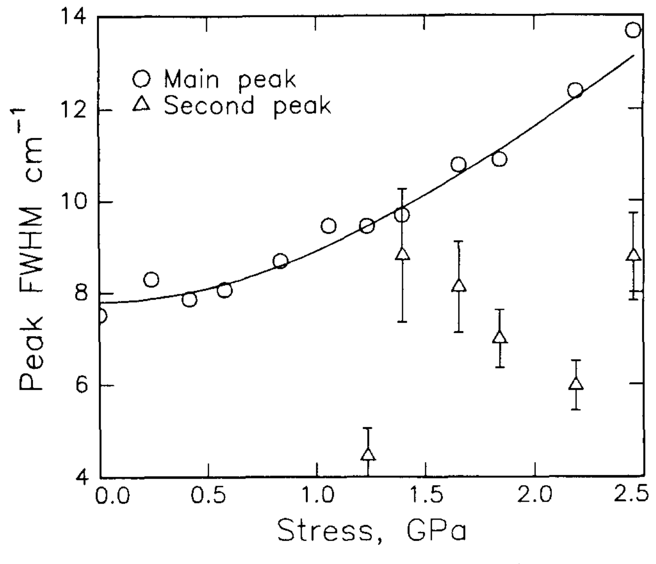

Figure 3 Fitted widths (FWHM) of the $1064\ \mathrm{cm}^{-1}$ band of the Raman spectrum of an S1000 fibre loaded at liquid-nitrogen temperature

The best fit that is drawn through the data in *Figure 3* using this equation has $a = 7.8\ \mathrm{cm}^{-1}$ and $b = 4.3\ (\mathrm{cm\ GPa})^{-1}$. As the position of the peak shifts by $-6.8\ (\mathrm{cm\ GPa})^{-1}$ at higher stresses, as shown in *Figure 2*, the FWHM of the stress distribution is about two-thirds of the mean stress. In this distribution, chains have from about zero strain up to twice the mean strain. The X-ray (0 0 2) linewidth of a single S1000 fibre as a function of stress at room temperature gave a FWHM of the stress distribution approximately equal to the mean stress[34].

The fitted width of the small low-stress peak has a larger scatter, indicating inaccurate fitting. The FWHM is approximately constant and near the FWHM of the main peak at zero stress, in the region of $6–9\ \mathrm{cm}^{-1}$. Its area is also constant at 10–15% of the major peak area. The second peak can be clearly seen only at stresses about 1.5 GPa, and the maximum stress that will not break the fibre is about 2.5 GPa. The shift factor for the motion of the small peak with stress is very unreliable because of the narrow range of stresses available. Averaging many results between 1.5 and 2.5 GPa, the shift factor is $-1.3 \pm 0.5\ (\mathrm{cm\ GPa})^{-1}$.

The $1130\ \mathrm{cm}^{-1}$ band can also be fitted to two Gaussians, with very similar results. The position of the smaller peak in this case appears to be almost constant. These results are very similar to those found for experimental Dyneema fibres at 240 K[29,30,35] where two peaks are resolved at strains of over 1%. For a fibre of modulus 149 GPa the low-stress peak of the $1130\ \mathrm{cm}^{-1}$ band has been fitted as at a constant shift of $4\ \mathrm{cm}^{-1}$ (ref. 35) and that of the $1064\ \mathrm{cm}^{-1}$ band as having a constant shift factor of $1.5\ \mathrm{cm}^{-1}/(\%\ \text{fibre strain})$[30].

As the low-stress peak in high-modulus fibres loaded at low temperature seems to be at near zero stress whatever the load applied to the fibre, it could possibly relate to breaking chains or other irreversible processes. An S1000 fibre was cycled between 0 and 2 GPa and another S1000 fibre between 1.4 and 2.5 GPa where the two peaks are always separable. In both cases the Raman effects of stress remained the same after several cycles.

The two peaks in each of the Raman bands in S1000 fibres under stress do not seem to be associated with any irreversible process, and relaxation is completely suppressed at 77 K. We therefore expect that the bimodal stress distribution that produces these peaks is caused by the inhomogeneous structure originally present in the fibre, and exists at all stresses. The bands appear as a single peak at low stresses because the separation of the two peaks is too small to be resolved. This interpretation requires a low shift factor such as $1–1.5\ (\mathrm{cm\ GPa})^{-1}$ for the low-stress peak. An extrapolation of both the peak positions back to zero stress then gives a value close to the observed position of the whole band at zero stress.

To see if this interpretation fits the data, the band shape was simulated at all stresses using the data obtained at stresses over 1.5 GPa where the two peaks can be separated. The data used are shown in *Table 2*, where the stress σ is in GPa. *Figure 4* shows the data and the Gaussian curves created to fit them. The errors in this simulation of the band shape are much smaller than the

Table 2 Parameters used to fit 1064 cm^{-1} band shape at 77 K as two Gaussians at all stresses

	Peak position (cm^{-1})	Peak width (cm^{-1})	Peak area
S1000			
Peak 1	$1065 - 6.8\sigma$	$[7.8^2 + (4.3\sigma)^2]^{1/2}$	1
Peak 2	$1065 - 1.3\sigma$	7.5	0.15
S900			
Peak 1	$1065 - 6.5\sigma$	$[7.5^2 + (6\sigma)^2]^{1/2}$	1
Peak 2	$1065 - 2.5\sigma$	$[7.5^2 + (3\sigma)^2]^{1/2}$	0.25

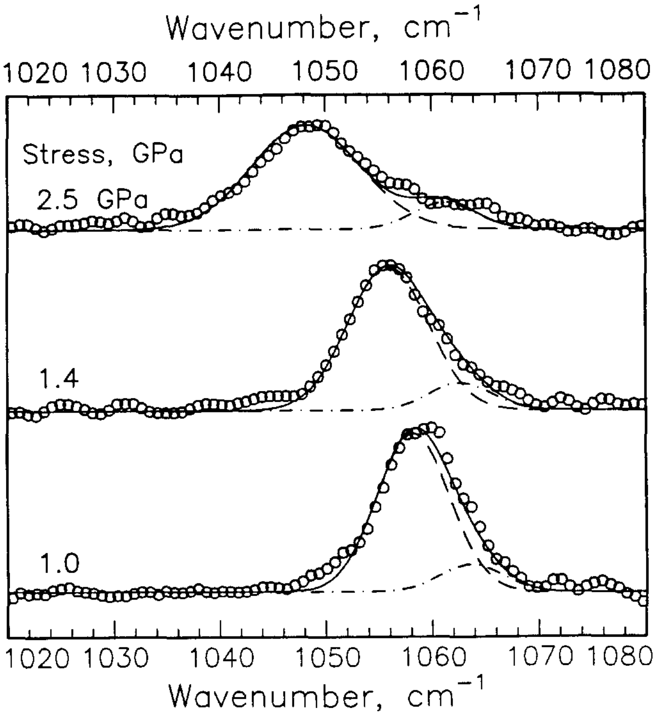

Figure 4 The 1064 cm^{-1} band of the Raman spectrum of an S1000 fibre loaded at liquid-nitrogen temperature: (○) data, (——) simulation using two Gaussian curves at all stress levels

size of the symbols in the figure. The excellent fit supports the idea that there are two components to the fibre, and the mean stress of each component and the width of the stress distribution increase linearly with applied fibre stress.

Initially spectra obtained from S900 under load at 77 K seemed to be out of line with the results presented for S1000 and for DSM fibres at 240 K[29]. The data were best fitted by a single peak at all stress levels for the 1064 cm^{-1} band and for the 1130 cm^{-1} band. However, after repeating the measurement with particular care to reduce noise, the 1064 cm^{-1} band could be seen to be not completely symmetric at stresses of 1.9 GPa and above. *Figure 5* shows these accurate data as circles, with the best fit using a single symmetrical peak drawn as a full curve. From such a fit, the shift factor for the 1064 cm^{-1} band was found to be -5.6 $(cm\ GPa)^{-1}$ and the width increased rapidly to 16 cm^{-1} at 1.8 GPa. Both parameters are shown in *Figure 6*. The deviations from symmetry are too small to make any fit using two peaks from the data.

Because the simulation using two Gaussian peaks worked so well for S1000 fibres, the same procedure was used on the S900 data. It was assumed that the peaks are Gaussian and have the same form of increase in width with stress. A very reasonable fit to the observations at all stress levels was then obtained by trial and error. *Figure 7* shows the data and the Gaussian curves used to fit them. As the peaks are never well separated, there is no check that the form of the fit is correct and the fitting parameters obtained, which are shown in *Table 2*, are not very reliable. Whatever the curve shape, the fraction of the low-stress peak is greater than it is in S1000 fibres; the fit gives 25%.

Fibre structure

The data in *Table 2* allow us to describe the molecular stress distribution in the fibres in terms of the mean stress on the all-*trans* molecules. These molecules will all have the same shift in vibrational frequency for a given

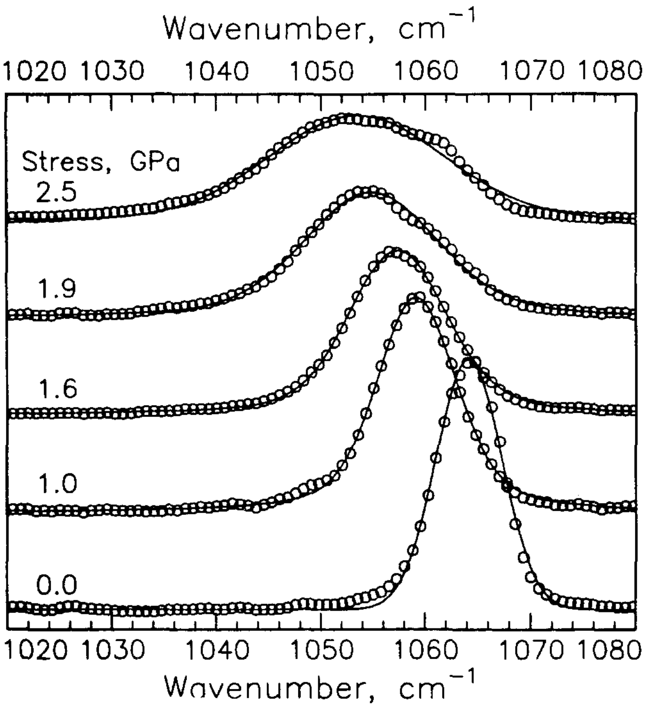

Figure 5 The 1064 cm^{-1} band of the Raman spectrum of an S900 fibre loaded at liquid-nitrogen temperature: (○) data, (——) fitted Gaussians

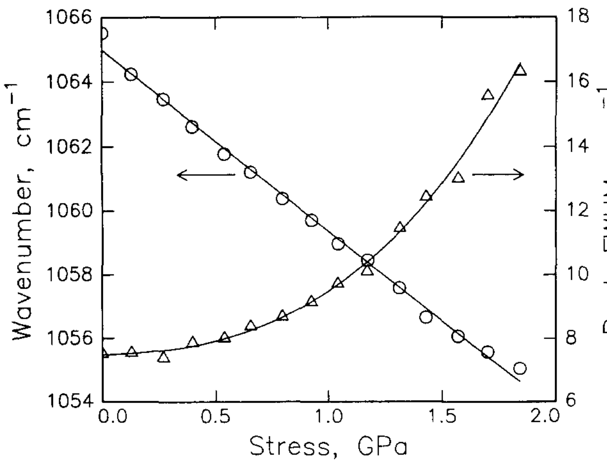

Figure 6 Fitted positions and widths (FWHM) of 1064 cm^{-1} band of the Raman spectrum of an S900 fibre loaded at liquid-nitrogen temperature

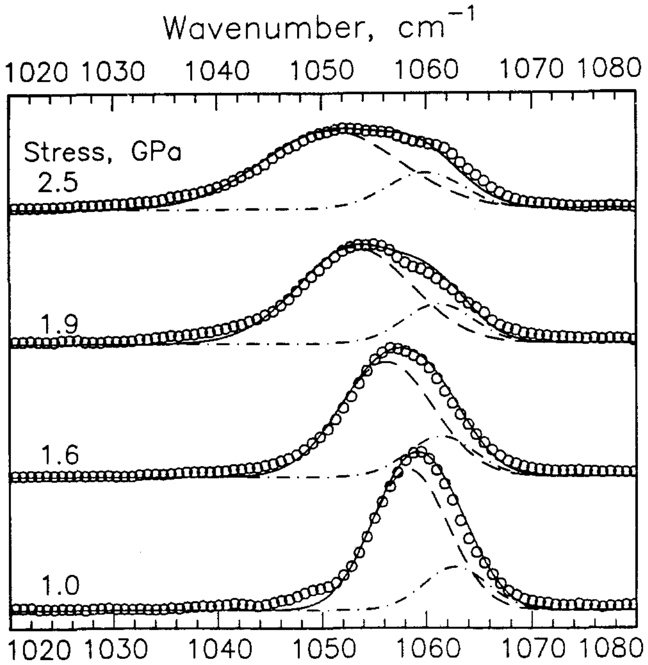

Figure 7 The 1064 cm^{-1} band of the Raman spectrum of an S900 fibre loaded at liquid-nitrogen temperature: (○) data, (——) simulation using two Gaussian curves at all stress levels

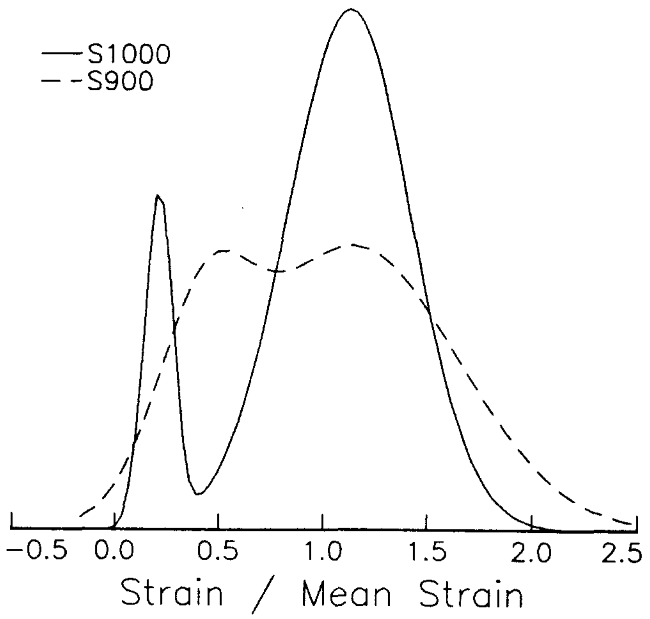

Figure 8 Calculated molecular stress distribution of S1000 and S900 fibres with no relaxation, as at liquid-nitrogen temperature

molecular load or strain, so a ratio between two shifts is a ratio between the two molecular stresses. For S1000 fibres the mean shift of the whole band is −6.1 (cm GPa)$^{-1}$ and the most probable shifts in the two peaks are 1.1 and 0.2 of this mean. The FWHM of the major peak is 0.7 of this mean shift. The width of the minor peak is given as a constant, so apparently there is no stress distribution in this peak. A narrow stress distribution cannot be detected; for example, a FWHM factor of 1.3 (cm GPa)$^{-1}$ would increase the peak width from 7.5 cm^{-1} to only $(7.5^2 + 3.2^2)^{1/2} = 8.2$ cm^{-1} at a stress of 2 GPa. *Figure 8* shows the stress distribution calculated on this basis, using 1.5 (cm GPa)$^{-1}$ for the width of the minor peak in S1000 fibres, and the tabulated values for S900. As these results come from dead-loaded fibres at 77 K, they relate to the original fibre structure.

The sharp bimodal distribution in S1000 fibres is straightforward to model as a series–parallel arrangement of crystals and disordered material. In structural terms it is tempting to refer back to the solution-grown fibrous crystal that began the discovery of gel drawing. These have two distinct populations of crystals, one fibrous and load-bearing, the other lamellar. The lamellae are under low stress because they are mechanically in series with disordered compliant material. Small-angle X-ray scattering (SAXS) shows a declining intensity in the meridional two-spot pattern that indicates lamellar structures as the stiffness of fibres increases[4]. None is visible in high-modulus fibres such as S1000, but SAXS peaks require a regular periodic arrangement of the lamellae, and it is possible for a fraction of the material to exist in this form without sufficient regularity. The degree of regularity would depend on the processing conditions.

The stress distribution calculated for S900 immediately shows why the data are always very close to a single peak, and it is clear that other fits are possible for this material, for example reversing the relative intensities of the two peaks.

Creep at room temperature

Figure 9 shows the effect of time of loading on an S1000 fibre under a load of 135 g, that is, a stress of 2.2 GPa. The data collection time for each spectrum was 60 s; the spectra are shifted vertically by an equal arbitrary amount and slightly smoothed for clarity. The times marked by each spectrum are the time the data collection was started, with zero at the moment the load was applied. Both the 1064 and the 1130 cm^{-1} bands behave in the same way. There is one major peak for each band;

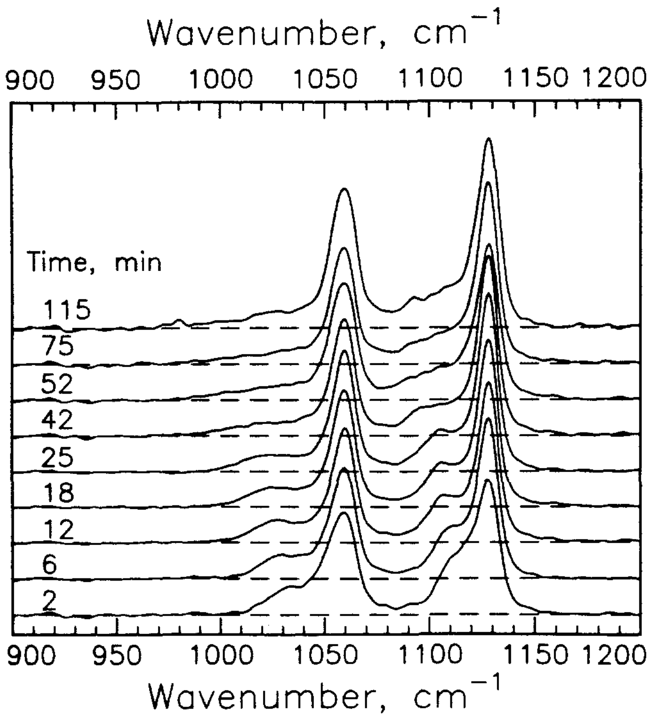

Figure 9 Raman spectra of an S1000 fibre dead-loaded to 2.2 GPa at room temperature as a function of time of loading

it is shifted to a lower wavenumber by the applied stress but its position does not change with time.

There is a second peak shifted further to lower wavenumbers. It appears quite clearly in the first spectrum at 2 min of loading and over the next 15 min this second peak becomes more distinct. This can be seen particularly well at 1110 cm^{-1} in the figure. While this second peak is well defined, it does not seem to change its position by much. At longer times the second peak begins to broaden, so that by 52 min of creep, no second maximum can be distinguished. The broadening continues so that after 115 min of loading the curve does not return to the baseline until 950 or 960 cm^{-1}, a shift of -100 cm^{-1} from the original position of the band. At -4.9 (cm GPa)$^{-1}$, this would correspond to over 20 GPa of fibre stress or over 10% of molecular strain.

It is important to put these main qualitative features in perspective before dealing with the quantitative information in these curves, which will depend on a choice of complex curve-fitting procedures. The previous experiments on the Raman spectroscopy of PE fibres were all strain-controlled. One set gave a single peak and a long tail for the 1064 cm^{-1} band stressed at over 1.2 GPa[27] and the other showed two clear peaks under the same stresses[28]. Although the fibres used were different, it was disturbing to find such very different behaviour. Now we find that the same specimen can show both types of result, depending on the time under load.

The experimental fibres from DSM Research used by Kip *et al.*[28] showed two peaks 45 min after a strain was applied. The commercial Allied fibre used here showed the second peak turning to a long tail between 42 and 52 min of creep. But it may be expected that different starting polymers, different production methods and perhaps different 'room temperatures' may cause the rate of change from one stress distribution to the other to be different. To see an extended tail in the stress distribution after relaxation would require a long relaxation time, with an initial stress below the failure stress and a final stress still greater than 1.2 GPa. Creep and stress relaxation do refer to the same basic processes, and so the results should not be fundamentally different[38].

To get numerical information on the process of creep, best fits were made to the 1064 and 1130 cm^{-1} band region. Each spectrum had a cubic background removed, using regions adjacent to the 1064 and 1130 cm^{-1} bands. As there are extensive tails at low wavenumbers, it is difficult to select a good background. If regions too near are used, part of the peak may be removed; too far, and noise prevents accurate fitting. The regions chosen were 800–920 cm^{-1} and 1200–1260 cm^{-1}. Spectra were then limited to the region 860–1200 cm^{-1} and normalized to uniform total area. They were fitted to a sum of four curves of the same shape. Gaussian, Lorentzian and a Gaussian–Lorentz sum function[27,39] were tried. To limit the number of variables involved in the sum function, the two parts had equal widths (as FWHM) and equal heights. The different curve shapes are shown in *Figure 10*; the main difference is the presence of a significant tail in the Lorentzian and sum function curves.

The total error in the fit was very similar for the Lorentzian and the sum function, and two to three times greater for the Gaussian fits. A set of fits to the 12 min creep time data is shown in *Figure 11*. The sum function fit is better in following the shape of the overlapping peaks; its errors are at the periphery, where they could be due to problems of background selection. *Figure 12* shows the area of the high-stress peak near 1040 cm^{-1} as a fraction of the total area in the 1064 cm^{-1} band, as determined using the three curve shapes. The time is plotted logarithmically, as is usual for creep data. All the fits had errors of similar magnitude; the errors are shown only for the sum function, as otherwise overlap makes the plot unreadable. Whatever curve shape is chosen, the fractional area is constant with time, but the actual area varies from 20 to over 50%. A very similar result was obtained for the 1130 cm^{-1} band, as shown in *Figure 13*. The errors and the difference between the fitting functions are somewhat smaller for this band.

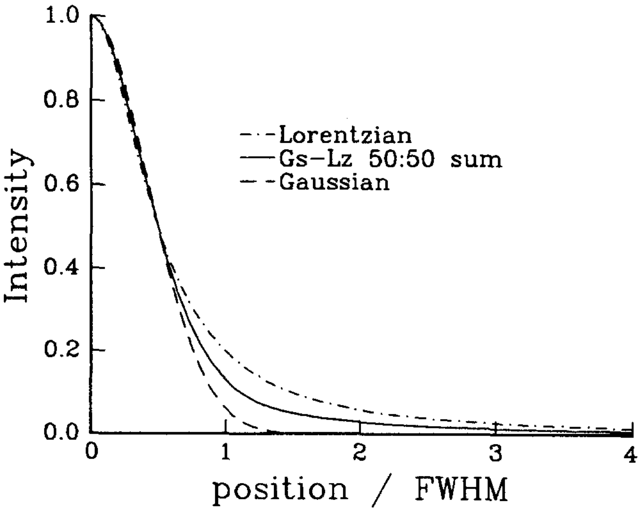

Figure 10 Curve shapes used to fit the 1064 and 1128 cm^{-1} bands of the Raman spectrum of an S1000 fibre during creep at room temperature

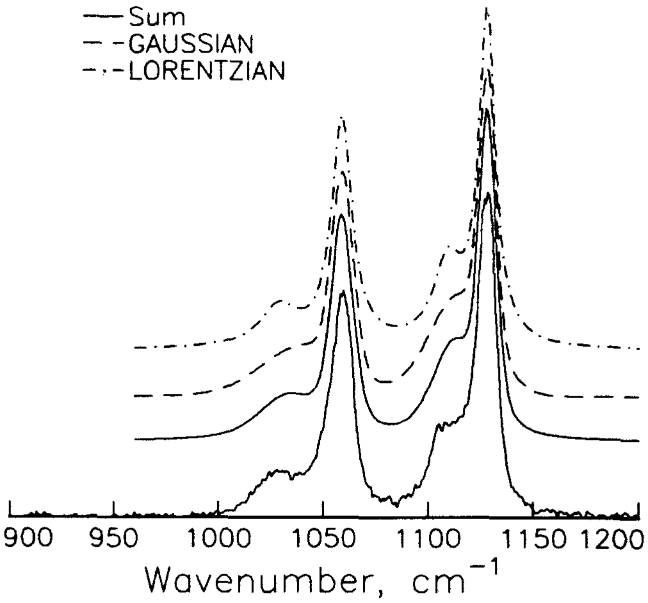

Figure 11 Raman spectrum of an S1000 fibre after 12 min creep at 2.2 GPa and room temperature: (below) data, and (above) fitted functions

Numerical values clearly depend on fitting choices; as the sum function gave the best fit, its results are used in all further analysis. On this basis, the high-stress peak in the 1064 cm^{-1} band has 30 ± 10% of the band area and the high-stress peak in the 1130 cm^{-1} band has 40 ± 5% of the band area. We might expect these

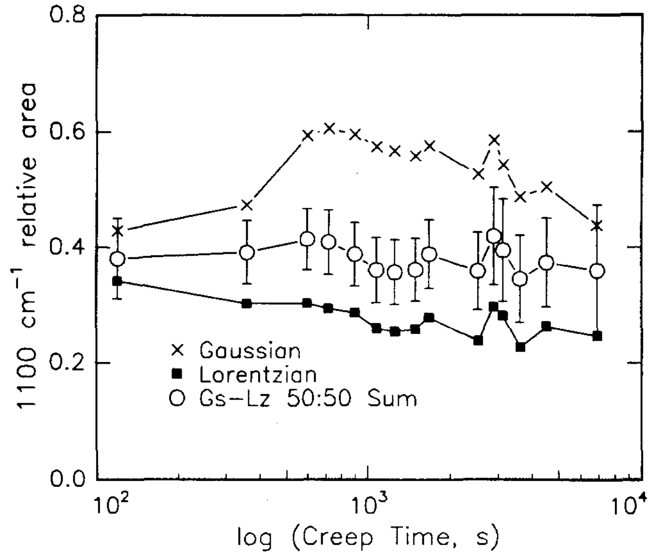

Figure 12 Area in the high-stress peak of the 1064 cm^{-1} band of the Raman spectrum of an S1000 fibre during creep at room temperature, as a fraction of the total area in the band

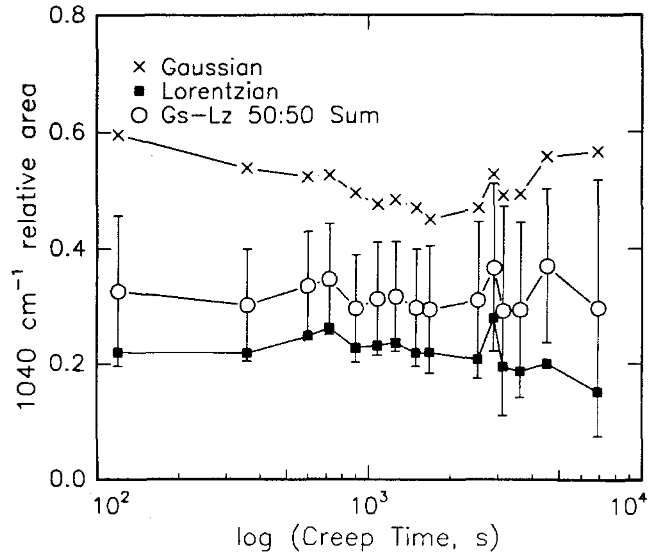

Figure 13 Area in the high-stress peak of the 1130 cm^{-1} band of the Raman spectrum of an S1000 fibre during creep at room temperature, as a fraction of the total area in the band

fractions to be the same, as they reflect the same stress distribution, and take as a best value 35 ± 5%. Our previous experiments on the same material found a tail containing 10–15% on the 1064 cm^{-1} band[27], but these new results are not a contradiction. As we found only a tail and never a peak in the previous work, the area of the asymmetric tail was measured. Now the same tail is fitted with a symmetric function, so the measured area should double. Kip *et al.*[28] found that the area in the high-stress peaks of these bands was 30–45%, using Gaussian curves to fit them, and remarked that differences between their results and the 10–15% in ref. 27 could be due to use of different materials and to use of different fitting procedures. We can now see that the different materials produce a similar result when similar fitting is done.

Figure 14 shows the peak shift as a function of time of loading, and *Figure 15* shows their FWHM. The two major low-stress peaks, at about 1060 and 1128 cm^{-1}, reduce in width and in shift very slightly over the first 10 min, and then remain constant. The change in position is about 1 cm^{-1} for the 1060 cm^{-1} peak and 0.5 cm^{-1} for the 1128 cm^{-1} peak. The high-stress peaks increase in shift and in width. For the 1040 cm^{-1} peak the shift goes from −27 to −35 cm^{-1} but the fit is quite erratic at long times; the 1128 cm^{-1} peak moves only from −18 to −22 and is more stable. For both the high-stress peaks, the width doubles, from 28 to over 60 cm^{-1} and from 18 to 35 cm^{-1}.

The poor fitting of peak position for the 1040 cm^{-1} peak is to be expected from the data. After 42 min or 2500 s, there is only a shoulder with no clear maximum, so it must be difficult to determine the peak position. When the width is large, the exact peak position will make little difference to the fit.

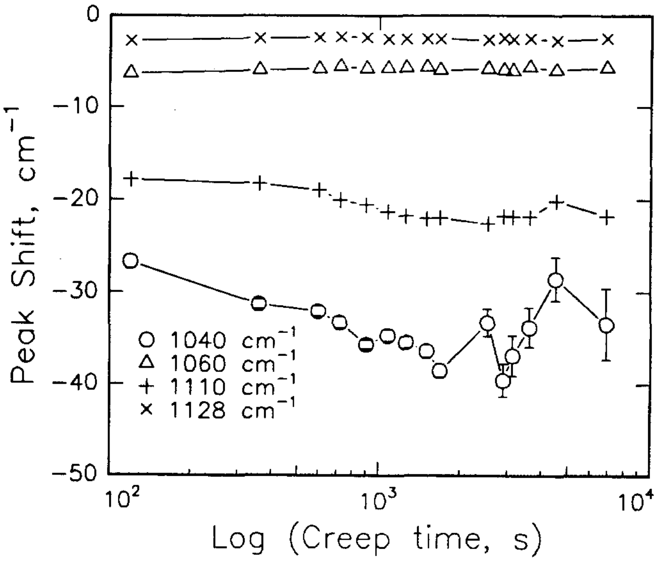

Figure 14 Peak shifts in the C–C stretching bands of the Raman spectrum of an S1000 fibre during creep at room temperature, as fitted with a Lorentzian–Gaussian sum function

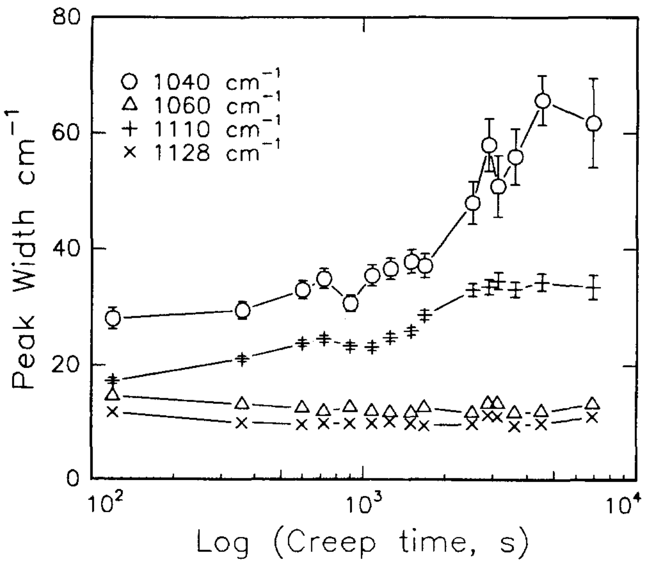

Figure 15 Peak widths in the C–C stretching bands of the Raman spectrum of an S1000 fibre during creep at room temperature, as fitted with a Lorentzian–Gaussian sum function

Transformation of structure in creep

There are two peaks in each C–C stretching band during creep at high stress in S1000 fibres, so there is a bimodal stress distribution that has two-thirds of the material in the low-stress peak. There is also a bimodal stress distribution in the original fibre structure with only one-sixth of the material in the low-stress peak.

Reports of stress relaxation are that there are always two peaks in the stress distribution, and their positions do not change with time[29]. Here from *Figure 14* the peak positions for the 1064 cm^{-1} band at a stress of 2.2 GPa are about 1059 and 1030–1035 cm^{-1} at room temperature. At 77 K the peak positions are 1064 and 1053 cm^{-1} (*Figure 2*). If this correctly describes the initial state of the fibre and the temperature effect on the 1064 cm^{-1} band position is only 1 cm^{-1}, then there must be considerable rearrangement at short times.

To show this directly, an S1000 fibre was loaded to 1.6 GPa at 77 K, producing the 1064 cm^{-1} band shown in the lower curve of *Figure 16*. It was then allowed to warm up to room temperature slowly over a period of 3 h under the same load. The spectrum changed to that shown in the upper curve of the figure. In this fibre the low-stress peak at low temperature is very small, so it could remain at the same position on warming, hidden by the broad low-stress peak at room temperature. There is no obvious correlation between the peaks at different temperature; the major peak at 77 K appears to split on heating. This view is encouraged by the poorer definition of the second peak at short times of loading at room temperature (*Figure 9*).

The upper curve in *Figure 17* is a spectrum collected for the first 30 s of loading at room temperature. It shows an asymmetric peak in each band which is very noisy, and cannot be fitted to two curves by the methods used for the other spectra taken during creep. Better spectra were obtained by cooling the fibre to 273 K in ice/water and collecting data for 60 s. The first spectrum collected, at 0–60 s, is the lower curve in *Figure 17*. It is shifted vertically and the best fit obtained using the Gaussian–Lorentzian sum function is shown below it.

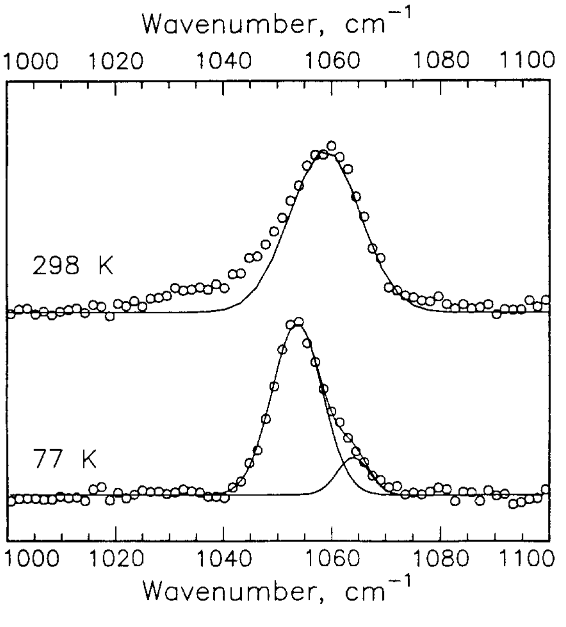

Figure 16 Raman spectra of an S1000 fibre loaded to 1.6 GPa at 77 K (lower curve) and then warmed to room temperature under load (upper curve)

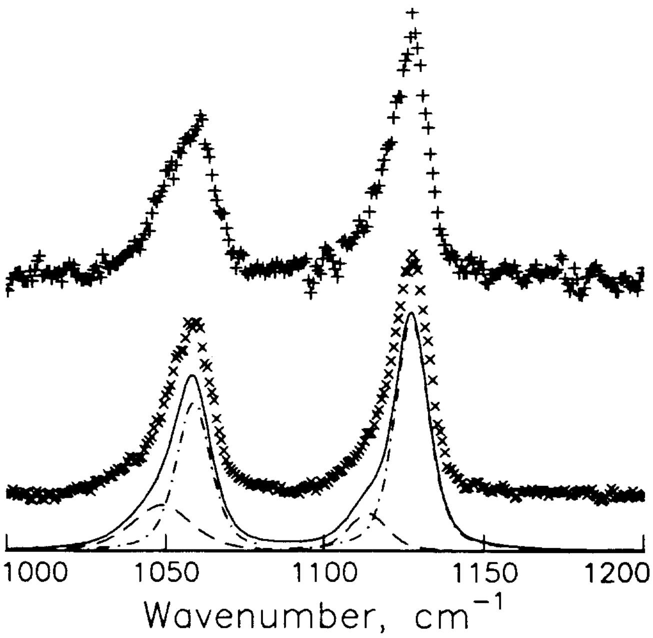

Figure 17 Raman spectra of an S1000 fibre: (+) at 2.2 GPa, room temperature, 30 s of loading; (×) at 1.8 GPa, in ice/water, 60 s of loading

The peak positions are 1048, 1059, 1114 and 1127 cm^{-1}, and the area fractions in the high-stress peaks are 0.23 and 0.14. Comparing the data for the 1064 cm^{-1} band, the major peak position has already reached the value seen at long times at room temperature. The high-stress peak is not distinguishable as a maximum, and is much closer to the low-stress peak with a shift of only 17 cm^{-1}. Fitting gets less reliable as the peaks become closer and the different area fractions are an indication of error, as they are expected to be the same.

Although creep concerns irreversible flow of the sample, the spectra considered here relate only to elastic deformation of the molecules. In a previous experiment it was shown that the original band shape was recovered in S1000 fibres after several hours at zero stress at room temperatures[27]. The high stress levels shown in the tail of the distribution after long periods of creep can be recovered, and they can also be locked in by cooling. *Figure 18* shows the 1064 cm^{-1} band of an S1000 fibre that had been loaded for a long period at room temperature, cooled to 77 K under load and unloaded at low temperature. The major peak position at zero applied stress is now above 1067 cm^{-1} corresponding to 0.4 GPa of fibre stress in compression. The mean position, counting the long tail to low wavenumbers, is 1065 cm^{-1}, equal to the normal position of this band at zero stress. On loading to 1.3 GPa the peak shifts but does not increase in width, since the stress is changing in sign but little in magnitude. The peak continues to shift linearly to the highest stresses applied, at -4.7 $(cm\,GPa)^{-1}$. This is close to the value of -5.4 $(cm\,GPa)^{-1}$ observed at low stress and low temperature (*Table 1*), an indication that the structure is fixed and the observed shift is the mean shift for all molecules in that sample.

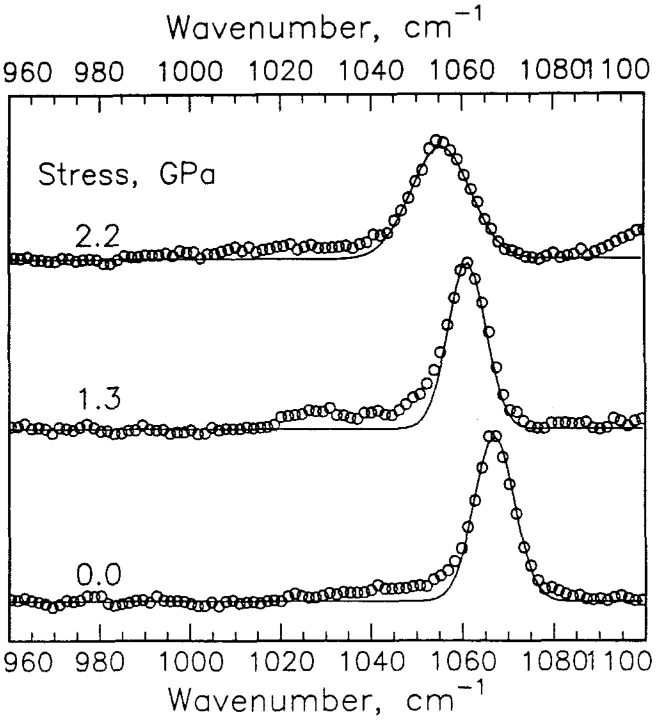

Figure 18 Raman spectra of an S1000 fibre pre-loaded to 2 GPa at room temperature, cooled under load to 77 K, then unloaded and reloaded at 77 K

SUMMARY

When a bimodal stress distribution was seen in PE fibres at 240 K it could have been due to some relaxation process. Now the same effect is seen at 77 K, where relaxation is completely suppressed, so it must relate to two components in the original fibre structure. X-ray diffraction from stressed fibres at 240 K indicates that both components are crystalline[35]. One component is inefficiently coupled to the applied stress and carries little load. In Spectra 1000, a high-modulus fibre, this component is 15% of the total crystalline material and each element in it carries one-fifth the average load. Some 97% of the total load is carried by the major component at 77 K.

Such a stress distribution seems inconsistent with many models of fibre structure. Those with distributed defects would produce a more continuous distribution of stresses[40,41]. Those where tie molecules or crystal bridges link crystals have a bimodal stress distribution in the molecules, but the minority are more highly stressed that the average[42–44]. These models relate more to the structure of the highly continuous fibrous elements that carry the load; they largely ignore less continuous and more compliant material, which Raman spectroscopy shows to be present.

The stress distribution can be obtained from a series–parallel model[26,33,45,46]. As the fibre crystallinity is 0.85, there will be a continuous crystal fraction, width 0.85 × 0.85 in parallel with the 0.85 × 0.15 wide compliant component and the 0.15 wide disordered part. The compliant component is a series combination of crystal and disordered material; the crystal will take up 80–90% of it. If the crystal modulus is 300 GPa, then the fibre modulus in this model will be 220 GPa. This is not too far from the room-temperature, high-strain-rate result of 180 GPa for Spectra 1000. Morphologically the compliant component might be obtained from a lamellar structure, as seen in flow-induced crystallization, but this is speculation at the moment.

On the series–parallel model, the immediate elastic effects of warming the fibre would be to soften the compliant component further, so the small peak ought to move to zero stress. The width of the major peak prevents this from being checked experimentally. No series–parallel model can correctly predict the distribution of stress that is seen within a single component.

At longer times, in creep, a peak appears at higher stresses and spreads out over time so that some material has a very broad stress distribution. It is not yet clear how this relates to the original fibre structure. X-ray diffraction measurements of (0 0 2) position under load as a function of time and temperature are planned to find out more about the process of creep in high-modulus polyethylene fibres.

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