JOURNAL OF MATERIALS SCIENCE **33** (1998) 4721–4725

The Raman spectra of high modulus polyethylene fibres by Raman microscopy

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Raman-microscopy has been used to analyse a series of high modulus polyethylene fibres. The high degree of orientation within the material means that upon 90° rotation of the samples and/or polarisation analyser, marked variations in band intensities occur throughout the spectra. Measurements of the 1131 : 1064 cm^{-1} band intensity ratio of the fibres are made and related to their Young's modulus. This relationship is useful in morphological studies of polyethylene fibres. © *1998 Kluwer Academic Publishers*

1. Introduction

It is known that illuminating an oriented polymer specimen such as a bundle of fibres of polyethylene with a polarized laser gives Raman spectra sensitive to the sample's orientation [1–2]. The reverse argument, once the assignment of the Raman bands is understood, is that the anisotropy of the Raman scatter can in principle yield the degree of orientation, but the detailed analysis is complex [3]. The mechanical properties, especially the Young's modulus of the fibres which are, of course, related to the degree of orientation may then be determined indirectly from the Raman spectrum. Recently, an account has been given of the anisotropic Raman scatter from a specimen of ultra high modulus polyethylene rod [4]. The method used was to illuminate the sample with a polarized laser operating at 1.064 μm analysing the scattered light with a Fourier transform spectrometer. The polarization of the scattered light was analysed with a Polaroid film and a series of six experiments were carried out. This is the normal procedure in this type of Raman analysis.

Drawn polymeric specimens are normally cylindrically oriented; hence, there is considerable redundancy in the experiments described above. Thus, there is value in making the very simplest experiment aligning the polarized laser with its direction perpendicular to the molecular axis but with the electric vector parallel or perpendicular to the sample orientation. A third experiment is possible in which the illumination is along the fibre axis. The experiment and its interpretation are discussed by Bentley and Hendra [4]. When a Fourier transform instrument is used a relatively large section of the specimen is illuminated and viewed (typically a cylinder 1 mm in length and 0.5 mm in diameter), hence it is impossible to examine a single fine fibre.

However, Raman microscopes, which were introduced in the mid 1970s [5], provide an alternative. In analyses using the Raman spectrometer–optical microscope combination, the radiation source can be a tightly focused laser beam, which may have a focal cylinder waist diameter of only about 1–2 μm, and can hence examine a micron sized area across the specimen [6]. We have, in our laboratories samples of polyethylene produced in an unusual process involving molten metal baths (to be described elsewhere). The fibres are $\sim 100\ \mu$m in diameter and no appropriate X-ray diffraction (XRD) equipment is available. To study these by infrared spectroscopy is not trivial unless an infrared microscope is used. We therefore decided to use Raman microscopy to relate the Raman scattering anisotropy to the mechanical performance of the filaments.

2. Experimental procedure

The polyethylene fibres were prepared from high density linear polyethylene Hostalen GF4760 using a molten metal bath [7]. The section of polyethylene fibre was placed parallel with respect to the polarization direction of the incident laser beam of the Raman microscope and the spectrum was recorded (see Fig. 2). The spectra were also recorded through a polarization analyser, and with both polarization analyser and a $\lambda/2$ plate. The polarization analyser was set to pass vertically polarized radiation and the spectrum was then recorded in backscatter. A spectrum was also recorded after adding a $\lambda/2$ plate with the same polarization analyser position, which is equivalent to setting the polarization analyser to pass horizontally polarized radiation. These steps were repeated having rotated the sample to the remaining two mutually perpendicular directions.

Raman spectra were recorded using a Renishaw Raman imaging microscope (System 1000) [8] powered by a He–Ne laser. The objective lens, with a magnification of 50×, was used to both focus the laser beam onto the sample and collect the back-scattered radiation. Illumination of the specimen by a white light source was used to aid focus and provide a visual image. Spectra were recorded at room temperature with

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the use of 10 mW of radiation at 632.8 nm wavelength at the sample. Spectra were accumulated for 3.5 min and taken with a slit width equivalent to 4 cm^{-1} resolution.

For comparison purposes a similar set of spectra of the polyethylene pellet used to produce the fibres studied was also recorded.

3. Results and discussion

Raman spectra of a high modulus polyethylene fibre (diameter: 75 μm, modulus: $\sim$25 GPa) are presented in Fig. 1. The spectra were recorded with the fibre cylindrical axis parallel, perpendicular and across the laser polarization direction as described in Fig. 2. In each case, the spectra are shown in the order: no polarization analyser, with a polarization analyser and with both polarization analyser and a $\lambda/2$ plate. It is evident that the spectra are highly anisotropic for fibre with its cylindrical axis parallel and perpendicular to the polarization direction of the incident laser; marked variations in band intensities occur throughout the spectra. To explain the observation it is essential to understand the origin of each band.

Polyethylene crystallizes with two chains per unit cell and unusually both the isolated chain and cell are isomorphous and of D_{2h} point group [9]. The orthorhombic unit cell requires that each mode of an isolated chain becomes two in the unit cell. This splitting is observable in some cases, e.g. the well known line pair near 720 cm^{-1} in the infrared due to the CH_2 rock. The assignment of polyethylene's Raman spectrum is given in Table I, from which it is clear that, for example, the CH_2 twist near 1295 cm^{-1} of B_{3g} symmetry becomes, in the crystal two modes, one with both chains moving in phase at 1295.5 cm^{-1} (B_{3g}) and the other at 1293 cm^{-1} (B_{2g}) where the chains move out of phase. The experiments in Fig. 1 can all be classified under Porto's nomenclature (see Table II).

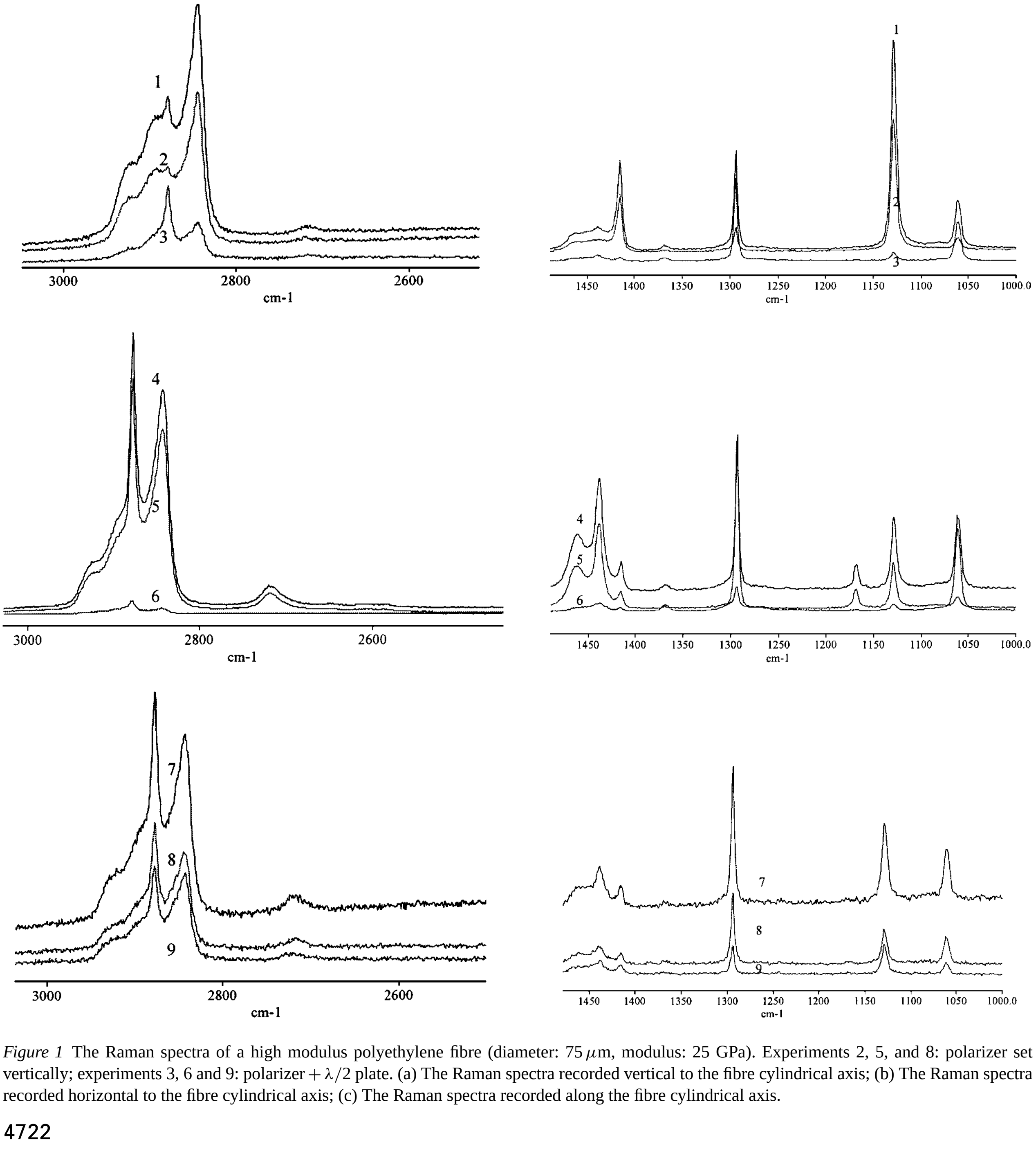

Figure 1 The Raman spectra of a high modulus polyethylene fibre (diameter: 75 μm, modulus: 25 GPa). Experiments 2, 5, and 8: polarizer set vertically; experiments 3, 6 and 9: polarizer + $\lambda/2$ plate. (a) The Raman spectra recorded vertical to the fibre cylindrical axis; (b) The Raman spectra recorded horizontal to the fibre cylindrical axis; (c) The Raman spectra recorded along the fibre cylindrical axis.

Experiments 1 and 2, which were designed to excite only the α_{zz} components, excite only A_g modes and hence favour one class of vibration alone. A_g modes occur as one component of the C–C stretching doublet unresolved near 1131 cm^{-1}, and of the CH_2 rock at 1170 cm^{-1}. A_g class modes also appear within the complex multiplets between 1470 and 1410 cm^{-1} and 2890 to 2840 cm^{-1}. It is obvious that when compared with the other experiments, 1 and 2 emphasize the bands at 1131, 1415 and 2847 cm^{-1} but certainly not the weak band near 1170 cm^{-1}, which vanishes.

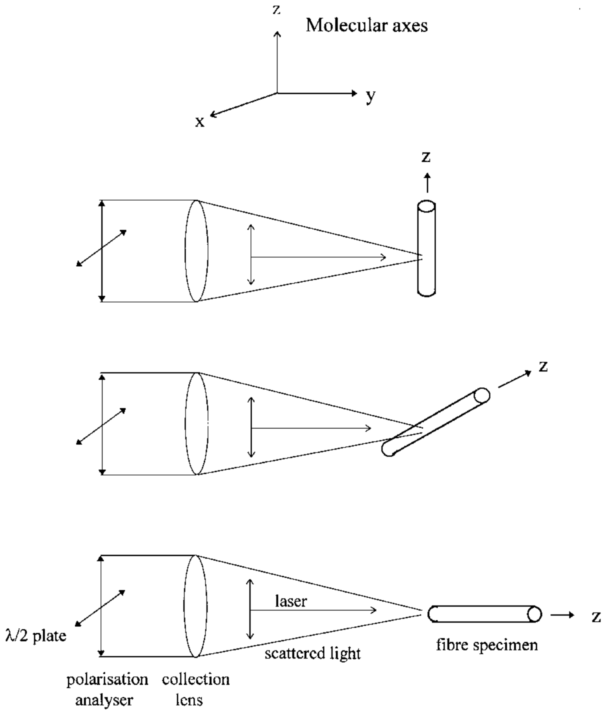

Figure 2 The various experimental geometries exploited in the Raman studies of high modulus polyethylene fibre.

It is noted that in all cases when the polarization analyser was set to pass vertically polarized radiation, the spectra recorded in backscatter are similar but of lower intensity to those without the polarization analyser. This is, of course, to be expected; however, the Raman spectra obtained with the polarization analyser have much weaker bands at 1064 and 1295 cm^{-1} because of a pair of modes of the B_{2g} and B_{3g} classes for the fibre cylindrical axis parallel and perpendicular to the laser polarization direction.

It is of interest to note that experiments 3 and 6 planned to excite B_{2g} and B_{3g} class modes emphasize the bands at 1064 and 1295 cm^{-1} as expected, assignable to C–C skeletal stretching of B_{2g} class and CH_2 twisting mode of B_{3g}, respectively. Those bands ascribed to A_g modes almost disappear.

We now turn to experiments 4, 5, 7, 8 and 9. In experiments 4 and 5, the features at 1441 and 1463 cm^{-1} are more prominent than they are in experiments 1, 2 and 3, and that at 1170 cm^{-1} is also evident. These band profiles are very close to those from polyethylene pellet (see Fig. 3). These spectra should all be similar and certainly the last three are almost identical when due

TABLE I The complete vibrational assignments of polyethylene [10]

Frequency (cm^{-1})					
Infrared		Raman			
298 K	77 K	298 K	77 K	Assignment	Symmetry[a]
2920	2917			$\nu_{as}(CH_2)$	$B_{2u} + B_{3u}$
2851	2848			$\nu_{as}(CH_2)$	$B_{2u} + B_{3u}$
		2882	2882	$\nu_{as}(CH_2)$	$A_g + B_{1g}$
		2847	2846	$\nu_s(CH_2)$	$A_g + B_{1g}$
1473	1475				B_{3u}
1465	1460			$\delta(CH_2)$	B_{2u}
		1463	1466	$\delta(CH_2)$	B_{1g}
		1453	1453	Fermi	A_g
		1440.5	1441.5	resonance	$A_g + B_{1g}$
				+	
		1416	1415	overtones	A_g
		1372	1372	$\omega(CH_2)$	$B_{2g} + B_{3g}$
		1295	1295.5		B_{3g}
			1293	$\tau(CH_2)$	B_{2g}
1176	1174			$\omega(CH_2)$	B_{1u}
		1170	1171	$\rho(CH_2)$	$A_g + B_{1g}$
		1131	1133	ν_s(C–C)	$A_g + B_{1g}$
		1064	1064.5		B_{2g}
			1063	ν_{as}(C–C)	B_{3g}
1050	1050			$\tau(CH_2)$	B_{1u}
730	733				B_{3u}
720	721.5			ρ (CH_2)	B_{2u}
			133	Rotary	B_{1g}
		104	109	LM	A_g
	110			Translation	B_{2u}
77	72			LM	B_{3u}
		34	34	LAM ($m = 3$)	A_g
		12	12	LAM ($m = 1$)	A_g

[a] $\nu_{s,as}$, symmetric, asymmetric stretching; τ, twisting; ρ, rocking; δ, bending; ω, wagging; LM, lattice mode; LAM, longitudinal acoustic mode.

TABLE II The Raman scattering activities of cylindrically symmetric samples of oriented polyethylene fibres

Spectrum	Fibre axis with respect to the polarization direction of the incident laser	Polarization direction	Scattering geometry	Space group symmetry
1	parallel		x(zz)x + y(zz)y	A_g
2	parallel	ll	x(zz)x + y(zz)y	A_g
3	parallel	⊥	x(zy)x + y(zx)y	$B_{2g} + B_{3g}$
4	perpendicular		x(yx)x + y(xy)y	$A_g + B_{1g}$
5	perpendicular	ll	x(yx)x + y(xy)y	$A_g + B_{1g}$
6	perpendicular	⊥	x(yz)x + y(xz)y	$B_{2g} + B_{3g}$
7	across		z(xy)z + z(yx)z	$A_g + B_{1g}$
8	across	ll	z(xy)z + z(yx)z	$A_g + B_{1g}$
9	across	⊥	z(xx)z + z(yy)z	$A_g + B_{1g}$

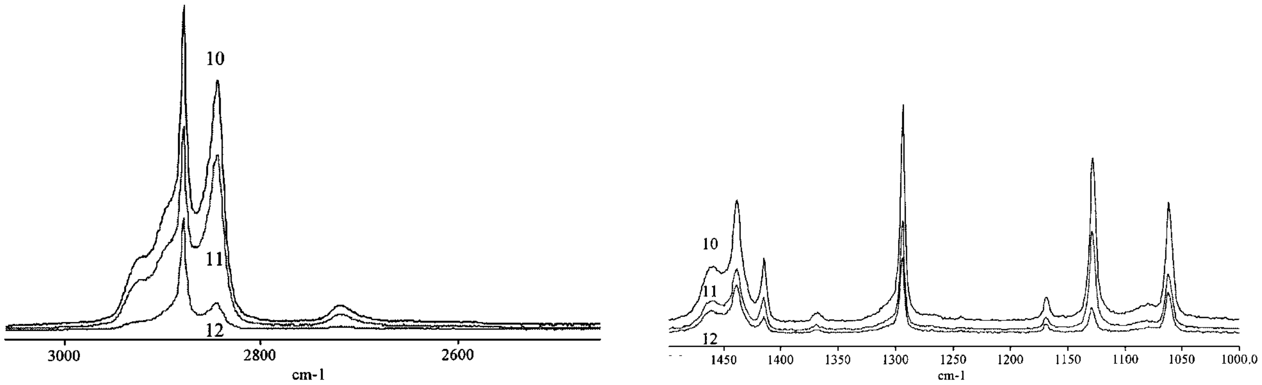

Figure 3 The Raman spectra of a single polyethylene pellet of the fibre starting material.

allowance is made for the application of polarization analyser and $\lambda/2$ plate.

Experiment 9, compared with experiment 8, has no obviously enhanced bands at 1064 or 1295 cm^{-1}, indicating the presence of almost perfectly cylindrical symmetry of the fibre. The complex vibrational behavior that generates the bands near 1470 and 1440 cm^{-1} requires additional explanation. It can be seen that the overall profile remains relatively constant from experiment to experiment but that the intensities in experiments 1 and 2 are very low, suggesting that in the melange of overtones effected by Fermi resonance the A_g contribution is of modest intensity.

In a manner similar to the deformations, the CH stretching vibration bands near 2930 and 2870 cm^{-1} in experiments 1 and 2 are very low in intensity. Like the deformations, Fermi resonance plays a complex part in dictating the appearance of the these spectra all originating in A_g and B_{1g} motions.

The Raman spectra of polyethylene pellet are shown in Fig. 3. Experiment 12 also exhibits relatively enhanced bands at 1064 and 1295 cm^{-1}, like experiments 3 and 6, suggesting the presence of slightly preferred orientation. This is certainly possible and would originate in the pellet production process, where polyethylene melt is extruded through a die and cut into pellets, introducing a low level of molecular orientation. However, for our purpose, the orientation within the pellet is so slight that it can be treated as unoriented.

It is clear that spectra 1 and 2 show the most anisotropic characteristics when compared with other spectra. The band at 1131 cm^{-1} caused by the C–C stretching modes is most prominent. The relative intensity of the feature near 1131 cm^{-1} compared with that at 1064 cm^{-1} is found to be related to the modulus of the fibre specimen, which is in turn determined by the molecular orientation along the fibre axis. It should be noted that it is sufficient to investigate the anisotropy of the fibre simply by changing its cylindrical axis with respect to the direction of polarization of the incident laser. The advantage here is the convenience and the greater signal strength resulting from the elimination of the polarisation analyser and/or $\lambda/2$ plate. Fig. 4 shows the relationship between band intensity ratio (1131 : 1064 cm^{-1}) and Young's modulus of fibres. It indicates that the 1131 : 1064 cm^{-1} band

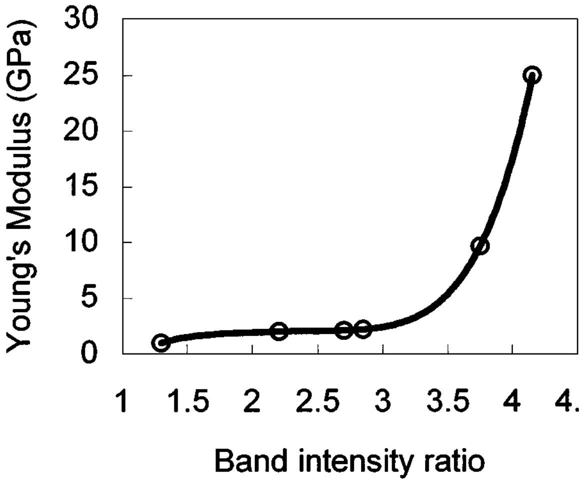

Figure 4 The 1131 : 1064 cm^{-1} band intensity ratio as a function of Young's modulus of the polyethylene fibres.

intensity ratio increases rapidly as Young's modulus increases above 5 GPa. This is only a preliminary result and the Young's modulus range of the fibres available is limited. It should also be noted that the band intensity ratio values are based on a single point on the fibre specimen, therefore, care must be taken to choose a representative area for examination. However, it can be envisaged that, with caution and a wider range of fibre samples, it is possible to establish a curve relating the 1131 : 1064 cm^{-1} band intensity ratio and Young's modulus of the fibres, which can be a better indication for the molecular orientation of fibre along the cylindrical axis.

4. Conclusions

Raman microscopy can be used to examine the molecular orientation of thin polyethylene fibre. The A_g characteristics revealed in spectra 1 and 2 are those where the movement vectors lie across the chain axes; experiment 1 is recorded with the source vector parallel to the chain axis and experiment 2 with both the source vector and polarisation analyser direction parallel to the chain axis. These two experiments are the most easily distinguishable from others and hence could be used to indicate molecular orientation. The 1131 : 1064 cm^{-1} band intensity ratio can be related to Young's modulus of fibres and can be used to evaluate molecular orientation of the fibres.

Acknowledgements

The authors wish to thank the Engineering and Physical Science Research Council for the funding of the project and Renishaw for loan of the Raman microscope.

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Received 10 March
and accepted 14 July 1998