Chain stretching in a poly(ethylene terephthalate) fibre*

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Molecular deformation during the mechanical straining of single filaments in a high-tenacity poly(ethylene terephthalate) (PET) technical yarn has been investigated using Raman spectroscopy. A significant shift of over 2.5 cm^{-1} in the peak position of the 1616 cm^{-1} phenylene ring stretching Raman band was found during deformation up to fibre fracture, and this has been related to chain stretching of the polymer molecules in the fibres during macroscopic deformation. It is found that the change in the position of the Raman band is more closely related to stress than to strain, and the behaviour has been shown to be similar to that of deformed PET films and of high-performance fibres such as aromatic polyamides (aramids).

(Keywords: poly(ethylene terephthalate); fibres; deformation)

INTRODUCTION

In the past decade there has been an upsurge of interest in the use of Raman spectroscopy to follow molecular deformation processes in a variety of high-performance polymer fibres. The original work was concerned with the deformation of single crystal fibres of substituted diacetylene polymers[1–3], but this was followed by investigations into aramid fibres[4–6], rigid-rod polymer fibres[7–9] and gel-spun polyethylene fibres[10–12]. In each case it is found that Raman bands associated with backbone groups on the polymer molecules shift in wavenumber on the application of stress or strain. This behaviour can be interpreted as being the result of macroscopic deformation of the polymer fibre causing chain stretching in the polymer molecules in the fibre, and hence it can be used as a method of relating macroscopic and molecular deformation processes. For example, it has been possible to follow the deformation of the molecules in aramid fibres from the shift in wavenumber of the *p*-phenylene ring symmetric stretching band at about 1610 cm^{-1} and to assign the overall deformation into a combination of crystal rotation and chain stretching, with the chain stretching process being the most prominent process in the highest modulus fibres[9].

The application of the Raman technique has so far been most successful in high modulus fibres, because they tend to have the most well-defined Raman spectra and have main-chain bands which shift considerably under the application of stress or strain (typically by more than -5 cm^{-1} (% strain)$^{-1}$). Attempts to use Raman spectroscopy to follow the deformation process in conventional polymers such as polypropylene[13] have met with only limited success, and shifts of the order of only 1 cm^{-1} are obtained up to the failure stress of the polymers. Fina *et al.*[14] were rather more successful in using Raman spectroscopy to analyse the deformation of oriented poly(ethylene terephthalate) (PET) films; they were able to monitor accurately the shift of the 1616 cm^{-1} ring stretching band with applied stress and showed that shifts of the order of up to -6.5 cm^{-1} GPa^{-1} could be obtained. In the past, several groups of workers have used i.r. spectroscopy to investigate molecular deformation processes in polyesters. In 1977 Mocherla and Statton[15] reported that there was a shift of the wavenumber of the 973 cm^{-1} i.r. absorption band in PET films during deformation, and more recently van der Heuvel *et al.*[16] have shown, using i.r. spectroscopy, that there is a similar shift in wavenumber of the band at $\sim$970 cm^{-1} for PET yarns subjected to stress.

In this present communication we show how Raman spectroscopy can be used to monitor molecular deformation in PET single filaments and the behaviour is compared with similar measurements on high-modulus polymer fibres such as aramids.

EXPERIMENTAL

The PET fibre used in this study was Akzo Diolen 855T, 1100 dtex f210, which is the same material as employed by van der Heuvel *et al.*[16]. It is a technical PET yarn with a tenacity of 80 cN tex^{-1}; full details of its physical properties are given elsewhere[16].

For tensile testing, individual PET fibres were mounted across windows cut out of paper cards using a slow setting cold-curing epoxy resin adhesive. A minimum of 24 h was allowed for the adhesive to set completely at room temperature in order to minimize slippage errors. Tensile stress–strain curves were obtained using an Instron 1121 universal testing machine following the testing procedure given in ASTM D3379–75. In this study a fibre gauge

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length of 50 mm was employed with an initial strain rate of $1.6 \times 10^{-3}\,s^{-1}$ and measurements were taken using a 1 N load cell. Fibre diameters were measured using an Olympus optical microscope with an Image Manager system and a minimum of 20 specimens were tested at 23 ± 1°C and 50 ± 5% relative humidity.

Raman spectra were recorded from the PET fibres during deformation using a Raman microprobe system. This is based upon a SPEX 1000M single monochromator with a holographic laser-line filter. The 632.8 nm red line of a 7 mW He-Ne laser was used to excite the spectra and this was focused to a 1–2 μm spot on the fibre using a modified Olympus microscope with a 50 × objective. The laser beam was polarized parallel to the fibre axis for all of the measurements (cf. the Vv arrangement in ref. 14) and the spectra were recorded using a highly sensitive Wright Instruments Charge Coupled Device (CCD) camera with associated AT1 software.

For Raman deformation studies individual fibres were fixed, using aluminium foil tabs and a cyanoacrylate adhesive, onto a straining rig, which then fitted directly on the microscope stage. A gauge length of 50 mm was again employed and displacement of the fibre was controlled using a micrometer attachment which could be read to ± 0.005 mm. This gave a precision of the order of 0.01% for strain measurement. The fibres were loaded to failure in steps of the order of 0.5% and the exposure time used to obtain a spectrum was about 30 s. Hence the period of time taken to deform the fibres to failure in the Raman deformation experiment was of the order of 30 min.

RESULTS AND DISCUSSION

Figure 1 shows the effect of deformation upon the strong phenylene ring stretching Raman band at 1616 cm^{-1} for the PET fibre. It can be seen that the band shifts to lower wavenumber, decreases in peak intensity and broadens somewhat upon the application of 12.5% strain. This behaviour is essentially similar to that reported by Fina *et al.*[14] for oriented PET films. *Figure 2a* shows the dependence of peak position of this band upon strain and it can be seen that the peak shifts to lower wavenumber but the dependence upon strain is not linear, unlike the behaviour of the same band for aramid fibres[4–6].

In order to determine the origin of the non-linear behaviour, the stress–strain characteristics of the PET

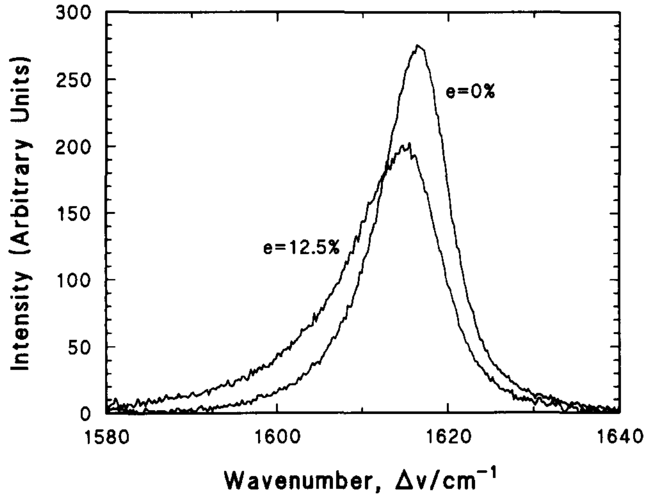

Figure 1 The Raman band at about 1616 cm^{-1} for a single filament of the PET yarn unstrained and at a strain, *e*, of 12.5%

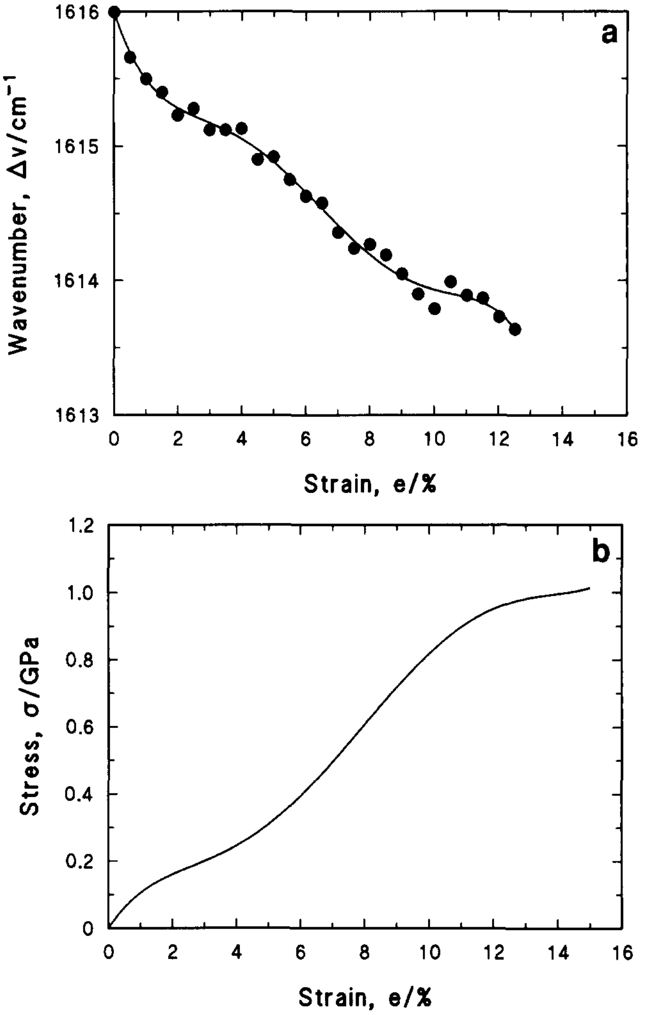

Figure 2 (a) Change in the wavenumber, Δ*v*, of the peak position of the 1616 cm^{-1} Raman band with strain for a single filament of the PET yarn. The curve is a fit of the data points to a fifth-order polynomial. (b) Stress–strain curve for a single filament of the PET yarn

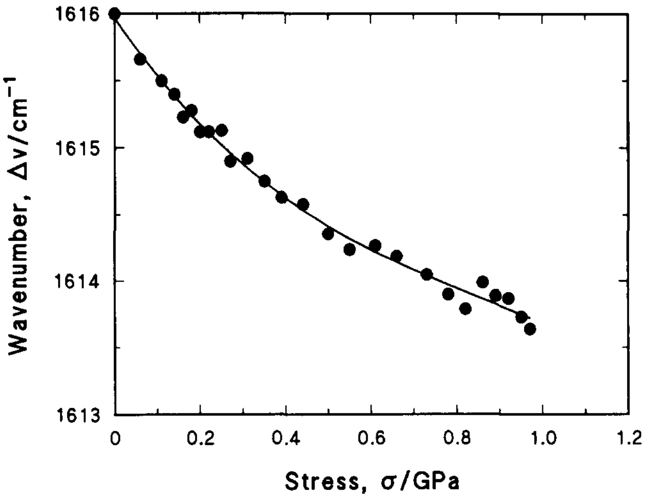

Figure 3 Variation of the wavenumber of the peak position of the 1616 cm^{-1} Raman band with stress for a single filament of the PET yarn derived from the data in *Figure 2*. The curve is a fit of the data points to a third-order polynomial

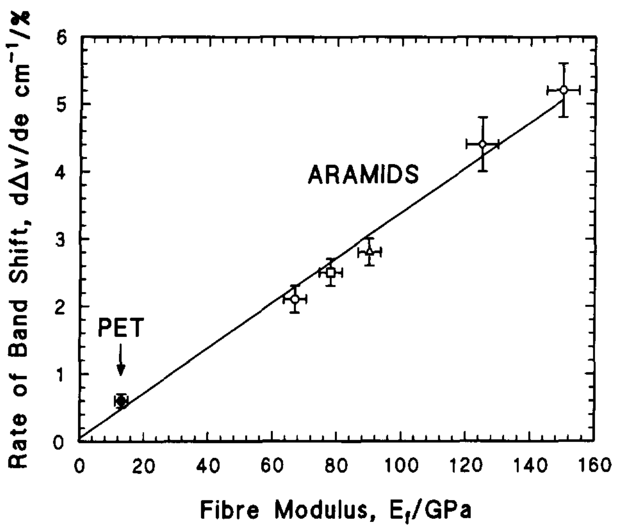

Figure 4 Rate of Raman band shift per per cent strain, $d\Delta\nu/de$, for the 1610 cm^{-1} band in five aramid fibres[6] and for the 1616 cm^{-1} band of the PET fibre investigated in the present study as a function of the fibre modulus, E_f. The data for the PET fibre were taken from the initial slopes of the curves in *Figure 2*

fibres were also examined. *Figure 2b* show a stress–strain curve for the PET fibre. The curve is very similar to that reported for multifilament yarns of the same fibres[16], and it can be seen that the shape of the stress–strain curve essentially mirrors the change in Raman band position with strain shown in *Figure 2a*. The implication of this is that the change in Raman band position is essentially a measure of molecular stressing in the PET fibres. This implication is exemplified in *Figure 3*, where the data from *Figure 2* are replotted as Raman band peak position *versus* stress. In this case it can be seen that the data points fall on a smooth curve, and changes in slope of the curves in *Figure 2* are lost.

It is of interest to see to what extent the behaviour of the PET fibres can be related to similar Raman deformation experiments on PET films. Fina *et al.*[14] found stress-induced shifts in the peak position of the 1616 cm^{-1} Raman band of -6.5 and $-5.3\,cm^{-1}\,GPa^{-1}$ for films with moduli of about 6.6 and 9.5 GPa, respectively. These figures are similar to the initial slope of the curve in *Figure 3*, which is of the order of $-5\,cm^{-1}\,GPa^{-1}$ for our 13 GPa modulus fibre. It appears, therefore, that there is a slight decrease in the rate of Raman band shift (per unit stress) with increasing fibre modulus and therefore degree of orientation. Fina *et al.*[14] expressed surprise at this decrease but our present findings have confirmed the trend. It is also worth noting that Fina *et al.*[14] were only able to subject their films to stresses of up to 0.2 GPa, whereas we were able to deform our high-tenacity fibres to stresses of over 1 GPa. Nevertheless, they also found that there were deviations from linear behaviour in Raman band position *versus* stress curves at higher stress. Another interesting finding of Fina *et al.*[14] was that the rate of Raman band shift was about a factor of 3 higher when the polarizer and analyser were parallel to the draw direction of their films than when they were in the perpendicular orientation. The reasons for this are not clear and it would be interesting to undertake similar experiments upon the higher-modulus fibres.

It is also of interest to compare the behaviour of the PET fibres with similar experiments on high-performance polymer fibres[4–12] which have much higher values of Young's modulus. The most detailed studies in this area have focused on the position of the 1610 cm^{-1} *p*-phenylene ring stretching band for aromatic polyamide (aramid) fibres such as Kevlar[4–6]. Strain-induced Raman band shifts of over $-5\,cm^{-1}$ (% strain)$^{-1}$ can be obtained for this band in the highest modulus fibres such as Kevlar 149. *Figure 4* shows a plot of the rate of shift for this Raman band $d\Delta\nu/de$ ($=-0.6\,cm^{-1}\,\%^{-1}$) *versus* fibre modulus E_f (~ 13 GPa), for the PET fibre studied in this present work, along with similar measurements on aramid fibres[6]. It can be seen that the data fall close to a straight line through the origin, implying that the molecular deformation processes in the two types of fibre are similar. The PET fibre appears to have inferior mechanical properties to the aramids owing to the presence of amorphous material and a poorer level of molecular orientation. It is worth noting that when the rates of band shift per unit stress $d\Delta\nu/d\sigma$ are compared, the figure is about $-3.5\,cm^{-1}\,GPa^{-1}$ for the aramids compared with the value of $-5\,cm^{-1}\,GPa^{-1}$ for PET. This implies that there may actually be a higher level of molecular stressing in the PET fibres than in the aramids, assuming that the intrinsic sensitivity of the vibrational modes in the two fibres is the same (which may or may not be the case). This aspect of the work is worthy of further investigation, since it may lead to methods of improving the mechanical properties of PET fibres.

CONCLUSIONS

It has been demonstrated that Raman spectroscopy is a powerful method for following chain stretching in single filaments of a high-tenacity PET technical yarn. It has been found that the behaviour is very similar to that of high-performance fibres such as aramids, and hence that the technique is of much wider application than was hitherto thought. There is clearly considerable scope to use Raman deformation studies to gain a detailed understanding of the molecular deformation processes in a variety of other industrial and textile fibres. These implications are currently under investigation.

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