

Chain stretching in aramid fibres

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The frequency shift in the resonance Raman spectra due to an applied mechanical stress has been measured for aramid fibres with different initial moduli. The observed shifts agree well with the values calculated with a single-phase series model for the elastic extension of aramid fibres.

(Keywords: aramid; poly(*p*-phenylene terephthalamide); Raman scattering; fibre deformation)

Introduction

This paper is concerned with the deformation processes in fibres of poly(*p*-phenylene terephthalamide) (PPTA), or aramid, during tensile loading. In earlier publications¹⁻³ it was shown that the deformation in this material involves both crystallite extension or chain stretching and crystallite rotation due to shear deformation. In this work resonance Raman spectroscopy was used to study the extensional strain component in aramid fibres as a function of the initial modulus.

Experimental

Three experimental yarns with different elastic moduli were spun at the Akzo laboratories using the standard dry-wet spinning technique. The mechanical properties, in particular the initial modulus, were determined with a computerized tensile testing machine. Measurements were performed on monofilaments, using a gauge length of 100 mm and a loading rate of 10%/min. The resonance Raman spectroscopy measurements were performed at Queen Mary College. Monofilaments were stretched in the beam of an HeNe laser operating at 632.8 cm⁻¹ and the Raman spectra were recorded at 0.2% strain intervals. The optical and mechanical components of the Raman set-up are described elsewhere^{4,5}. Changes in resonance frequency could be measured with a precision of approximately ±0.5 cm⁻¹. The measurements reported here deal with the Raman band with an undeformed vibrational frequency of 1610 cm⁻¹. Earlier measurements⁵ have shown that the strain dependence of this band is the largest in the 1100 to 1700 cm⁻¹ region. All measurements were performed at room temperature and 60% relative humidity.

Theory

The deformation model for a well-oriented, single phase paracrystalline fibre has been described in detail elsewhere¹⁻³. In this model the fibre is regarded as a 'chain' of end-to-end linked crystallites each having a slight disorientation with respect to the fibre axis. A

tensile stress, σ , applied along the fibre axis causes stretching of the crystallites and a rotation towards the fibre axis due to shear deformation. The total strain is the sum of both deformation processes:

$$\epsilon_{\text{total}} = \epsilon_{\text{stretch}} + \epsilon_{\text{rotation}} \quad (1)$$

OR

$$\epsilon_{\text{total}} = \frac{\sigma}{e_3} + 0.5 \langle \sin^2 \phi_0 \rangle [1 - \exp(-\sigma/g)] \quad (2)$$

where e_3 is the PPTA chain modulus ($\approx 220 \text{ GN m}^{-2}$), $\langle \sin^2 \phi_0 \rangle$ an orientation parameter describing the average molecular orientation with respect to the filament axis and g the shear modulus ($\approx 2 \text{ GN m}^{-2}$). The initial orientation parameter can be calculated from Young's modulus of the fibre:

$$\frac{1}{E_0} = \frac{1}{e_3} + \frac{\langle \sin^2 \phi_0 \rangle}{2g} \quad (3)$$

The above equations describe the stress-strain curve for relatively small strains ($\epsilon_{\text{total}} < 2\%$). It is clear from the above equations that the ratio of the extensional and the rotational strain component varies with the fibre modulus; the extensional strain component increases with increasing fibre modulus.

Since the shift in the Raman spectra is due to the stretching of the covalent bonds along the chains, the Raman shift should be proportional to $\epsilon_{\text{stretch}}$ only and independent of $\epsilon_{\text{rotation}}$.

Results

The stress-strain curves of the three types of fibres are shown in *Figure 1*. The initial moduli are 49, 72 and 102 GN m⁻² for the low modulus (LM), the medium modulus (MM) and the high modulus (HM) fibres, respectively.

The results of the resonance Raman measurements on the MM fibre are shown in *Figure 2*. In this figure the strain dependence of the leading (L) and trailing (T) edges at half-maximum intensity of the band, as well as that of the peak (P) are indicated. The shift in frequency is approximately proportional to the applied strain. The

same linear behaviour was found for the LM and the HM fibre. In all cases there is some peak broadening. The proportionality constant between fibre strain and resonance frequency, i.e. the Raman shift factor, increases with increasing fibre modulus as shown in Table 1. In this table the results of an earlier experiment⁵ on a heat-treated (HT) aramid fibre are also included.

Using these data and equations (2) and (3) we can calculate the proportionality constant between the Raman shift and $\epsilon_{\text{stretch}}$: $-6.8 \text{ cm}^{-1}/\%$ or $-3.1 \text{ cm}^{-1}/\text{GN m}^{-2}$. This value depends slightly on the value of ϵ_{total} used in the calculations (here $\epsilon_{\text{total}} = 0.5\%$) due to the non-linearity of equation (2). We can now predict the fibre Raman shift factor as a function of the fibre modulus. Figure 3 shows that the theoretical and experimental results are in good agreement.

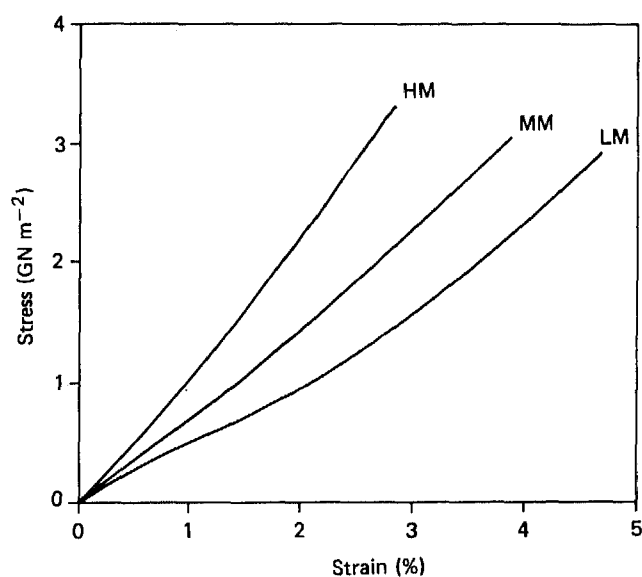


Figure 1 Stress-strain curves for low (LM), medium (MM) and high-modulus (HM) aramid fibres

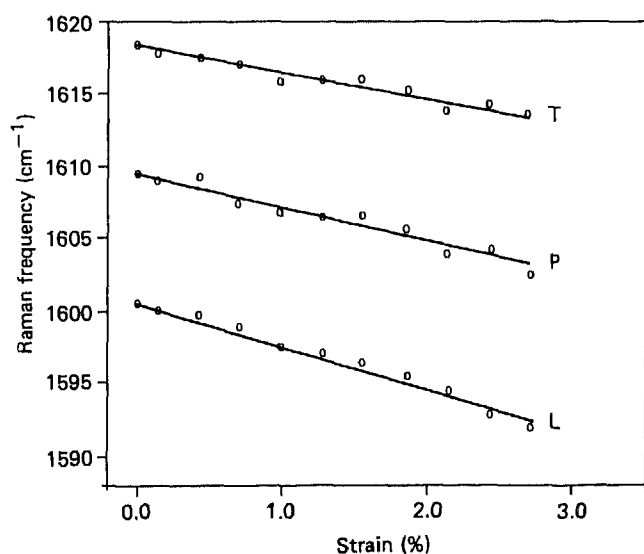


Figure 2 Strain dependence of the 1610 cm^{-1} Raman band for the medium modulus (MM) aramid fibre. L, P and T indicate the results for the leading edge, the peak and the trailing edge, respectively

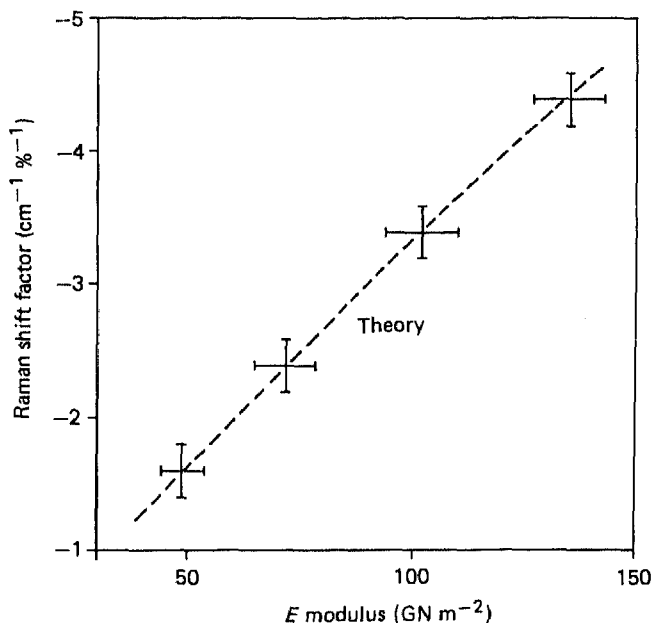


Figure 3 Raman shift factor as a function of the initial fibre modulus. The broken line is according to the theory for a total strain of 0.5%

Table 1 Results of mechanical and resonance Raman measurements on aramid fibres

Material	Modulus GN m^{-2}	Raman shift factor in $\text{cm}^{-1}/\%$		
		L	P	T
LM	49	-2.4	-1.6	-1.2
MM	72	-3.0	-2.4	-1.8
HM	102	-3.8	-3.4	-2.6
HT	135	-5.7	-4.4	-3.8

Because of the orientation distribution individual chains are stretched differently depending on their orientation. This gives rise to a distribution of Raman shifts and hence to the observed peak broadening.

Conclusions

The change in frequency in the 1610 cm^{-1} Raman band per percent applied fibre strain depends on the initial fibre modulus. This dependence is due to the fact that there are two mechanisms that contribute to the elastic extension in aramid fibres: a crystallite stretching parallel to the chains and a crystallite rotation due to a shearing deformation. With Raman spectroscopy only the stretching mode is measured. The results are in good agreement with a model describing the deformation in aramid fibres in terms of these two processes.

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