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Stress induced twinning of polydiacetylene single crystal fibres in composites

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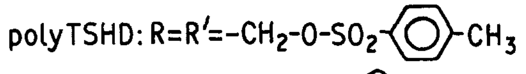
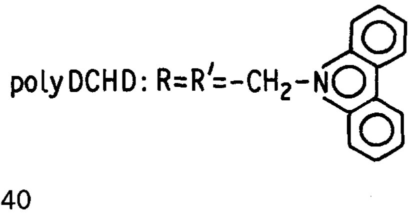
Scanning electron microscopy has been used to show that twins induced by compression of DCHD-polydiacetylene fibres occur on a single crystallographic plane. Other twinning modes appear to be prohibited by the nature of the sidegroup packing. Under the optical microscope identical twinning patterns have been observed on fibres in composite specimens where matrix shrinkage had been induced by post-curing the epoxy at 100° C. Resonance Raman spectroscopy has been used to monitor the strain in a single fibre embedded in an epoxy matrix which was subjected to uniaxial compressive stress. The initiation of twinning was found to occur when the axial strain in the fibre was approximately 0.2%.

1. Introduction

In compression a reinforcing fibre in a composite is in unstable equilibrium since the applied stress can be relieved by buckling of the fibre. The critical stress required to initiate buckling can thus be a major factor in determining the compressive strength of the composite. This is certainly the case for composites containing fibres such as Kevlar 49 which possess a very high degree of mechanical anisotropy [1–9]. Compressive failure of Kevlar 49 composites has been found to occur at strains of approximately 0.3% and be accompanied by the appearance of kink bands on the surface of the fibres. Within a kink band the polymer chain direction was found to deviate abruptly from the fibre direction with the angle of deviation varying considerably among different kink bands.

Polydiacetylenes are another type of fibre with anisotropic mechanical properties which have been considered for use in composites [10]. The single crystals produced by the solid-state polymerization of various diacetylene monomers have provided a model system for the study of the mechanical properties of crystalline polymers [11]. The polymer chain has the structure $\nmid \mathrm{RC{-}C{\equiv}C{-}CR'} \nmid_n$ where R and R′ are the sidegroups. Where needle-like crystals have been produced the polymer chain has been found to be parallel to the long dimension. The mechanical anisotropy thus arises from having covalent bonds in the fibre direction and van der Waals' bonding in the transverse direction. Two of the most studied polydiacetylenes have sidegroups with the chemical formulae


(1)


(2)

Both types of polymer crystal have the crystallographic structure $P2_1/b$ (in the second setting) with the polymer chain parallel to the c-axis [12, 13].

Deformation of polydiacetylene crystals has, like Kevlar 49, produced kink-like bands on the surface. In contrast to Kevlar 49 the bands on polyTSHD single crystals have been found by optical and electron microscopy and electron diffraction to be crystallographic twins [14–16]. Twinning planes have been identified and good agreement has been found between the measured angles of chain rotation and those predicted by crystallographic analysis. In a few cases it was noted that the twins disappeared after several weeks storage of the crystals; this suggested the twin deformation was reversible.

In the present paper this study is extended to investigate the twinning modes of polyDCHD single crystal fibres. To study the effects of compressive stress on polyDCHD composites both single and multiple fibre specimens have been prepared with an epoxy matrix. In the initial experiments the stress was introduced by post-curing the specimens at 100° C where matrix shrinkage might be expected. Previous experiments on Kevlar 49/epoxy composites had demonstrated that matrix shrinkage could cause the formation of kink bands [8, 9]. More controlled compressive stresses have been applied to a single fibre specimen by mechanically loading it in the fibre direction. The strain in the fibre was monitored by resonance Raman spectroscopy. Previously it had been demonstrated that the atomic vibrational frequencies of polydiacetylene single crystal fibres decrease approximately linearly with increasing elastic strain in the polymer chain direction [17–19]. The establishment of a strain-frequency relation has enabled us to use the fibre as an internal molecular strain gauge.

2. Experimental details

Needle-like crystals of the disubstituted diacetylene

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1,6-di(N-carbazolyl)-2,4-hexadiyne (DCHD) were prepared from toluene solution by slow evaporation of the solvent [20, 21]. Crystals of uniform diameter and free from obvious defects such as twins or cracks were polymerized by exposure to 30 to 40 Mrad of ^{60}Co γ-radiation. Typical crystal fibres were approximately hexagonal in cross section, 15 mm long and 50 μm thick. The polymer chain was along the fibre axis, the [0 0 1] direction, with (0 1 0), (2 1 0) and $(2\,\bar{1}\,0)$ facets on the long sides of the crystals [11].

Isolated twins were introduced into the crystals by bending them a few degrees about an axis perpendicular to the polymer chain direction. Much greater densities of twins were produced by tying a fibre into a tight knot.

Single fibre composite specimens were prepared with Ciba-Geigy HY 1927 two-part solvent-free cold-setting epoxy using 100 parts of resin to 36 parts of hardener by weight. It had been previously demonstrated that polyDCHD fibres bond well to an epoxy [22]. The PTFE mould was filled with epoxy and the fibre aligned in the centre to within $\pm 5°$ of the direction of applied stress using fine needles and a stereo microscope. The specimens were allowed to set and cure at room temperature for 1 week before the surfaces were polished to give good optical transmission. Finally, thin film resistance strain gauges of gauge factor 2.15 were attached to the surface of the specimen at the centre of the fibre. The matrix strain could thus be measured to an accuracy of $\pm 0.01\%$.

Compressive and tensile stresses were applied to the composite specimens in the fibre axial direction by a small loading device [19]. Optical micrographs were taken of specimens under load by placing the device on the stage of a Zeiss photomicroscope. The resonance Raman spectra were measured with 180° backscattering geometry using a double monochromator and photon counting system [23] with the 632.8 nm line from a 10 mW HeNe laser. The 2085 cm^{-1} Raman line of the polyDCHD fibres could be measured with an absolute accuracy of $\pm 2\,\mathrm{cm}^{-1}$, with shifts in the frequency usually measured with greater precision. The frequency of this Raman line had been found to decrease by $19.7 \pm 0.4\,\mathrm{cm}^{-1}$ for a 1% tensile strain [19]. Using this calibration it was possible to determine the strain of the fibre in the composite to $\pm 0.1\%$.

3. Results and discussion

3.1. Identification of twins

A large number of twinned fibres were examined in the scanning electron microscope and Fig. 1a shows a typical example. Contrary to the experience with polyTSHD where several different modes of twinning were found [14], only a single twin type was found in polyDCHD fibres. The K_1 plane that defines the interface between twinned and parent crystal in this case was $(2\,\bar{1}\,2)$ with the twins leaving traces on the crystal surface very similar to those shown in Fig. 6 of [14] for the $(2\,\bar{1}\,2)$ twin on the surfaces of polyTSHD fibres. For this twin the K_2 plane that defines the rotated plane of the simple shear is $(2\,\bar{1}\,0)$ and for the polyDCHD crystal structure the magnitude of the shear, s, of the twin is 0.6. A sketch of the $(2\,\bar{1}\,2)$ twin at the molecular level in polyDCHD is shown in Fig. 1b.

The existence of a single $(2\,\bar{1}\,2)$ twin is probably due to the structure of the polymer chain; the planar backbone and bulky sidegroups make it difficult to kink the molecule in certain directions. Fig. 2 shows a projection of the molecular arrangement of polyDCHD onto the a–b plane with the polymer chain direction perpendicular to the figure [24]. The molecular cross-section resembles a squat "H" in shape with the plane of the polymer backbone lying in the cross piece of the H. The structure of the polymer chain thus has some semblance to a ribbon and clearly it must be easier to bend the ribbon about an axis in its plane than one perpendicular to it. The traces of the K_2 twin planes which are also indicated in Fig. 2 confirm this expectation. The $(2\,\bar{1}\,0)$ trace defines the axis of rotation of the polymer chain for the $(2\,\bar{1}\,2)$ twin; clearly this is the easy axis of rotation for a ribbon-like structure. The constraints of molecular packing thus appear to prohibit the formation of the (0 1 2) twin which has the more favourable shear of 0.4.

Fig. 3 is a scanning electron micrograph of a polyDCHD fibre which has been tied in a tight knot.

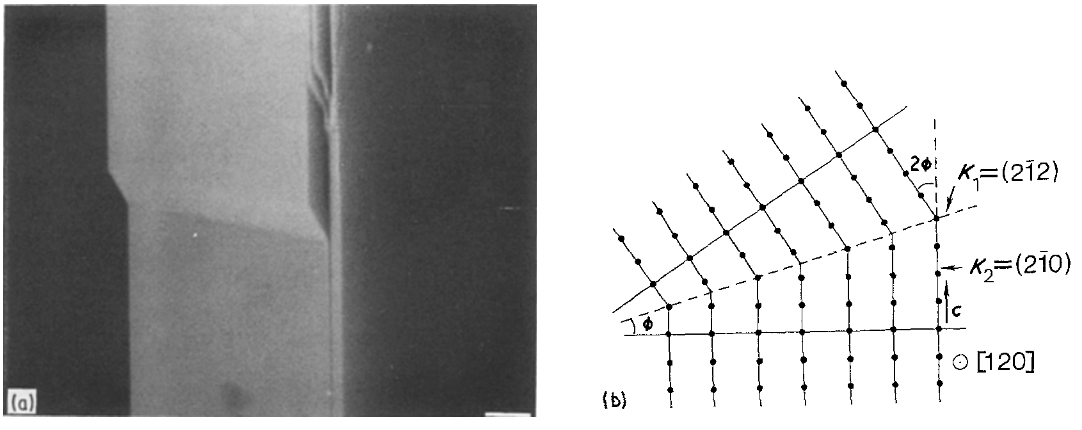

Figure 1 (a) Scanning electron micrograph of a $(2\,\bar{1}\,2)$ twin on the $(2\,\bar{1}\,0)$ face of a polyDCHD single crystal. The viewing direction is approximately normal to the (2 1 0) face in the right side of the micrograph. The scale bar represents 2 μm. (b) Schematic illustration of the $(2\,\bar{1}\,2)$ twin viewed in the plane of the shear. The K_1 and K_2 twinning planes are perpendicular to the plane of the figure. The angle of chain rotation, 2ϕ, is equal to 33.6°.

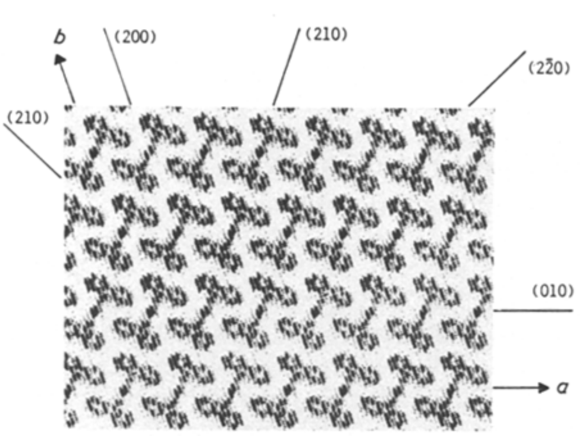

Figure 2 Projection of the molecular structure of polyDCHD onto the *a–b* plane [24]. The major axes and traces of the K_2 twin planes are indicated.

In this case of extreme deformation the compressive stress is still relieved by twinning in the single $(2\bar{1}2)$ mode. Some delamination of the fibre can be seen but less structural damage has occurred than has been observed on Kevlar 49 fibres treated in the same manner [3, 7].

The importance of the polymer chain in determining the allowed twinning mode is emphasized by the fact that several different types of twin have been observed in DCHD monomer crystals [25]. Twins with K_1 planes (0 1 2), (2 0 2), (0 2 2), and (2 1 2) have been detected as well as the $(2\bar{1}2)$ which were the most numerous. In polyTSHD crystals the most common twin has the K_1 plane (0 1 2). The plane of the backbone in polyTSHD has different crystallographic indices than that in polyDCHD. As for polyDCHD the bending of the polymer backbone for the (0 1 2) twin in polyTSHD is about an axis which is perpendicular to the chain direction and nearly in the plane of the backbone.

3.2. Twinning induced by matrix shrinkage

Optical microscopy of the polyDCHD fibres indicated that they were unaffected by the epoxy matrix provided they were cured only at room temperature. By contrast Fig. 4a shows a transmission optical micrograph of a single polyDCHD fibre in an epoxy matrix which had been subjected to further curing at 100° C for 24 h. Numerous bands can be seen on this (0 1 0) crystallographic face. These have been identified as twins in which the K_1 twinning plane is $(2\bar{1}2)$ as was found for isolated polyDCHD fibres. The sharpness of the twin bands in the photographs shows that the twinning plane is approximately perpendicular to the (0 1 0) plane and that the bands are narrow, typically less than 10 μm wide. The appearance of the twins suggested that shrinkage of the matrix occurred during the high temperature cycle of the curing procedure. This suggestion was confirmed when the specimen was subjected to tensile stress. Figs 4b to d show the same region of the fibre as the matrix strain was increased from zero by applying a uniaxial tensile stress. With increasing strain the twin bands become fewer until by about 1% strain they have essentially disappeared. At this strain the shrinkage in the matrix has been overcome and the single crystal fibre restored to its original condition.

Figs 4e to g show the same region of the specimen as the applied tensile stress was removed. The elastic compressive stress of the matrix reasserted itself and twinning of the specimen again became apparent. The elastic nature of the twins is demonstrated by the fact that an almost completely different set of twin bands appeared on relaxation of the applied tensile stress. There is some evidence of hysteresis as for the same matrix strain the twin density is greater on unloading than loading. As the twin bands were not present in specimens cured at room temperature, Fig. 4 presents strong evidence that shrinkage of the epoxy matrix occurred during the post-curing at 100° C. Since the twin bands disappeared at approximately 1% tensile strain of the matrix then a similar degree of shrinkage must have occurred during that curing. Hence the degree of shrinkage of an optically transparent matrix could be determined by observation of an included polydiacetylene fibre.

3.3. Determination of the critical strain for twin formation

Measurement of the strain in the fibre by resonance

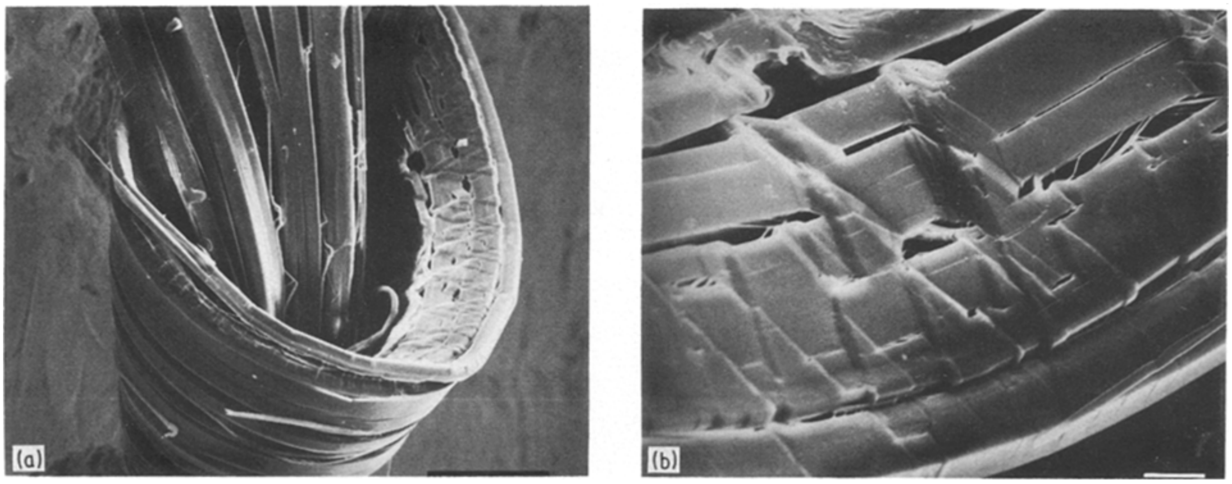

Figure 3 (a) Scanning electron micrograph of a polyDCHD fibre drawn into a tight knot. The scale bar represents 100 μm. (b) Detailed view of part of the knot. The scale bar represents 10 μm.

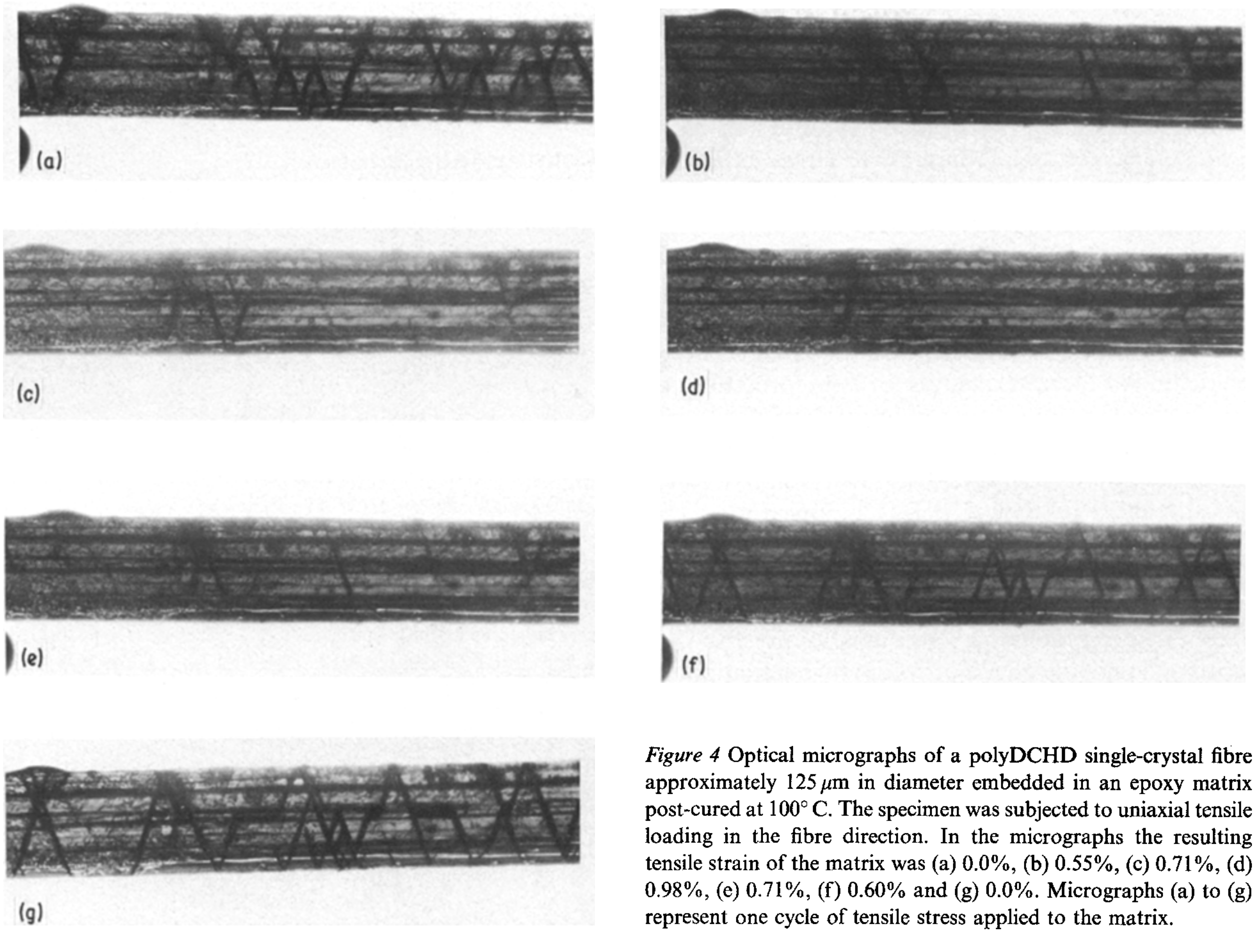

Figure 4 Optical micrographs of a polyDCHD single-crystal fibre approximately 125 μm in diameter embedded in an epoxy matrix post-cured at 100° C. The specimen was subjected to uniaxial tensile loading in the fibre direction. In the micrographs the resulting tensile strain of the matrix was (a) 0.0%, (b) 0.55%, (c) 0.71%, (d) 0.98%, (e) 0.71%, (f) 0.60% and (g) 0.0%. Micrographs (a) to (g) represent one cycle of tensile stress applied to the matrix.

Raman spectroscopy has determined the critical strain for twin formation during axial compression. Loading of a single-fibre composite specimen which had been cured at room temperature produced the results shown in Fig. 5. For an applied tensile stress the mid-point strain in the fibre was equal to the matrix strain within experimental uncertainty. Under a compressive stress the fibre strain was also compressive as the Raman frequency was observed to increase. The fibre strain approximately followed that of the matrix until at 0.22% compressive strain there was an abrupt levelling off with no further increase. Under the optical microscope we observed that twin bands began to appear on the specimen when this critical value of the compressive strain was reached.

There has been some uncertainty about the critical compressive strain for Kevlar 49 fibres as no direct measurement of that strain has yet been made. Estimates vary between 0.3 and 3% but the lower value appears to be the currently accepted one [9]. The high value of approximately 14 for the ratio of the longitudinal to transverse elastic modulus has been suggested as an important contributory factor to this low compressive strength. For polyTSHD sound velocity measurements indicate that the value of the ratio is between 5 and 8 [26]. PolyDCHD should have

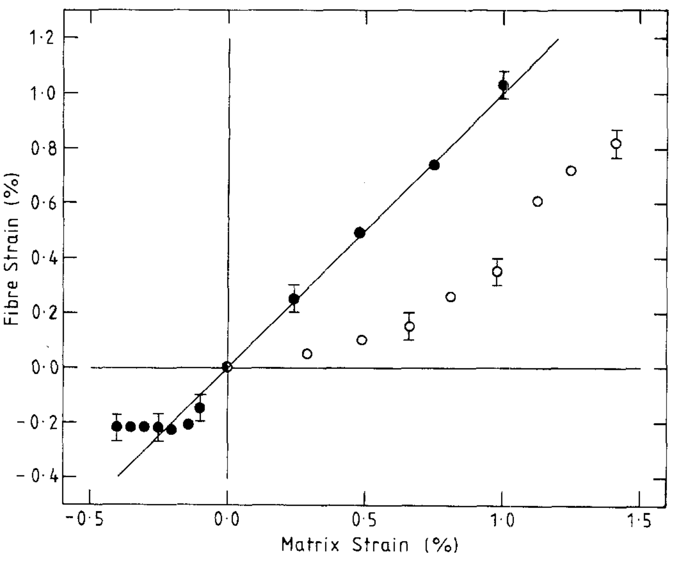

Figure 5 Axial strain at the midpoint of a polyDCHD fibre in an epoxy matrix as a function of tensile (positive) and compressive (negative) matrix strain. The closed circles represent the present data for a specimen cured at room temperature; (○) [19], Fig. 3, for a specimen additionally post-cured at 100° C. The straight line represents the case of equal fibre and matrix strains. The error bars indicate the uncertainty in the strain associated with locating the peak of the Raman band. This uncertainty was approximately the same for all points but for clarity only a few error bars are included.

a similar degree of anisotropy and yet appears to have a slightly lower compressive strength than Kevlar 49. Clearly there are more important factors in determining the compressive strength than the elastic anisotropy.

Most models for the buckling of fibres in composites subjected to a compressive stress assume a sinusoidal wave type of deformation [27]. These models have not been very successful in predicting the critical compressive strain for Kevlar 49 fibres which kink so it is unlikely that, as they stand, the models would have any greater success treating polydiacetylene fibres which twin. It has been suggested that accurate forecasting of the critical stress for twin formation, at least in metals, is impossible as it is probably linked to defect structure which can be extremely variable [28]. The succession of micrographs in Fig. 4 shows, however, that the twins in polyDCHD disappear when the compressive stress is removed and that on reapplication of the stress a new set of twins appears which is almost orthogonal to the original. This implies that defects in the fibre, which presumably are fixed in position, do not play a major role in twin initiation. A realistic model for stress initiated twinning in polyDCHD fibres will need to take into account the elastic properties of the matrix, the mechanical anisotropy of the fibre and, at the molecular level, an estimate of the work required to shear one plane of molecules past another.

Also shown in Fig. 5 are the results for the same experiment performed on a specimen which had been post-cured at 100° C. The strain of this fibre initially increased much more slowly with matrix strain than that in the specimen which was cured at room temperature. With the evidence in Fig. 4 it is now clear that most of the initial strain in the matrix was not converted into tensile strain of the fibre but instead effected removal of twins which had been introduced in the fibre by shrinkage of the matrix during curing. This effect could therefore also be used to measure shrinkage in composite specimens with an optically transparent matrix. The substantial lag of the fibre strain behind the matrix strain during the initial stages of the application of uniaxial tensile stress which was previously reported [19] was a consequence of the specimen preparation procedure. During the experiments reported in that paper the possibility of matrix shrinkage had been considered. It had been discounted, however, since it was expected that any shrinkage would result in compressive stress on the fibre which would be reflected by an increase of the Raman frequency. The present results show that the compressive stress was so great that it was essentially eliminated by crystallographic twinning so the observed Raman frequencies were similar to those appropriate to unstressed fibres.

4. Conclusions

PolyDCHD fibres have been shown to have a single twinning mode in which the K_1 twin plane is $(2\bar{1}2)$. This mode has been demonstrated to be a major mechanism of stress relief for fibres in polyDCHD/epoxy composites which are subjected to uniaxial compressive loading. Twin formation was induced both by direct loading and as a consequence of matrix shrinkage during curing. In the latter case the twin bands could be removed by the application of uniaxial tensile stress thus demonstrating their elasticity.

Acknowledgements

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