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Study of model polydiacetylene/epoxy composites

Part 2 *Effect of resin shrinkage*

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A model composite has been prepared consisting of a polydiacetylene single-crystal fibre in an epoxy resin matrix. The strain at points along the length of the fibre has been measured, using Raman spectroscopy, as a function of matrix strain and the post-cure temperature of the matrix. Good quantitative agreement has been found between the behaviour of the cold-cured system and the shear-lag model of Cox. The critical length of the fibres was measured as a function of fibre diameter and compared with recent calculations using finite difference methods. Higher post-cure temperatures have been shown to lead to compressive deformation of the fibres due to matrix shrinkage on cooling. The deformation is manifest as twinning, which disappears reversibly during tensile deformation. The amount of matrix shrinkage was determined by measuring the level of strain required to remove the twins. This was found to be in good agreement with the shrinkage determined from the linear thermal expansivity of the matrix.

1. Introduction

It was established in Part 1 of this series [1] that polydiacetylene fibre/epoxy composites are excellent model systems for the study of the micromechanics of composite deformation. It was shown that Raman spectroscopy could be used to measure the point-to-point variation of strain in a model system consisting of a polydiacetylene single-crystal fibre embedded in an epoxy resin matrix. The results of the study were compared with the theoretical analyses of Cox [2] and others [3, 4] where there was broad qualitative agreement. However, more recent work [5] has shown that shrinkage of the epoxy resin matrix can lead to reversible twinning of the polymer fibres which complicates the analysis of stress transfer.

In the present work a study has been made of the micromechanics of deformation in the model system using an epoxy resin cured at room temperature which eliminated the problems of shrinkage stresses. In addition, a systematic study has then been made of the effect of post-cure temperature upon the behaviour of the system so that the effect of matrix shrinkage can be quantified.

The compressive deformation of high-modulus polymer fibres through matrix shrinkage is a potential problem in any composite system consisting of high-modulus polymer fibres in a polymeric matrix. It is well-known that other types of fibres, such as Kevlar, are susceptable to failure by kinking [6] induced by compressive deformation which leads to such composites having poor compressive properties [7]. As there is a close relationship between twinning in polymer crystals and kink-band formation in fibres, the present study has enabled the model system to be used to follow the consequences of shrinkage.

2. Experimental details

2.1. Preparation and characterization of fibres

The substituted diacetylene monomer derivative, 1, 6-di-(*N*-carbazolyl)-2,4-hexadiyne (DCHD), was synthesized as described previously [8, 9]. Fibre-like monomer crystals were prepared by slow evaporation from toluene solution. The axial direction corresponds to the crystallographic *b*-axis and the sides and ends of the single-crystal fibres were faceted [10]. The cross-sections of the crystals were approximately hexagonal and diameters could be controlled in the 1 to 200 μm range by adjusting the rate of crystallization. However, a range of fibre diameters was invariably produced. The fibre diameters were calculated for equivalent fibres with a cylindrical cross-section and the same cross-sectional area as the DCHD fibres. The fibre lengths were in the range 1 to 15 mm.

Individual uniform DCHD fibres of appropriate dimensions and free from any obvious defects were selected for use in the single-fibre composites. The DCHD fibres were polymerized by exposure to 35 to 40 Mrad ^{60}Co γ-radiation. The polymer chains (polyDCHD) form parallel to the long axis of the fibres as a result of the topochemical reaction, thus creating single-crystal fibres [9]. The fibres have a Young's modulus of 45 ± 1 GPa in the axial direction

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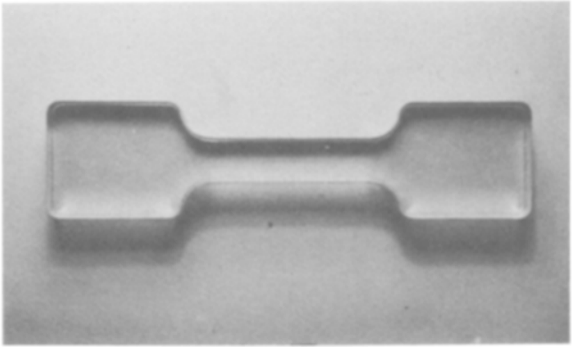

Figure 1 Epoxy resin tensile specimen containing a single polyDCHD fibre.

[10]. The values of Young's moduli in other directions are expected [11] to be significantly lower, but they have not yet been measured for polyDCHD.

2.2. Single-fibre composites

Single-fibre composites were prepared as before [1] using Ciba-Geigy XD927 two-part solvent-free cold-setting epoxy resin, using 100 parts (by weight) of resin to 36 parts of hardener. It had been demonstrated previously [12] that polyDCHD fibres bond well to the resin and that the epoxy resin is sufficiently transparent and free from fluorescence that Raman spectra could be measured for embedded fibres. A "dog bone"-shaped PTFE mould was half-filled with the resin/hardener mixture and allowed to set partially before the fibre and the rest of the epoxy were added. In this way a tensile specimen could be produced with fibre aligned within ± 5° of the axial direction at the centre of a 6 mm thick section as shown in Fig. 1. After setting for 24 h at room temperature (24 ± 3° C), thin film resistance strain gauges of gauge factor 2.1 were attached with adhesive to the surface of the specimen at the centre of the fibre. It was possible to measure matrix strain to an absolute accuracy of ±0.01% with a DVM. Some specimens were post-cured for 24 h at various temperatures up to 150° C.

All specimens were polished to give smooth, transparent surfaces and holes were drilled at both ends to accommodate the clamps used to apply the tensile stress. After completion of the measurements, the specimens were sectioned at several points to determine the fibre diameters. The Young's modulus of the matrix was determined to be 2.8 ± 0.1 GPa at room temperature from measurements upon dummy specimens, without fibres, deformed in a mechanical testing machine.

2.3. Raman spectroscopy

A small tensile loading device was used to apply stress in the fibre direction. The device was mounted on a micrometer slide so that the whole length of the specimen could be traversed through the incident laser beam. The Raman spectra were obtained with 180° backscattering geometry using a double monochromator and photon counting system [13]. Two types of radiation were employed; the 676 nm line of a krypton-ion laser and the 638 nm line of a helium/neon laser. Results obtained using the two types of laser were essentially identical. A focal spot size of about 25 μm and beam power of 5 mW were used in both cases. This enabled good spectra to be obtained without damaging the fibre through excessive heating.

Earlier studies had demonstrated that intense Raman spectra can be obtained from polydiacetylene fibres and that the 2085 cm^{-1} Raman line of polyDCHD single-crystal fibres shifts to a lower frequency when the crystals are subjected to a tensile strain [14]. A Raman spectrum is shown in Fig. 2 for a polyDCHD fibre, the shift of the 2085 cm^{-1} line is -19.7 ± 0.4 cm^{-1}/%. Because the position of the line can be measured to ±2 cm^{-1} the strain in polyDCHD fibres can be measured to an absolute accuracy of ±0.1%. Because the epoxy resin is essentially transparent to the laser beam, measurements can be made from regions of 25 μm diameter on fibres inside composites. Because the effective skin depth for Raman scattering at around 650 nm is only about 10 nm for polyDCHD [13] the Raman technique measures strain at the surface of a polyDCHD fibre.

3. Micromechanics of deformation

3.1. Distribution of strain along a fibre

The distribution of strain along a single polyDCHD fibre (~ 110 μm diameter) is shown in Fig. 3 for three different levels of applied matrix strain (0%, 0.5% and 1.0%). It can be seen that when the matrix is deformed the strain increases from the end of the fibre and then saturates along the central portion such that the fibre and matrix strain are equal ($e_f = e_m$) within experimental accuracy. The length over which the fibre strain rises from the value at the end to that of the

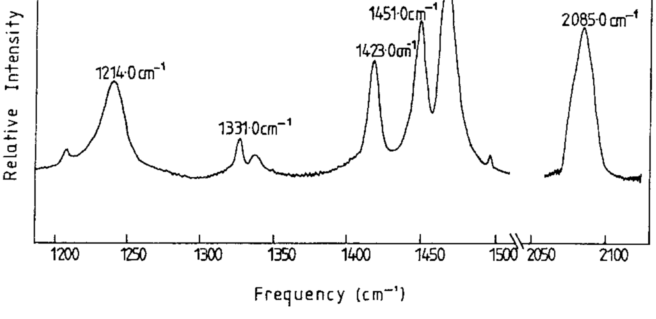

Figure 2 Raman spectrum obtained from a single polyDCHD fibre showing the position of the main peaks.

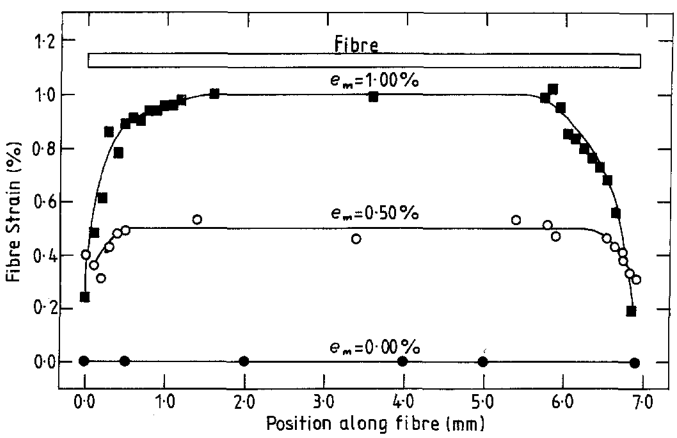

Figure 3 Variation of fibre strain with position along the fibre for three different levels of applied matrix strain.

central section is equivalent to half of the "critical length", l_c. This length is closely related to the critical length determined from fibre pull-out tests [15], although the Raman technique enables it to be measured elastically without the necessity of fracturing fibres.

It appears from Fig. 3 that the critical length increases with the level of applied strain. Analyses of the micromechanics of fibre deformation in composites [2–4] invariably assume that the deformation of both the fibres and the matrix is linear elastic. However, in the regions of high stress concentration at the fibre ends it is highly likely that the matrix may undergo inelastic or plastic deformation. The effect of this will be to lead to an increase in critical length with increasing fibre strain. Non-linear deformation and yielding may be a particular problem in the potentially under-cured, cold-cured resin used in this present study, although the stress/strain curve of the resin was not found to be significantly different from that of the same resin post-cured at 100° C.

The behaviour of the single-fibre specimen in Fig. 3 should be contrasted with similar specimens used in Part 1 of this series [1]. Although the behaviour appears qualitatively to be similar, it was found earlier [1] that when the epoxy resin was post-cured at 100° C the fibre strain way always substantially less than the matrix strain ($e_f < e_m$). A recent study [5] has shown that shrinkage of the epoxy resin matrix during curing causes axial compression in the fibres leading to fibre twinning. An application of tensile strain to the specimen must first of all untwin the fibre before subjecting it to tension. The twins are elastic and are found to reform when the applied strain tension is removed. Hence the fibre strain is always less than the matrix strain during the deformation of hot-cured samples. The fibre embedded in the specimen used in this present study was examined optically before deformation and was found to contain no twins. Hence close strain matching between the central region of the fibre and the matrix was obtained.

3.2. Determination of critical length

It was demonstrated in Part 1 [1] that the model of Cox [2] and dimensional analysis both predict that the critical length, l_c, should be proportional to the fibre diameter, d. Fig. 4 gives a plot of critical length against fibre diameter for the single-fibre cold-cured samples. The critical length in this case was defined as twice the length over which the fibre strain increases to reach 99% of its value at the fibre mid-point; the measurements being made at a matrix strain of 1.0%.

The transfer of stress between the matrix and fibre in single-fibre composite samples has recently been analysed theoretically by Termonia [16] using finite difference techniques. He showed that the slope of a plot, such as Fig. 4, depends upon the ratio of fibre to matrix modulus E_f/E_m. The slope increases as E_f/E_m increases and is approximately 30 for our present system where E_f = 45 GPa [10] and E_m = 2.8 GPa. It can be seen, although there is scatter in the data, that the measured critical length increases with diameter, but falls below the theoretical line. It is clear from Fig. 3 that the situation is considerably more

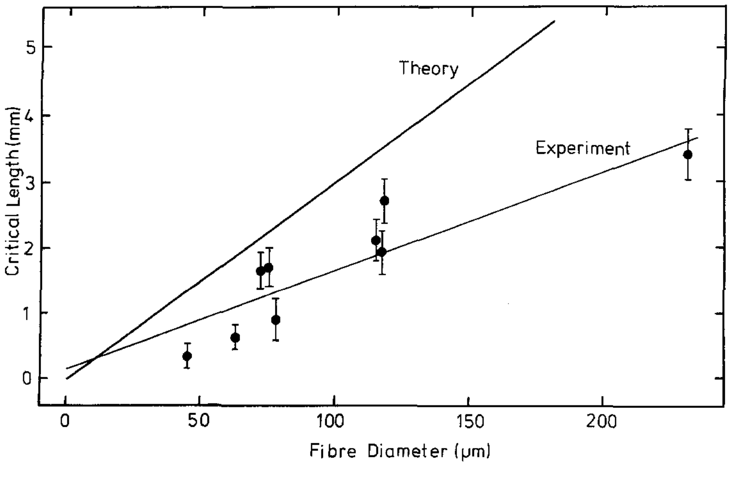

Figure 4 Variation of critical length with fibre diameter. The experimental line is a least-squares fit of the data. The theoretical line is due to Termonia [16].

complicated than assumed by theoretical analyses. For example, the critical length appears to increase with increasing matrix strain whereas the elastic analyses of Termona [16] and Cox [2] do not predict this. They assumed linear elastic behaviour with no yielding and their elastic analyses will not strictly be valid for the present situation. It is clear that the theoretical analyses will have to be modified to take into account non-linear and plastic deformation so that real systems can be modelled.

It is important to point out at this stage that the critical length, l_c, measured in the present study is not the same as the critical length measured using pull-out tests. This is also often assigned the symbol l_c, but is given by the well-known relationship [17]

$$\frac{l_c^*}{d} = \frac{\sigma_f}{2\tau} \qquad (1)$$

where d is the fibre diameter, σ_f is the fibre fracture strength and τ is the interfacial shear strength. In this case l_c^* is actually a "pull-out length" and the asterisk denotes the difference. It is a function only of the fibre strength and interfacial shear strength.

The present study, earlier work by the authors [1] and the work of Termonia [16] have shown that l_c/d depends only upon the fibre modulus, E_f, and matrix modulus, E_m. In this case l_c is really an "elastic transfer length" and it does not depend directly upon either σ_f or τ. Unless this careful distinction is made, anomalies arise. For example, of τ is altered by changing surface treatment of the fibres, then Equation 1 clearly shows that l_c^*/d will change. However, the elastic transfer length l_c will not change because it is a function principally of E_f and E_m.

Hence, the term "pull out length" is only applicable to the fracture of a composite specimen where fibre fracture and/or pull-out take place. On the other hand, the elastic transfer length, measured in this present study, is applicable only to the elastic deformation of composites and relates only to the elastic transfer of stress between the matrix and fibre.

3.3. Resin shrinkage

It is clear from the observation highlighted in Section 3.1 that resin shrinkage has an important effect upon the micromechanics of the deformation of single-fibre composites. Because of this, a systematic study was made of the dependence of the strain at the fibre mid-point upon the temperature of post-curing. The measurements are shown in Fig. 5, where the strain in the centre of the fibre is plotted against the matrix strain for different post-cure temperatures. It can be seen that for the room-temperature cured specimen $e_f = e_m$ but that as the post-curing temperature is increased e_f becomes significantly less than e_m. This mismatch in strain was found to correlate with the appearance of shrinkage-induced twins in the fibres.

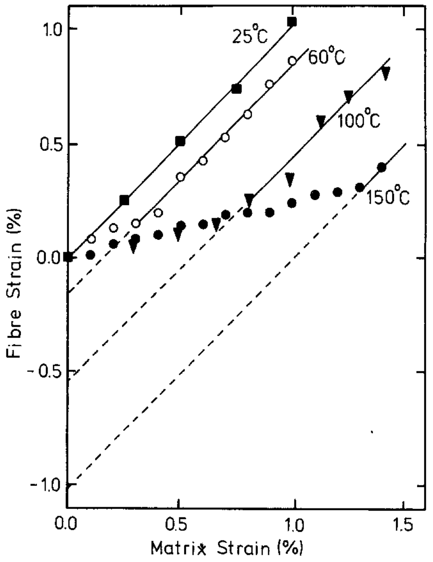

Figure 5 Variation of fibre strain (e_f) with applied matrix strain (e_m) for four different post-cure temperatures. The extrapolation back to $e_m = 0$ gives the shrinkage strain (e_s).

It is possible to quantify the degree of resin shrinkage by analysing further the data in Fig. 5. In the high-temperature-cured specimens the fibre strain increases slowly as the matrix strain is increased until a certain level of strain when the increase in e_f becomes parallel to the $e_f = e_m$ line. This region of relatively slow increase corresponds to the untwinning of the fibre and so the point at which the more rapid increase occurs corresponds to the point at which the twins have been removed and the fibres are subjected to tensile straining. Hence, extrapolating the data back to $e_m = 0\%$ allows the level of compressive strain due to the matrix shrinkage (e_s) to be quantified. Fig. 6 gives a plot of e_s against ΔT, the difference between the post-cure temperature and room temperature ($\sim 25^\circ$ C). It can be seen that these data fall upon a straight line with an intercept upon the ΔT axis. However, it is necessary to point out that it was found in a previous study [5] of twinning in this system that a critical compressive strain of the order of 0.2% is necessary to induce twinning in polyDCHD fibres. Hence, in order to gain a more accurate idea of the resin shrinkage, 0.2% must be added to e_s. This has also been done in Fig. 6 and it can be seen that the data fall on a straight line which now passes through the origin. The slope of the line is $1 \times 10^{-4}\,K^{-1}$. It implies that Fig. 6 is essentially a measure of the linear thermal expansivity of the epoxy resin matrix, because

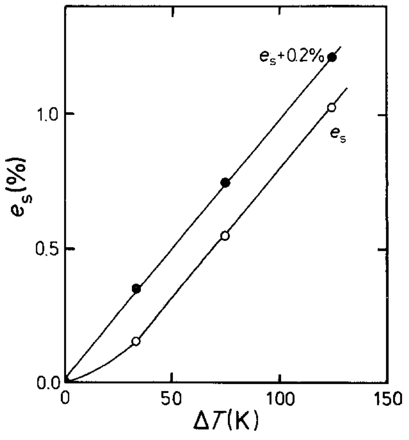

Figure 6 Variation of shrinkage strain (e_s) with ΔT, the difference between the post-cure temperature and room temperature. (○) e_s (●) e_s + 0.2%.

it is known that the expansivities of polydiacetylenes in the chain direction are nearly a factor of 100 smaller [18].

The picture that emerges is, therefore, as follows. During the room-temperature curing process, the epoxy resin hardens, but there is very little shrinkage during this period to put the fibres under stress and so they are virtually twin-free. Any shrinkage would appear to be taken up by relaxation in the curing system. Important changes do take place when the specimen is heated to the post-cure temperature. Further curing takes place and the resin relaxes again. However, it appears that it is the resin shrinkage during cooling, from the post-cure temperature back to room temperature, that causes considerable internal stresses leading to axial compression in the fibre and twinning to occur.

It would seem that this quantitative measurement of the consquences of resin shrinkage should be of considerable significance for polymer fibre-reinforced polymer–matrix composites, such as Kevlar/epoxy composites. For example, it may be possible to screen resin systems and produce optimum cure cycles which minimize the shrinkage stress when they are employed as composite matrix materials.

4. Conclusions

It has been demonstrated that the single-fibre composite systems used in this present study are excellent models for the study of the micromechanics of composite deformation. In particular, it has been shown that good quantitative agreement can be obtained from the distribution of stresses in a fibre with those determined from theoretical models.

It has also been shown that resin shrinkage has an important effect upon the micromechanics of deformation in the model composite system. The shrinkage is due to a thermal expansion mismatch between the fibres and the matrix and occurs when the system is cooled down from the post-cure temperature. It causes compressive deformation of the fibres which leads to twinning. The twinning is reversible and is removed when the fibres are subjected to tensile deformation. The levels of shrinkage and twinning are found to increase with cure temperature and the thermal expansivities of $1 \times 10^{-4}\,\mathrm{K}^{-1}$ estimated from this present study are similar to those determined using conventional methods.

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