The solid-state polymerization and physical properties of bis(ethyl urethane) of 2,4-hexadiyne-1,6-diol: 3. Mechanical properties

C. Galiotis and R. J. Young

Department of Materials, Queen Mary College, Mile End Road, London, E1 4NS, UK (Received 3 November 1982)

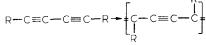
The mechanical properties of partly and fully polymerized single-crystal fibres of a substituted polydiacetylene have been investigated. In particular the Young's moduli, fracture stresses and creep properties have been measured. The Young's modulus was found to increase with conversion from monomer to polymer up to a maximum value of 62 GPa. The fracture stress was found to vary with both the degree of conversion and fibre diameter. Strengths of up to 1.4 GPa have been determined for fully polymerized, 20 μ m diameter fibres. It has not been possible to detect any creep or time-dependent deformation for the fibres. The variation of the mechanical behaviour with conversion from monomer to polymer has been explained in terms of the Voigt and Reuss models and related to the structure of the crystals. The dependence of the fracture stress upon fibre diameter has been accounted for in terms of the presence of defects upon the surface of the crystals.

Keywords Polydiacetylenes; mechanical properties; deformation; fracture; fibres; defects

INTRODUCTION

Much effort has been expended over recent years in obtaining molecular extension and alignment in solid polymers with the aim of exploiting the high strength and stiffness of the covalently bonded backbone. It is expected that an extended polymer chain such as that of polyethylene should have a stiffness similar to that of steel¹. Some of this potential is realized to a limited extent in conventional polymer fibres but there have been recent advances in the preparation of high-modulus aromatic polyamide² and aromatic polyester³ fibres by solution spinning and melt spinning respectively. The molecules in these polymers tend to be rigid and rod-like and the strongest fibres appear to be obtained if the solutions or melts have liquid crystal structures^{2,3}. Another way of making high-modulus polymers is by producing samples of a polymer such as polyethylene which has a high crystal modulus in the chain direction, and in which there is a very high degree of molecular alignment. This has been achieved by tensile drawing of solid polymers^{4,5} or a polymer gel⁶, solid-state extrusion^{5,7} and extensional flow in solution⁸.

The present study is concerned with the preparation and deformation of polydiacetylene single-crystal fibres made by the solid-state polymerization of substituted diacetylene monomers^{9,10}. The general polymerization reaction¹⁰ is:



The derivative studied in this present investigation was a symmetric diacetylene derived from 2,4-hexadiyne-1,6-diol with:

$$R = -CH_2 - O - C - N - C_2H_5$$

0032-3861/83/081023-08\$03.00 © 1983 Butterworth & Co. (Publishers) Ltd The polymer of this ethyl urethane derivative will be referred to as poly-EUHD. The monomer was synthesized and purified and fibres were grown from a variety of solvents. They were then polymerized and their mechanical properties evaluated. A previous study by Baughman *et al.*⁹ has indicated that polydiacetylene single-crystal fibres have interesting mechanical properties. In this present investigation the factors controlling the Young's modulus and fracture strength, and creep behaviour of poly-EUHD fibres have been examined in detail.

EXPERIMENTAL

Fibre preparation

The chemical synthesis and purification of the EUHD derivative has been described elsewhere¹¹. Monomer fibres were produced by crystallization of the EUHD monomer from an acetone/petroleum ether mixture or distilled water. Details of the crystallization conditions have also been given elsewhere^{11,12} and monomer fibres $10-100 \,\mu\text{m}$ in diameter and up to 5 cm long were obtained (*Figure 1*). The crystals to be used for mechanical testing were selected in the monomer state and any split or tapering fibres were excluded. Some fibres were polymerized using γ -rays from a ⁶⁰Co source at a rate of 1 Mrad h⁻¹. Other fibres were polymerized thermally by heating at 80°C for different lengths of time. The degree of conversion to polymer was by determined extraction of the monomer using suitable solvents¹².

Mechanical testing

Partly and fully polymerized fibres were mounted across holes between 10 mm and 20 mm in diameter (depending upon fibre length) in rectangular paper tabs 0.22 mm thick. The fibres were bonded to the paper with 'Durofix'TM adhesive. The tabs were suspended between

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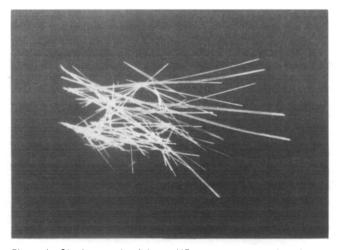


Figure 1 Single crystals of the EUHD monomer crystallized from distilled water

spring-loaded fibre testing jaws attached to an Instron mechanical testing machine. After the fibres in the tabs had been carefully aligned the edges of the tabs were burnt away so that the fibres could be stressed parallel to their length.

The fibres were deformed at different strain rates of between 0.002 and 0.02 min^{-1} using load cells with a maximum capacity of 0.05 kg or 1 kg. The extension of each fibre was measured directly by monitoring the movement of marks on the gauge length of the fibre using a travelling microscope fixed firmly to the body of the testing machine. The extension could be measured to an accuracy of ± 0.005 mm giving an error of $\pm 5\%$ at 1% strain for a 10 mm gauge length.

The load was recorded automatically on a chart as a function of crosshead displacement. The stress was calculated from the load divided by the original cross-sectional area of the fibres. This area was determined by examining each fibre after failure in a scanning electron microscope (JEOL 50A) and measuring the dimensions of the undamaged part. The cross-sections of the fibres were approximately square and the size of the facets and the angle between them was determined for each fibre. The crystal sizes are all quoted as 'effective diameters', i.e. the diameter of a cylindrical fibre with the same cross-sectional area. These measurements gave an error in the stress of the order of $\pm 5\%$.

Room-temperature $(22^{\circ} \pm 2^{\circ}C)$ creep tests were also performed on the same Instron mechanical testing machine. However, in this case the instrument was switched off and the load applied by hanging a known weight from the fibre. The extension of the fibre was again monitored, using a travelling microscope, to an accuracy of ± 0.005 mm.

RESULTS

Stress-strain curves from both partially and fully polymerized EUHD fibres were obtained for monomer crystallized from different solvents and polymerized using either heat or γ -rays. The Young's modulus E was determined from the initial slope and the fracture stress $\sigma_{\rm f}$ from the maximum stress.

Stress-strain behaviour

Stress-strain curves for a thermally polymerized and a γ -ray polymerized poly-EUHD fibre are given in Figure 2a and b respectively. The curve for the thermally polymerized fibre is linear up to a strain of about 1.5% with a slight decrease in slope above this strain. In the case of the γ -ray polymerized fibre (Figure 2b) the curve is linear up to the relatively low fracture strain of $\sim 1.2\%$. In both cases the loading and unloading points followed the same path, showing no hysteresis. Stress-strain curves were also obtained for partly polymerized EUHD fibres. The slopes of the curves and fracture stresses were found to increase with increasing degree of conversion to polymer, but for fibres of similar dimensions the fracture strain was found to be approximately constant.

Young's modulus

Table 1 gives measured values of Young's modulus E for different types of fully polymerized poly-EUHD fibres.

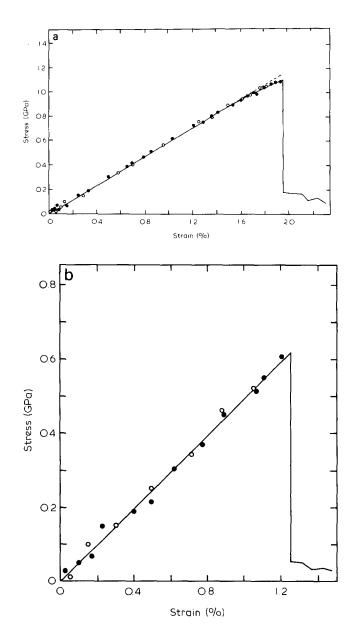


Figure 2 Stress-strain curve for a poly-EUHD fibres. The closed circles are for loading and the open ones for unloading. (a) Thermally polymerized fibre (23.3 μ m diameter); (b) γ -ray polymerized fibre (24.9 μ m diameter). (Strain rate=0.01 min⁻¹)

Fibre	Young's modulus,* E (GPa)	Effective diameter, d (µm)	Mean Youngʻs modulus, E (GPa)
EUHD water crystallized,	55.6	74.3	
98% polymerized (thermally)	59.2	98.3	
	60.7	45.9	
	62.3	141.0	61.5 ± 3.3
	63.4	111.2	
	64.5	86.5	
	64.8	62.1	
EUHD acetone/petroleum ether crystallized, 98% polymerized (thermally)	55.9	26.2	
	58.6	65.0	
	58.8	23.3	
	60.3	14.5	60.3 ± 2.5
	60.4	31.9	00.3 ± 2.5
	62.2	48.9	
	62.4	21.3	
	63.6	51.1	
EUHD acetone/petroleum	42.2	20.7	
ether crystallized, 99.5%	48.1	15.3	
polymerized (γ -rays)	49.5	24.9	49.4 ± 4.8
	53.3	51.8	
	54.1	42.0	

Table 1Measured values of Young's modulus for different fullypolymerized EUHD fibres

* Strain rate $\sim 0.01 \text{ min}^{-1}$

It is found that there is no systematic variation of modulus with fibre diameter but the modulus is found to depend upon the method of polymerization. Thermally polymerized fibres are found to have a modulus of 61 ± 3 GPa with no significant dependence upon the type of solvent used to crystallize the monomer fibres. On the other hand, γ -ray polymerized fibres have a significantly lower modulus of 49 ± 5 GPa. The modulus of the polydiacetylene fibres increases with the degree of conversion C_p (by mass) from monomer to polymer. A plot of modulus as a function of C_p is given in *Figure 3* for both γ -ray and thermally polymerized fibres, and again there is a clear increase of *E* with C_p . However, it is found for all conversions that thermally polymerized fibres have higher values of *E* than γ -ray polymerized ones.

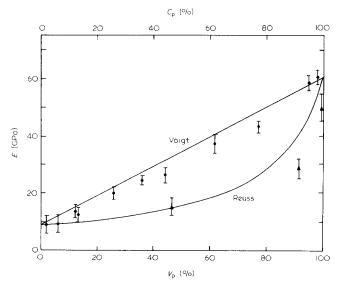


Figure 3 Variation of Young's modulus with conversion to polymer (C_p) and volume fraction to polymer (V_p). The circles are for thermally polymerized fibres and the triangles for γ -ray polymerized ones

No dependence of E upon strain rate was detected for any of the fibres.

Fracture stress

The fracture stress of the EUHD fibres was found to depend upon both the fibre diameter and the degree of conversion to polymer. The variation of σ_f for fully (thermally) polymerized poly-EUHD fibres with effective fibre diameter d is shown in *Figure 4*. There is an obvious decrease in σ_f with increasing diameter. The dependence of the fracture stress upon the degree of conversion is shown in *Figure 5* where σ_f is plotted against d for three different conversions. The fracture stress clearly increases with increasing degree of conversion and the effect of fibre diameter is similar in each case.

Creep behaviour

Some preliminary studies were made of the roomtemperature creep behaviour of poly-EUHD fibres, and the variation of strain with time for a thermally polymerized fibre held at a stress of 1.0 GPa ($\sim 70\%$ of σ_t) is given in *Figure 6*. The strain in the fibre was found, within the limits of experimental error, to remain unchanged with time up to 24 h when the experiment was terminated. Hence no creep could be detected for fibres deformed at room temperature.

DISCUSSION

Linearity of stress-strain curves

The stress-strain curves for the EUHD fibres (*Figure 2*) tend to be linear, following Hooke's law up to about 1.5% strain. Above this strain the slope of the curve decreases but the behaviour is completely reversible along the loading path, with no hysteresis. The fibre therefore show a certain amount of non-linear elastic behaviour. There is no fundamental reason why Hooke's law should be

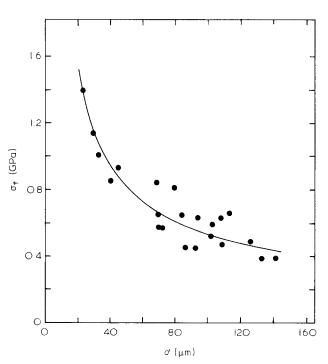


Figure 4 Dependence of fracture stress σ_f with effective fibre diameter for thermally polymerized poly-EUHD fibres crystallized originally from water

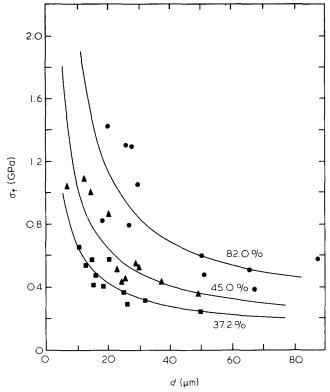


Figure 5 Variation of $\sigma_{\rm f}$ with effective fibre diameter for EUHD fibres thermally polymerized to the stated conversions crystallized originally from acetone/petroleum eether

obeyed, although most materials tend to obey it at vanishingly small strains. The non-linear behaviour of the EUHD crystals gives some indication of how the deformation takes place on the atomic or molecular level and suggests that the force constants for the stretching or bending of the bonds in the polymer backbone decrease with strain. This has been confirmed by measuring the Raman scattering from deformed polydiacetylene crystals^{13,14}. A continual decrease in the frequency of the various vibrational modes occurs as the strain in the crystals is increased and Batchelder and Bloor¹⁴ have suggested that this might be indicative of the bondstretching force constants decreasing with increasing strain. This will have the consequence of causing the value of E to decrease with increasing strain as is observed in practice.

Factors controlling polymer modulus

The measured value of modulus of 61 ± 3 GPa for the poly-EUHD crystals is the highest yet obtained for a

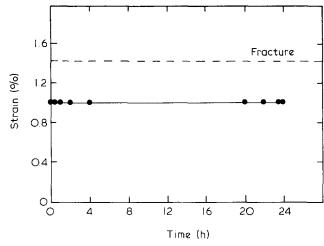


Figure 6 Creep data showing the variation of strain with time for a thermally polymerized poly-EUHD fibre held at a stress of 1.0 GPa

polydiacetylene single crystal. The difference in modulus for poly-EUHD crystallized originally from water (61.5 \pm 3.3 GPa) and acetone/petroleum ether (60.3 \pm 2.5 GPa) is probably not significant but may be due to slight structural differences between the two types of polymer¹¹. However, the relatively low value of modulus of 49.4 \pm 4.8 GPa for γ -ray polymerized material reflects the relatively short polymer chains and the radiation damage that has occurred during the irradiation with γ -rays¹³.

The Young's moduli of different diacetylene polymers are listed in Table 2 for measurements made in this present study and in previous publications^{9, 13-17}. Values are given for E determined both mechanically and using optical methods such as Raman scattering or Brillouin spectroscopy. It can be seen that the optical methods generally yield values of E which are 5-10% higher than mechanically measured ones. The value of the modulus also depends upon the particular derivative of the diacetylene being studied. In particular, it is controlled by the size of the side groups R on the polydiacetylene chain. Polymers with small side groups have higher values of Ethan those with large side groups. This effect can be seen clearly in Figure 7 where a linear relationship is obtained when the modulus of the polydiacetylene is plotted against the reciprocal of the cross-sectional area A supported by each polymer chain in the crystal. The values of A for each derivative are given in Table 2 and can be determined from knowledge of the crystal structure. The higher modulus values from optical measurements are reflected in the steeper slope of the line in Figure 7.

Table 2 Summary of the mechanical property data for different polydiacetylene derivatives

Derivative	Specific gravity	Area per chain, A (nm ²)	Young's modulus, E (GPa)	Method	Reference
poly-PUHD	1.37	0.974	45.0	Mechanical*	9
poly-TSHD 1.48	1.48	0.955	43.0	Brillouin	15
		50.0	Raman	14	
poly-DCHD 1.30	1.30	1.063	44.8	Mechanical *	12
		46.6	Brillouin	16	
poly-EUHD	1.31	0.651	60.9	Mechanical *	This work
			73.7	Raman	13

* Strain rate ~0.01 min⁻¹

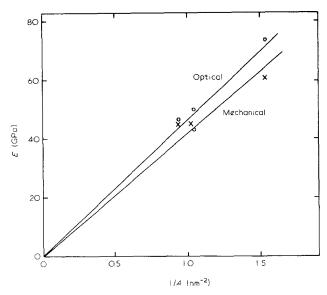


Figure 7 Variation of the Young's modulus *E* of different diacetylene polymers with the reciprocal of the area supported by each polymer chain in the crystal, 1/A. The circles correspond to optical measurements and the crosses to mechanical data given in *Table 2*

Further consideration of the effect of side-group size shows that these polydiacetylene crystals have modulus values which would be the same as polyethylene crystals if it were not for the large side groups. Extrapolation of the lines in *Figure* 7 to the value of 1/A for a polyethylene crystal (A = 0.184 nm²) gives a modulus value of the order of 250–300 GPa, which is close to the value currently accepted for polyethylene^{18–20}. Hence it appears that polydiacetylene crystals exhibit their theoretical values of chain direction modulus which, although relatively high (currently > 60 GPa), could be increased by reducing the size of the side groups. Work is under way at present to find methods of producing new derivatives with smaller side groups which should have even higher values of Young's modulus.

Dependence of modulus upon conversion

There is a large increase in the modulus of the EUHD fibres with the degree of conversion from monomer to polymer (*Figure 3*). Since there is a very slow approach to full conversion for both thermally and γ -ray polymerized poly-EUHD fibres¹¹, the maximum conversions that could be tested before the fibres became damaged were 98% for thermally polymerized fibres and 95% for γ -ray polymerized ones.

The partially polymerized polymer fibres can be regarded as composites consisting of high-modulus polymer molecules embedded in a low-modulus monomer matrix. The fibre modulus will therefore be between that of the polymer and that of the monomer, and the dependence of the modulus upon conversion can then be predicted using averaging procedures such as those due to Reuss or Voigt²¹. The Voigt model assumes that the strains in the monomer and polymer elements are equal and the modulus of the composite, *E*, is given by:

$$E = (l - V_{\rm p})E_{\rm m} + V_{\rm p}E_{\rm p} \tag{1}$$

where V_p is the volume fraction of the polymer and E_m and E_p are the monomer and polymer moduli respectively.

Equation (1) is plotted as a straight line in Figure 3 with $E_{\rm m}$ taken as 9 GPa and $E_{\rm p}$ as 61 GPa, the measured values of ~0% and ~100% converted material. The values of $V_{\rm p}$ have been determined from the measured conversions (by weight) and the known specific gravities of the monomer and polymer which are 1.23 and 1.31 respectively.

In the alternative Reuss model the stresses in the monomer and polymer components are assumed equal and the composite modulus is given by:

$$\frac{1}{E} = \frac{1 - V_{\rm p}}{E_{\rm m}} + \frac{V_{\rm p}}{E_{\rm p}}$$
(2)

This equation is plotted as the curve in *Figure 3*. It can be seen that the experimental points for the thermally polymerized EUHD crystals generally follow the Voigt line except at low conversion (<10%) where they lie closer to the Reuss curve. In contrast, the points for the γ -ray polymerized fibres are nearer to the Reuss curve over the entire range of conversion but tend to fall outside the bounds at high conversions.

This behaviour is entirely consistent with the known polymerization behaviour and structure¹¹⁻¹³ of the partially polymerized fibres. Analysis of the polymerization kinetics¹² has suggested that during thermal polymerization the length of the polymer chains increases with the degree of polymerization, whereas the polymer chains are relatively short for γ -ray polymerization and their length remains so throughout the reaction. It would be expected that short chains would lead to uniform stress in the composite (Reuss model), whereas long chains cause a uniform strain to pertain (Voigt model). Hence, as it is found experimentally, the Reuss model should apply to the γ -ray polymerized fibres and thermally polymerized ones at low degrees of conversion. Otherwise the Voigt model would be expected to apply. These observations are also consistent with the results of Raman scattering experiments¹³ upon partially polymerized fibres where it was found that the dependence of the frequency of the triple-bond-stretching mode upon strain for thermally polymerized fibres followed the Voigt model, whereas similar observations upon y-ray polymerized fibres could be explained better using the Reuss model.

The final question that needs to be answered is why the data points in *Figure 3* for the γ -ray polymerized fibres at high conversions (>80%) fall outside the bounds of the two models. This degree of conversion could only be achieved by using high doses of radiation (>50 Mrad) which lead to the crystals becoming visibly cracked and damaged¹² and hence having a lower modulus than more perfect crystals.

Dependence of fracture stress upon fibre diameter

The strong dependence of $\sigma_{\rm f}$ upon fibre diameter *d* is well established for polydiacetylene crystals⁹ and other high-strength fibres²². Baughman *et al.*⁹ suggested that the dependence might be of the form:

$$\sigma_{\rm f} = 1/d \tag{3a}$$

However, careful examination of the data in *Figures 4* and 5 shows that the relationship between σ_f and *d* is more accurately given by¹²:

$$\sigma_{\rm f} = 1/d^n \tag{3b}$$

where 0.6 < n < 0.7. Hence *n* is closer to 0.5 than to 1.0, and it is possible to explain a relationship of this form by considering the effect of defects on the surface of the fibres upon the fracture stress.

Examination of the EUHD fibres by scanning electron microscopy shows that they invariably have steps or notches on their surfaces and, indeed, it is thought that the monomer crystals grow by a dislocation mechanism involving steps. An example of a tapering surface step is given in *Figure 8*. The presence of surface defects will give rise to a concentration of stress when the crystals are deformed and the magnitude of the stress concentration will depend upon the geometry of the steps or notches. In general, the stress concentration factor η at the root of a step or notch is given by an equation of the form^{23,24}:

$$\eta = \frac{\sigma_0}{\sigma_a} = k_1 + k_2 \left(\frac{a}{\rho}\right)^{1/2} \tag{4}$$

where σ_a is the applied stress, σ_0 the stress at the root of the defect, *a* is the notch or step depth, ρ the radius of curvature at the root of the defect and k_1 and k_2 are constants which depend upon the geometry of the defect^{23,24}.

In this present study on EUHD fibres and in earlier work²³, it was found that the value of a was approximately proportional to the crystal diameter d. Hence

$$a \sim d/m$$
 (5)

where *m* is a constant (~15 for EUHD). Substituting equation (5) into equation (4), rearranging and setting $\sigma_a = \sigma_f$ at fracture gives:

$$\frac{1}{\sigma_{\rm f}} = \frac{k_1}{\sigma_0} + \frac{k_2}{\sigma_0 (\rho m)^{1/2}} d^{1/2} \tag{6}$$

where σ_0 is now the fracture strength of a defect-free crystal or the 'theoretical strength'.

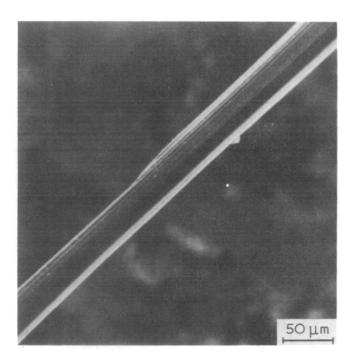


Figure 8 Scanning electron micrograph of a tapering step on the surface of a poly-EUHD fibre

Examination of the steps on EUHD crystals has shown that the value of ρ is very small (~30 Å) and does not depend upon the crystal diameter^{12,23}. Hence equation (6) predicts that a plot of $1/\sigma_f$ versus $d^{1/2}$ should be a straight line with an intercept of k_1/σ_0 and a slope of $k_2/\sigma_0(\rho m)^{1/2}$. The data from Figures 4 and 5 are replotted in Figures 9 and 10, and it is apparent that the correlation between the data and the theory is good. There is a slight discrepancy with the intercept on the $1/\sigma_f$ axis. This should be approximately zero as k_1 is small but positive²³ and σ_0 large, but the intercept is found to be slightly negative (Figures 9 and 10). However, within the accuracy of the theory and considering the assumptions made (e.g. equation (5)), the agreement of the theory with experimental data indicates strongly that the strength of the polydiacetylene crystals is controlled by the presence of defects.

Dependence of fracture stress upon conversion

Figure 5 shows that the fracture stress of the partially polymerized fibres depends upon both the fibre diameter and the degree of conversion to polymer. It might be expected that the fracture stress of the partially polymerized fibres can be presented by the Voigt and Reuss

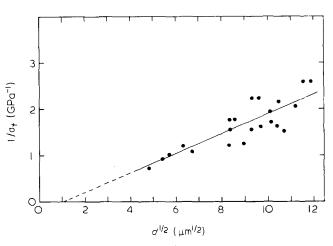


Figure 9 Variation of $1/\sigma_f$ with $d^{1/2}$ for poly-EUHD fibres for the data from *Figure 4*

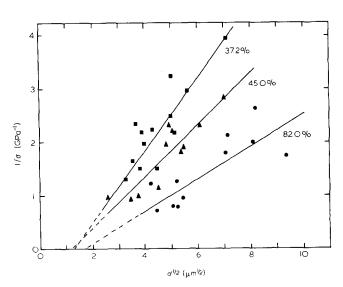


Figure 10 Variation of $1/\sigma_f$ with $d^{1/2}$ for partially polymerized EUHD fibres using the data from Figure 5

averaging procedures which were used for modulus predictions (*Figure 3*). However, it is difficult to compare fracture stresses directly because of their dependence upon fibre diameter and the presence of defects. The Voigt and Reuss models can only be used for crystals with identical defects or for defect-free crystals. If the fracture strength of a defect-free 'composite' (i.e. the polymer molecules reinforcing the monomer matrix) is given by σ_c then it follows using the Voigt average that:

$$\sigma_{\rm c} = \sigma_{\rm m} (1 - V_{\rm p}) + \sigma_{\rm p} V_{\rm p} \tag{7}$$

Alternatively the Reuss average gives

$$\frac{1}{\sigma_{\rm c}} = \frac{1 - V_{\rm p}}{\sigma_{\rm m}} + \frac{V_{\rm p}}{\sigma_{\rm p}} \tag{8}$$

where $\sigma_{\rm m}$ is the fracture stress of a defect-free monomer crystal and $\sigma_{\rm p}$ is the fracture stress of defect-free polymer (both determined at the same strain²⁴). The values of defect-free fracture stress cannot be determined without detailed knowledge of the defect geometry, but the slopes S of the lines in Figures 9 and 10 can be used instead of $\sigma_{\rm m}$, $\sigma_{\rm p}$ or $\sigma_{\rm c}$.

Equation (6) can be rewritten as:

$$\frac{1}{\sigma_{\rm f}} = \frac{k_1}{\sigma_0} + \frac{k_3}{\sigma_0} d^{1/2} = \frac{k_1}{\sigma_0} + S d^{1/2} \tag{9}$$

where k_3 is a new constant and σ_0 is the strength of any type of defect-free crystal. The ratio of the slopes of the lines in *Figures 9* and 10 for the polymer and composites (S_p/S_c) will be equal to the inverse of the ratio of their defect-free strengths and so can be used instead of the absolute values of strength (which depend upon crystal diameter). Hence *Figure 11* gives a plot of S_p/S_c against V_p with the line and the curve representing the Voigt and Reuss averaging procedures respectively. The value of S_m has been calculated by assuming that the monomer and polymer have the same fracture strain, so that the ratio of their fracture stresses equals the ratio of their moduli. Hence

$$S_{\rm p}/S_{\rm m} = \sigma_{\rm m}/\sigma_{\rm p} = E_{\rm m}/E_{\rm p} \tag{10}$$

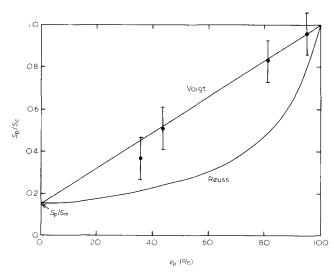


Figure 11 Variation of S_p/S_c for EUHD fibres with the volume fraction of polymer in the crystals, V_p

Since $E_{\rm m}$, $E_{\rm p}$ and $S_{\rm p}$ are known, $S_{\rm m}$ can be determined and $\sigma_{\rm m}$ and $\sigma_{\rm p}$ need not be evaluated.

It can be seen that, as for the modulus measurements upon thermally polymerized fibres, the data points fall between the Voigt and Reuss bounds. Hence the fracture stress of the partially polymerized fibres would appear to be controlled by the volume fraction of long high-strength polymer molecules in the monomer matrix.

Creep behaviour

One of the more interesting aspects of the mechanical behaviour of polydiacetylene single-crystal fibres is their complete lack of any time-dependent deformation or creep. This is normally a serious problem with conventional fibres such as ultra-high-modulus polyethylene⁴ and makes it somewhat difficult to utilize the materials in engineering applications. Hence polydiacetylene single-crystal fibres could be particularly useful in situations where creep might lead to problems.

In some respects the lack of any time-dependent deformation is not unexpected since the only way it can take place is by the slippage of molecules past each other, which is clearly a difficult process in a perfect chainextended crystal. This can be contrasted with the highly oriented polyethylene fibres which are polycrystalline and contain entangled chains and chain ends able to move past each other during tensile deformation. Over short periods of time, ultra-high-modulus polyethylene and poly-EUHD have similar values of Young's modulus (60–70 GPa). The values change with loading period or strain rate for the polyethylene but remain constant in the case of the poly-EUHD.

Experiments are currently under way to examine the time-dependent deformation of polydiacetylene single crystals at elevated temperatures.

CONCLUSIONS

It has been shown that single-crystal fibres of a substituted diacetylene polymer have interesting and unusual mechanical properties. They have high values of Young's modulus (up to 62 GPa) and strength (up to 1.4 GPa) and do not show any time-dependent deformation or creep. The value of Young's modulus of fully polymerized fibres has been shown to depend upon the crystal structure of the polymer being controlled by the size of the side groups on the polymer chain. It is thought that it may be possible to increase the modulus and fracture strength significantly by producing fibres of new derivatives which have smaller side groups.

ACKNOWLEDGEMENTS

This research was supported by grants from the Science and Engineering Research Council and the Ministry of Defence (Procurement Executive). The authors are grateful to D. Bloor, D. N. Batchelder, D. Ando and other members of the Polymer Group, for help with preparation of the materials and useful discussions. They would also like to thank R. J. Loneragan, R. L. Tickner and J. Roberts of the MOD for their encouragement and support. Mechanical properties of substituted polydiacetylene: C. Galiotis and R. J. Young

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