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The relation between filament diameter and fracture strength for ultra-high-modulus polyethylene fibres

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The effect of filament diameter on the failure stress of polyethylene fibres has been studied using Weibull analysis. Both gel-spun and melt-spun fibres have been examined, so that differences might be observed for changes in draw ratio or modulus as well as molecular weight. It is concluded that the strength of high-modulus melt-spun fibres relates to the concentration of flaws and is significantly dependent on filament diameter. Conflicting results for gel-spun fibres are discussed in the light of the present investigation, and it is concluded that the mechanism of failure in these fibres is different from that of the melt-spun fibres.

1. Introduction

The production of high-stiffness high-strength fibres from polyethylene has been developed over the last 20 years, by a melt-spinning/hot-drawing route [1, 2], by solution spinning of very high molecular weight polymer [3, 4] and by a gel spinning/hot-drawing route also for very high molecular weight polymers [5]. The modulus is directly related to the draw ratio reached [2], and in some cases has reached values very near to the calculated modulus [6]. The achieved tensile strengths are, by comparison, always much lower than the theoretically possible values. Hallam *et al.* [7, 8] have shown that for melt-spun and hot-drawn fibres there is an increase in achieved tensile strength with increasing molecular weight and Smith *et al.* [9] showed that to obtain the highest strengths, a very high molecular weight polymer is needed. Smith *et al.* [9] also compared the tensile strengths of fibres made by the melt-spun/drawn and solid-state extrusion methods. Differences in tensile strength were attributed to the fact that the two methods produce fibres with a significant difference in cross-sectional area, the strength decreasing as the fibre dimensions increase. Smook *et al.* [10] combined data for surface-growth/hot-drawn and gel-spun/hot-drawn fibres and observed a diameter effect in ultra-high molecular weight polyethylene (UHMWPE) fibres. Wagner and Steenbakkers [11] also reported similar results for the commercially produced Spectra gel-spun UHMWPE fibres.

From the results summarized above, the factors which govern the tensile strength of high-modulus polyethylene fibres can be divided into two groups. First, there are intrinsic factors, such as molecular weight or crystallite size. Secondly, there are extrinsic factors such as flaws or fibre diameter. It is of considerable importance to understand the role of all such factors in determining the strength of high-modulus fibres and the degree to which they make a contribution to the strength and extensibility to break. This paper describes a study of the effect of diameter on the tensile strengths of melt-spun/drawn polyethylene fibres for a wide range of diameters and molecular weights. It is a sequence to previous publications from this laboratory on the effect of molecular weight and molecular weight distribution [8] and separately strain rate [12], on the observed tensile strength. At high strain rates, above 20% min^{-1}, high-modulus polyethylene fibres fail in brittle manner. It is therefore appropriate to use Weibull analysis, which is a well-established method for studying brittle materials, to investigate the tensile behaviour of fibres with a wide range of diameters from polymers with a range of molecular weights. In this paper, a comparison will be made on fibres drawn to constant modulus, which is strongly correlated with the degree of molecular orientation [13, 14]. In addition to tests at room temperature, tests were also carried out at low temperatures, $-55\,^{\circ}C$, where the fibres definitely failed in a brittle manner.

Recently, McGarry and Moalli [15] have developed a transverse splitting test which provides quantitative information on the lateral integrity of highly drawn fibres. This test was adapted to the highly drawn fibres used in this study and the different behaviour of fibres at two levels of molecular weight has been related to the effects of diameter on tensile strength.

2. Theoretical background

2.1. Weibull analysis

The Weibull analysis is a statistical method which is widely used to study the failure mechanism of brittle materials such as glass [16], ceramic [17] and polymeric fibres which show brittle failure. It has been applied to oriented polyethylene, polydiacetylene and Kevlar fibres [18]. The method is based on two assumptions [19]: (a) the material is statistically

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homogeneous; according to this assumption the probability of finding a flaw of a given severity within an arbitary small volume of the material is the same throughout the material, or along its length in case of fibre; (b) failure at the most critical flaw leads to total failure of specimen; this latter assumption is often called the concept of the weakest link of a chain.

With the above two assumptions the following equation can be derived

$$P_f(\sigma) = 1 - \exp[-n\phi(\sigma)] \quad (1)$$

where $P_f(\sigma)$ is the probability of failure of specimen containing n links at stress σ.

Because $\phi(\sigma)$ is an unknown function, Weibull assumed an empirical form for this function given by

$$\phi(\sigma) = \left[\frac{\sigma - \sigma_n}{\sigma_0}\right]^m \quad \text{for } \sigma > \sigma_n \quad (2a)$$

and

$$\phi(\sigma) = 0 \quad \text{for } \sigma \leqslant \sigma_n \quad (2b)$$

where σ_n is the minimum failure stress, m is a constant, termed the Weibull modulus, and σ_0 is a normalizing factor.

Substitution of Equations 2a and b in Equation 1 gives

$$P_f(\sigma) = 1 - \exp\left[-n\left[\frac{\sigma - \sigma_n}{\sigma_0}\right]^m\right] \quad \text{for } \sigma > \sigma_n \quad (3a)$$

and

$$P_f(\sigma) = 0 \quad \text{for } \sigma \leqslant \sigma_n \quad (3b)$$

$P_f(\sigma)$ can be determined by ranking data in an ascending order of stress and the probability of failure of the ith ranked sample in a group of N determined from $P_f = i/(N + 1)$. Rearranging Equation 3a and assuming σ_n, the threshold stress for failure for any sample, to be zero, we have

$$\ln \ln\left[1\Big/\left(1 - P_f\right)\right] = \text{constant} + m \ln \sigma \quad (4)$$

Hence, a linear plot of P_f versus σ can be derived with a gradient m equal to the Weibull modulus.

Further transformation of Equation 3 gives [19]

$$\bar{\sigma} = \left(\frac{\sigma_0}{n^{1/m}}\right)\Gamma(1 + 1/m) \quad (5)$$

where $\bar{\sigma}$ is the mean strength of the fibre, and Γ is a gamma function.

Equation 5 shows the effect of the number of links or flaws on the mean strength of the fibre. If we assume that the number of flaws is either proportional to the surface area of the fibre or alternatively to the volume of the fibre we can derive further equations as follows: for the surface model

$$\bar{\sigma} = \left[\frac{\sigma_0}{(\pi d l)^{1/m}}\right]\Gamma(1 + 1/m) \quad (6)$$

for the volume model,

$$\bar{\sigma} = \left[\frac{\sigma_0}{(\pi d^2 l)^{1/m}}\right]\Gamma(1 + 1/m) \quad (7)$$

where d is the diameter of tested fibre, and l the gauge length of tested fibre.

By using Equation 5, a plot of ln strength versus ln diameter for fibres tested at constant gauge length will give a straight line with a slope $-1/m$ if the surface model is applicable, but in the case of the volume model the plot will give a slope $-2/m$. The plot of ln strength versus ln gauge length for fibres of identical diameter will give a slope $-1/m$ for both models.

An alternative approach was used by Smook *et al.* [10] in a study of UHMWPE fibre prepared by the surface-growth/hot-drawn and gel-spun/hot-drawn methods. They proposed that the results could be interpreted by Griffith-like dependence between strength and fibre diameter. The following equation was proposed

$$\frac{1}{\sigma_f} = \frac{1}{\sigma_0} + a\left[\frac{D - D_0}{G_{1c}E}\right]^{1/2} \quad (8)$$

where σ_f is the tensile strength, σ_0 is the strength of a flawless fibre or the theoretical strength of a perfect polyethylene fibre, D is the fibre diameter, D_0 is the diameter of a flawless fibre (in practice, this is taken as zero), G_{1c} is the energy needed for the creation of a crack of critical dimensions, E is the Young's modulus and a is a constant.

From Equation 8 it would be expected that a plot of $1/\sigma_f$ versus $D^{1/2}$ would give a straight line with an intercept equal to the reciprocal of the theoretical tensile strength of polyethylene. A similar type of equation was also derived by Galiotis and Young [20] in their study of polydiacetylene.

3. Experimental procedure

The molecular weight characteristics of the polymers used in this study are given in Table I. The fibres of NEWS 1950 and SCLAIR 2909 were prepared in the IRC laboratory by melt spinning and drawing, as detailed below.

1. Melt spinning. Polymer granules were melted in the heated cylinder of a rod spinner capable of holding about 15 g at temperatures of 225 and 150 °C for NEWS 1950 and SCLAIR 2909, respectively. A ram driving downwards at a controlled speed pushed the molten polymer through a spinneret of diameter 0.4–1.5 mm at the lower end of the heated cylinder. The emergent polymer in the form of a monofilament was allowed to solidify in air for the higher $\bar{M}_w$ and in

TABLE I

Polymer	$\bar{M}_w$	$\bar{M}_n$	Diameter range
SCLAIR 2909	67000	15000	0.060–0.280
Celanese	100000	18000	0.015
Snia Fibre	130000	17000	0.015
NEWS 1950	210000	13000	0.075–0.250
Tekmilon	800000	–	0.040
Spectra	1.5×10^6	–	0.030
Dyneema	1.5×10^6	–	0.015

water for the lower $\bar{M}_w$ and collected by winding on to a bobbin mounted 1.5 m below the die. The wind-up speed was adjusted in order to keep slight tension in the monofilament. The extrusion speed and wind-up speeds were adjusted in order to obtain spun fibres with range of diameters.

2. Drawing. In this step the spun filaments were drawn on a small drawframe by passing the filament several times round a feed roll, through a heated glycerin bath at 75–100 °C and winding up on a draw roll. The diameters of the feed roll and draw roll were chosen such that the surface speeds differed by the required draw ratio.

In order to cover a wider range of diameter and molecular weight, commercially produced gel-spun fibre "Spectra" and "Dyneema", a very high-molecular weight filament produced by a modified melt-spinning process "Tekmilon", and melt-spun filaments of low molecular weight polyethylene produced by Hoechst Celanese and Snia Fibre, were also used.

Tensile tests were carried out by using an Instron tensile tester and were conducted at room temperature (21 °C) and − 55 °C. For low-temperature work, the Instron was equipped with an environmental chamber which was operated at − 55 ± 3 °C. The standard gauge length used was 20 cm for room-temperature tests but due to limited working space in the low-temperature chamber the gauge length for the tests at − 55 °C was restricted to 10 cm. For both room-temperature and − 55 °C tests the strain rate was 50% min^{-1}.

Polyethylene sheets were used as grip liners to prevent severe damage to the samples. For the thicker filaments the sample cross-section diameter was measured with a digital micrometer. For the finer filaments the diameter was measured using a microscope with calibrated micrometer eye-piece.

The tensile strength and 1 % secant modulus were computed from the nominal stress values using the original cross-sectional area and the breaking load and the load at 1 % strain, respectively.

The tensile strength and modulus values quoted are, in all cases, at least an average of five determinations on each sample. For Weibull analysis, 50 determinations of tensile strength were made on each sample.

3.1. Filament splitting

To determine the transverse splitting tear energy, the ends of a short length, about 5 cm, of drawn fibre were flattened and a notch cut into the centre of the flattened end [15]. Both edges were gripped with tweezers and a split initiated along the length of the fibre. The two ligaments of the fibre were gripped in the Instron tensile tester and the fibre pulled apart at a crosshead speed of 0.1 cm min^{-1}. The load developed was recorded and the tear energy calculated from the equation

$$\text{tear energy} = \frac{2F}{d} \tag{9}$$

where F is the load developed and d is fibre diameter.

4. Results

4.1. Diameter effect

The relationship between diameter and tensile strength was determined for highly drawn polyethylene fibres of room-temperature modulus E = 10, 20 and 30 GPa. These fibres were produced by drawing to appropriate draw ratios, spun fibres produced under similar conditions but of various diameters. The fibres were tested at room temperature (21 °C) and − 55 °C. The latter temperature has been shown by Hallam *et al.* [7] to be removed from any transition regions so that the fracture behaviour does not depend on either temperature or strain-rate. Considering first the room-temperature results, Figs 1 and 2 display the effect of fibre diameter on the tensile strength of fibres of various modulus for the low $\bar{M}_w$ fibres and high $\bar{M}_w$ fibres, respectively. At low modulus, i.e. low draw ratios, the diameter has no effect on tensile strength (Fig. 1) but at high modulus, 30 GPa, the tensile strength decreases with increasing fibre diameter. Fig. 2 displays results for high-modulus (30 GPa) fibres of different molecular weight and in addition the strengths of some commercial high-modulus polyethylene fibres are included. It can be seen that the high molecular weight fibres show a stronger diameter effect than the low molecular weight ones.

Fig. 3 shows results at − 55 °C for the same series of fibres used to construct Figs 1 and 2. At the lower temperature, diameter has an effect on the tensile strength for fibres of all moduli. It is seen better in the natural logarithm plot form (Fig. 4) that as the modulus increases the gradient of the ln tensile strength/ln diameter line increases. This trend is observed for both the low and high molecular weight series of fibres.

4.2. Tensile strength distribution

As already indicated, the tensile strength quoted for some of the fibre samples is the mean of a large number, usually 50, tests which is a sufficient number for the distribution of tensile strengths to be analysed by the Weibull equation (Equation 4).

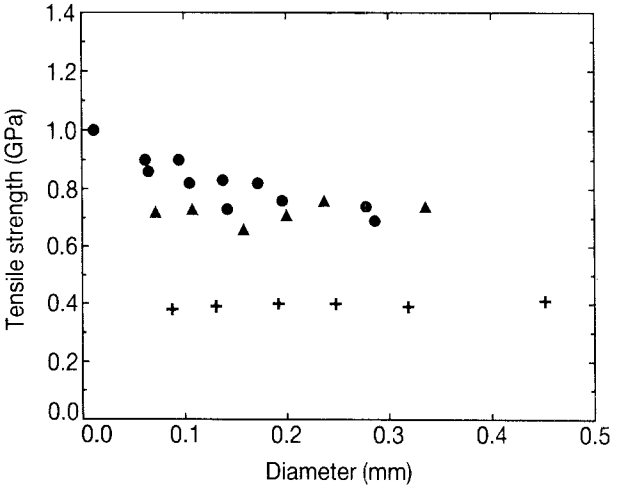

Figure 1 Tensile strength–diameter relationship of oriented SCLAIR 2909 fibres. (+) E = 10 GPa; (▲) E = 20 GPa; (●) E = 30 GPa.

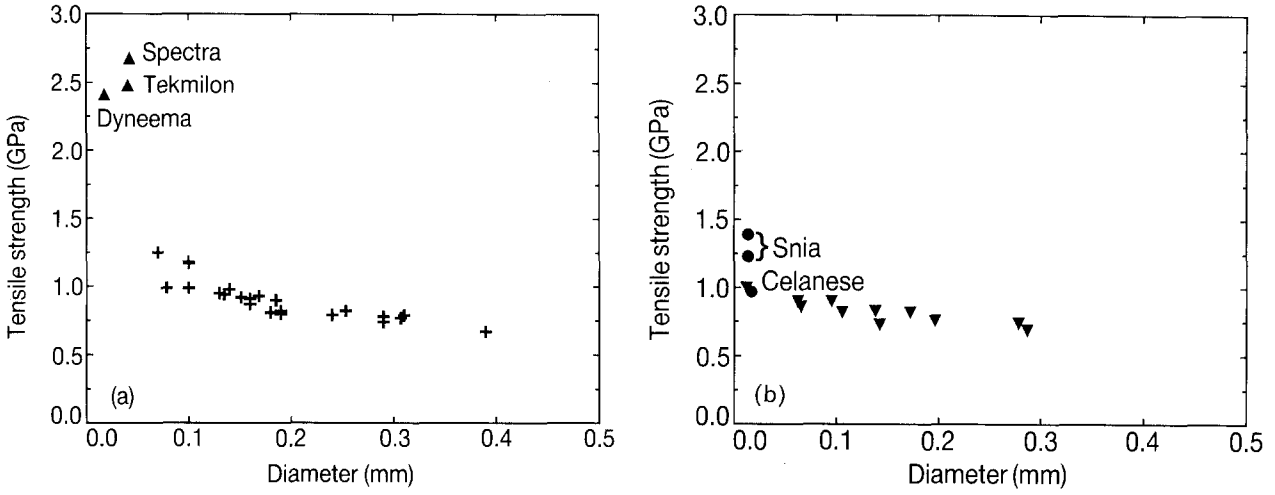

Figure 2 Tensile strength–diameter relationship of oriented polyethylene fibres. (a) (+) 30 GPa NEWS 1950; (▲) UHMWPE fibres. (b) (▼) 30 GPa SCLAIR 2909; (●) SNIA and Celanese fibres.

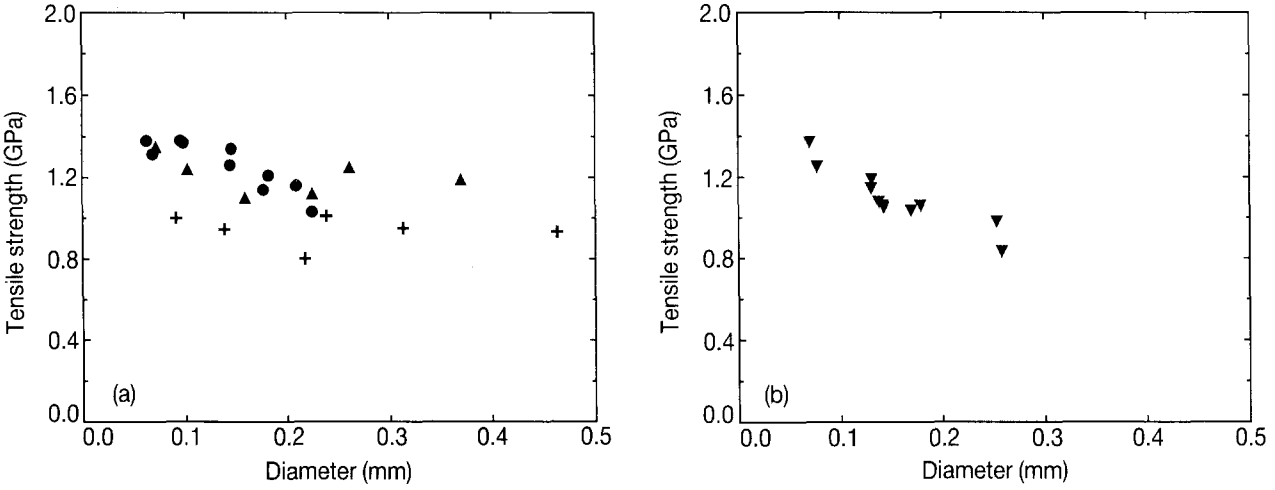

Figure 3 Tensile strength, measured at − 55 °C,–diameter relationship of oriented polyethylene fibres. (a) SCLAIR 2909; (+) E = 10 GPa; (▲) E = 20 GPa; (●) E = 30 GPa. (b) NEWS 1950; (▼) E = 30 GPa.

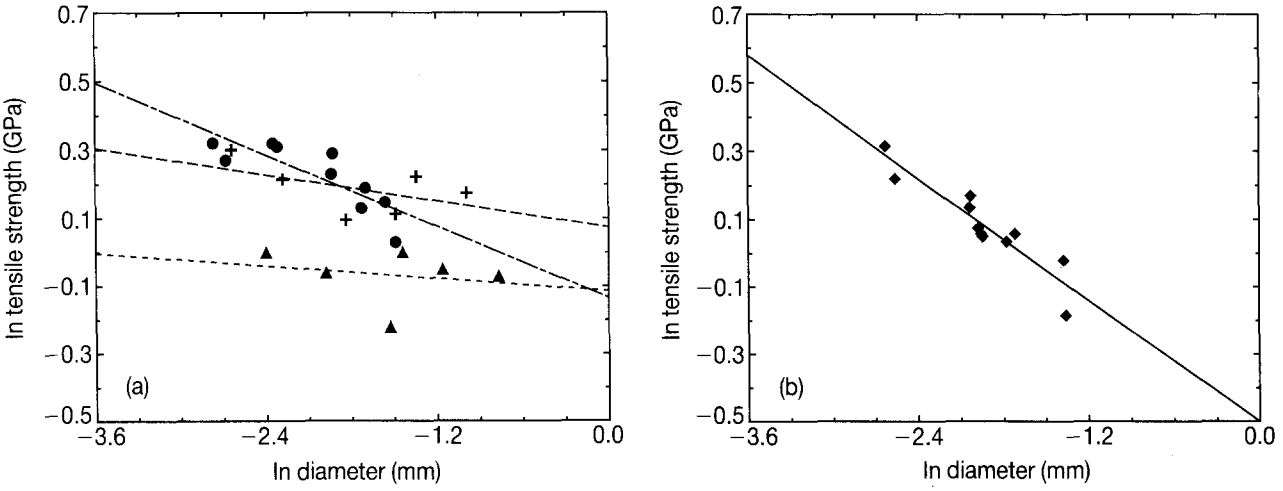

Figure 4 Ln tensile strength, at − 55 °C, versus ln diameter of oriented polyethylene fibres. (a) SCLAIR 2909; (▲) E = 10 GPa, (+) E = 20 GPa; (●) E = 30 GPa. (b) NEWS 1950; (◆) E = 30 GPa.

A typical Weibull plot is shown in Fig. 5. Lower m corresponds to a broad distribution of tensile strength and higher m to a narrow distribution.

The Weibull moduli computed from Weibull plots of fibres drawn to various draw ratios tested at room temperature and − 55 °C, respectively, are shown in Table II.

Table III shows Weibull modulus results for SCLAIR 2909 and NEWS 1950 fibres drawn to various moduli tested at both room temperature and

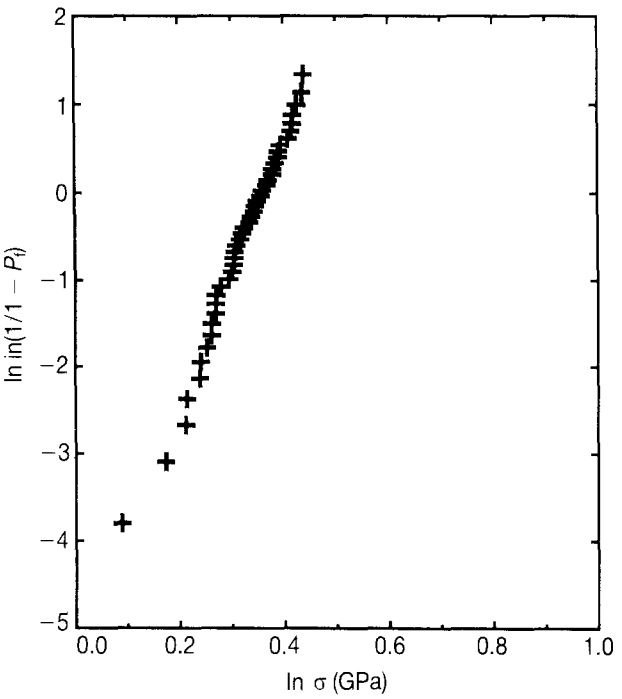

Figure 5 Typical Weibull plot of oriented polyethylene fibre obtained in this study.

TABLE II Weibull modulus of fibres prepared from NEWS 1950 drawn to various draw ratios

Draw ratio	Weibull modulus	
	Room temperature	− 55°C
15	27.9	–
20	19.2	15.6
25	17.0	14.8
30	14.8	–

TABLE III Weibull modulus of fibres drawn to various moduli and some commercial fibres tested at room temperature and − 55°C

Polymer	Modulus (GPa)	Weibull modulus	
		21°C	− 55°C
SCLAIR 2909	10	–	27.6
	30	22	18.4
NEWS 1950	30	17	14.8
Snia fibre	50	15.4	–
Tekmilon	70	8.2	10.2
Dyneema	85	2.4	–

− 55 °C. Results for some of the commercial high-modulus polyethylene fibres are also included in this table.

4.3. Lateral splitting test

The results of the lateral splitting tests for NEWS 1950 and SCLAIR 2909 fibres of various draw ratios are shown in Fig. 6. It can be seen that the tear energy decreases with increasing draw ratio for both the NEWS 1950 and SCLAIR 2909 fibres, changing from 4.9 kJ m^{-2} for NEWS 1950 at draw ratio 10 to 1.65 kJ m^{-2} at draw ratio 30. At the same draw ratios SCLAIR 2909 shows the lower values of 2.97 and 1.1 kJ m^{-2}, respectively.

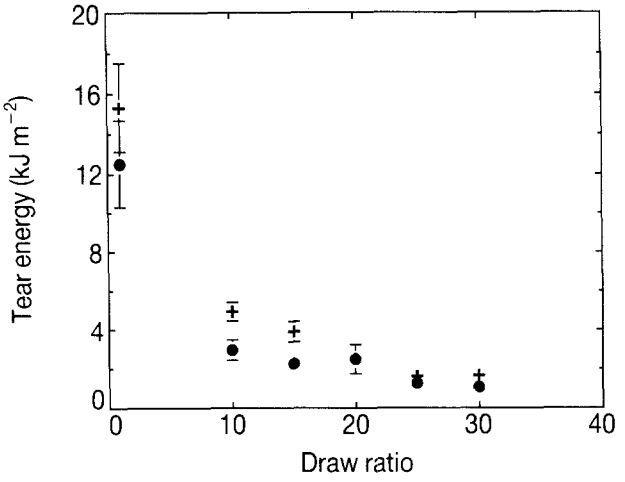

Figure 6 Lateral splitting results for oriented polyethylene fibres drawn to various draw ratios. (●) SCLAIR 2909; (+) NEWS 1950.

5. Discussion

It is known that drawn polyethylene fibres possess very high anisotropy [30]. To avoid end effects, according to St Venant's principle, samples with high aspect ratios must be used. In our study a gauge length of 20 cm was used to obtain reliable moduli, giving an aspect ratio of about 800. A preliminary investigation on these materials showed that gauge length has no effect on tensile strength in the range 5 cm sample length or greater. In addition, Weibull plots of two very different gauge lengths gave practically the same tensile strength and tensile strength distribution. This result was in line with the observations of Schwartz *et al.* [22].

The results of the present investigation show a very complex relationship between fibre diameter, modulus (or almost equivalently draw ratio), and molecular weight, on the measured tensile strength of polyethylene fibres. At ambient temperature and low draw ratio, i.e. low modulus, the fibres do not show any variation of tensile strength with diameter (Figs 5 and 7), and also at these moduli there is a very narrow distribution of tensile strengths, as indicated by the high Weibull modulus (Tables II and III) for each sample tested. These results would suggest that the tensile failure of these fibres is not determined by any external factors such as the macroscopic flaws seen in high draw ratio fibres but is an intrinsic property of the drawn fibre.

Hallam *et al.* [7, 8] have shown that for fibres of draw ratio 15 and 20, or of comparable modulus, the tensile strength is related to the polymer molecular weight. These results in the present investigation as far as low-modulus fibres are concerned would confirm Hallam's results that molecular weight in combination with draw ratio are the intrinsic properties controlling tensile strength. The type of flaw that may exist in these low draw ratio fibres is a molecular flaw which is distributed evenly throughout the fibre. These flaws

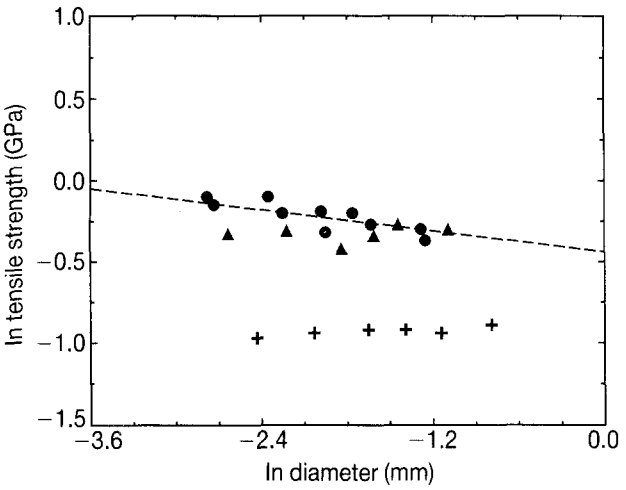

Figure 7 Ln tensile strength versus ln diameter of oriented SCLAIR 2909 fibres. (+) $E = 10$ GPa; (▲) $E = 20$ GPa; (●) $E = 30$ GPa.

arise from the discontinuities of the crystal structure in the drawn fibre which has been described as an arrangement of crystal blocks that are linked by taut tie molecules [13] and/or crystalline bridge [23]. It is therefore very likely that stress inhomogeneities will arise in these areas when the fibres are subjected to external load. Stress is concentrated around these molecular flaws and the over-stressed chains fail, leading to failure of the specimen. The increased tensile strength with increasing molecular weight may be attributed to the increase of the fraction of taut tie molecules and crystalline bridges in the high molecular weight fibre.

On the other hand, the high-modulus fibres tested at ambient temperature show a distinctly different pattern of response with regard to their variation with diameter (Figs 2, 4 and 8). For both the higher and lower molecular weight polymers the measured tensile strength definitely depends on the fibre diameter. These high-modulus fibres also have a wider distribution of tensile strengths as indicated by a lower Weibull modulus for individual samples from this group (Tables II and III). Fracture behaviour of this type, as was originally shown by Griffith [24] can be attributed to cracks or voids in the test samples. A real material will therefore have a distribution of cracks and voids both in size and orientation. This will result in an increased probability in finding a weak crack, the greater the diameter when constant length test samples are used. A mechanism of failure of this type, producing a scatter of failure strengths can be analysed by statistical methods and the approach used for these samples follows the Weibull analysis.

The key parameter in the Weibull analysis, the Weibull modulus, m, can be determined either directly from the slope of the Weibull distribution (Equation 4) or from the slope of ln tensile strength versus ln diameter line (Equations 6 and 7). The first determination of m from $\ln\ln(1/1 - P_f)$ versus $\ln\sigma$ can be regarded as simply a measure of the statistical distribution of tensile strengths. This first derivation of the Weibull equation is based on the assumption of an assembly of variable flaw sizes and orientations (with respect to the applied load) accounting for the observed scatter in tensile strength. The second derivation of m from the ln tensile strength–ln diameter gradient derives from the greater probability of finding a flaw when the volume of specimen is increased. The m value for high modulus/lower molecular weight SCLAIR 2909 fibres derived from the first method, the Weibull plot gives 22, in good agreement with the value obtained, 18.4, from the gradient of the ln tensile strength–ln diameter line assuming a volume distribution of flaws (See Table IV). We therefore conclude that the mechanism of failure for the low molecular weight/high-modulus fibres is by growth of a dominant flaw (LEFM). This is a distinct change in the mechanism of failure at high modulus for the lower molecular weight SCLAIR 2909 fibre from a dependence on molecular weight and draw ratio (which is intrinsic) to a flaw-dependent mode (which is extrinsic and to some extent overrides the effect of molecular weight).

This pattern of behaviour does not extend to the higher molecular weight NEWS 1950 samples. In this case the tensile strength is still diameter dependent but the gradient of the line is much steeper and shows no prospect of agreement between m determined from this gradient for either the surface ($m = 3.2$) or volume

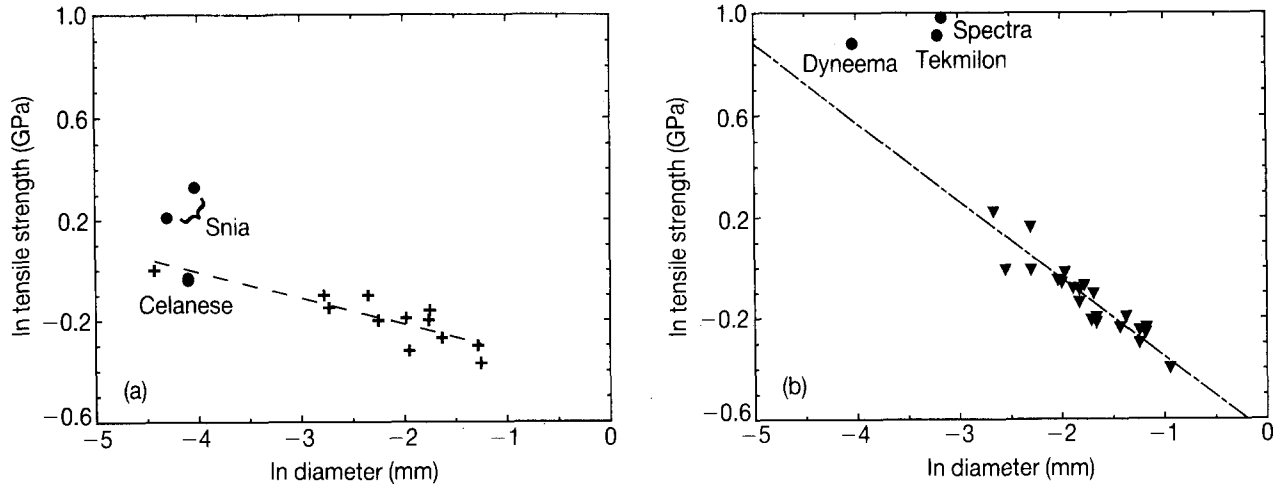

Figure 8 Ln tensile strength versus ln diameter of oriented polyethylene fibres. (a) (+) 30 GPa SCLAIR 2909; (●) commercial fibres. (b) (▼) 30 GPa NEWS 1950; (●) commercial fibres.

($m = 6.5$) assumption and m determined directly from the Weibull distribution ($m = 17$) (See Table IV). The simple brittle fracture mode of failure in this case deduced by linear elastic fracture mechanics for fibres of different diameter has been severely modified, giving higher tensile strengths for the finer fibres than would be predicted by the Weibull theory. Smook *et al.* [10] have determined an activation energy of about 60 kJ mol^{-1} for fracture of ultra-high molecular weight polyethylene fibres which implies that strength is mainly determined by lateral bond strengths between molecules. Our results on the splitting of high draw ratio fibres show a significantly increased tearing force for the higher molecular weight fibres over the lower molecular weight fibres. This result supports the conclusion of Smook *et al.* that there is an increased bond strength between the fibrils of the fibre for the higher molecular weight structure and could be due to the inter-microfibrillar tie molecules proposed by Prevorsek *et al.* [25] that arise with the higher molecular weight polymers used in these fibres. The effect of these stronger inter-fibrillar bonds would be to modify the crack development leading to failure, that occurs with the lower molecular weight fibre, by either stopping or deflecting the steady propagation of the cracks.

Smith *et al.* [9] have shown that for fibres of the same $\bar{M}_w$, prepared by either a gel-spinning or a melt-spinning route, the properties of the final drawn product are the same. They propose that the fibre properties depend only on the draw ratio achieved, because the drawing process for either type of spun fibre can be regarded as the deformation of similar molecular networks. It is therefore reasonable to compare the tensile properties of an ultra-high molecular weight gel-spun fibre with the high molecular weight melt-spun higher diameter filaments, even if the molecular weights are not quite comparable. When this is done it is seen that the tensile strength of some of these fine fibres (Fig. 8) fall remarkably close to the ln tensile strength–ln diameter line derived for the melt-spun fibres of a somewhat lower molecular weight. It was also found that the Weibull modulus of one particular gel-spun fibre, 'Dyneema', is very low (2.4) (Table III) which would suggest a very strong diameter dependence. These observations would appear to support our initial conclusions for the lower molecular weight fibres that the effect of diameter modifies any improvement in tensile strength that could be expected from the increased molecular weight and higher draw ratio. The source of this change in behaviour would appear to be the voided nature of these fibres when drawn to high draw ratio as revealed by scanning electron micrographs of melt-spun NEWS 1950 drawn to modulus of 30 GPa (Fig. 9). The microscopic examination of Dyneema fibre shows that it has a very irregular cross-section and this would equally account for the scatter of the measured tensile strengths and therefore a very low Weibull modulus. It is therefore not appropriate to conclude at this stage that the diameter dependence at high draw ratio can extend to these UHMWPE gel-spun fibres. This will be dealt with in a separate section later.

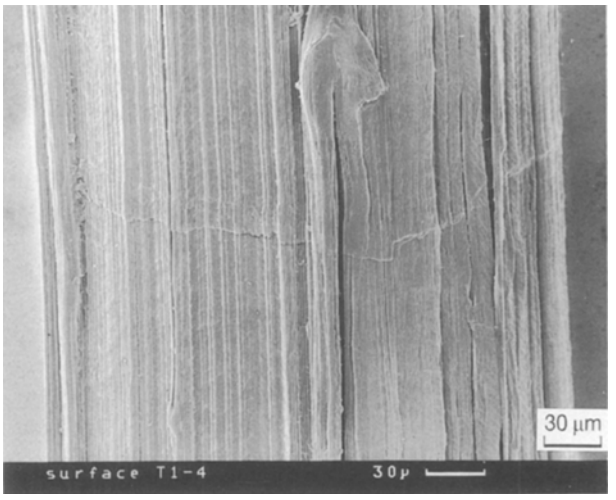

Figure 9 Scanning electron micrographs of the surface of highly drawn NEWS 1950 fibre.

A different pattern of behaviour is found at low temperature. Here, at all draw ratios (i.e. for all levels of fibre modulus) the fibres show a sensitivity of tensile strength to diameter (Figs 3 and 4). The cause of the diameter effect appears however, to change with modulus level. At low modulus (10 GPa), the slope of the tensile strength/diameter line is low (0.031), and in this case the directly determined Weibull modulus (27.6) agrees best with the interpretation that fracture is due to surface flaws, because the slope (0.031) gives a value of $m = 32.3$, whereas the volume condition $2/m$ is equivalent to an m value of 64.6 (See Table V). As the modulus increases, the flaw distribution changes to a volume effect for the lower molecular weight fibres, similar to that recorded at room temperature, and similar to the strong effect of diameter on tensile strength for the higher molecular weight fibres observed at room temperature. It is also to be noted from the results in Fig. 4 that, in general, the high $\bar{M}_w$ fibres tend to have lower tensile strengths at this temperature than the lower molecular weight fibres. This effect can be attributed to a difference in the polydispersity of the two polymers. Hallam *et al.* [26] reported that a wide distribution polymer will have a lower tensile strength than a polymer of comparable $\bar{M}_w$ with a narrow distribution. The $\bar{M}_w/\bar{M}_n$ ratio of 16 for the higher molecular weight polymer NEWS 1950 is very high compared to that of SCLAIR 2909 which is 4.3. It would appear that polydispersity of molecular weight can still have an effect on tensile strength even when chain-length effects have been overridden to a major extent by the influence of fibre diameter. In fact, the results of Hallam *et al.* suggested that $\bar{M}_n$ was the key parameter, as proposed by Flory [27] in 1945.

5.1. Gel-spun fibres

The examination of gel-spun fibres from UHMWPE has been restricted to two commercially available samples of "Dyneema" and "Spectra" and a modified melt-spun fibre "Tekmilon". It would appear from a superficial examination of Fig. 8 that the tensile

strengths of the gel-spun fibre are near to those expected for melt-spun fibres of a similar diameter. This observation in conjuction with the low Weibull modulus of Dyneema (Table III) would appear to indicate that a similar failure mechanism operates for these fibres. However, the suggestion that the tensile strength of gel-spun fibre is also diameter dependent is in conflict with the results of Bastiaansen [28] but in accord with results published by Smook *et al.* [10].

Bastiaansen compared the tensile strength of different diameter fibres at a constant modulus having shown that for his samples the relationship between tensile strength and modulus is the same for all samples irrespective of diameter. Smook *et al.* [10], however, compared fibres of different diameter in which the modulus increased over a wide range as the diameter decreases using data from Zwijnenburg and Pennings [3]. Because these fibres, like those used by Bastiaansen, have a similar modulus tensile-strength relationship to that shown by Smith *et al.* [9], the increased tensile strength of the lower diameter fibres is adequately explained by their higher modulus and need not be attributed to their lower diameters. It would, therefore, appear that the mechanism of failure of gel-spun fibres does not follow the flaw-induced failure mechanism of the melt-spun fibres and is more likely to be controlled by some intrinsic property of the polymer.

5.2. Griffith theory

As indicated above, an alternative approach to the study of the strength–diameter relationship, based on the Griffith theory of fracture, has been proposed by Smook *et al.* [10].

Figs 10–12 display the results of this present study presented in the form $1/\sigma$ versus $d^{1/2}$. By extrapolating to zero diameter the intrinsic strength of a fibre without flaws is obtained (Table V).

At room temperature, the intrinsic strength of flawless fibres prepared from the lower molecular weight polymer SCLAIR 2909 increases from 0.39 GPa to 1.13 GPa as the modulus increases from 10 GPa to 30 GPa, and at $-55\,^{\circ}C$ over the same range of modulus the intrinsic strength increases from 0.98 GPa to 2.07 GPa. For the higher molecular weight NEWS 1950 polymer the intrinsic strengths of fibres at room temperature and $-55\,^{\circ}C$ are 2.24 and 2.81 GPa, respectively.

TABLE IV Room-temperature result

Polymer	Modulus[a] (GPa)	Slope of ln σ versus ln ϕ	m_{sur}^{b}	m_{vol}^{c}	m from Weibull plot
SCLAIR 2909	10	0.038	–	–	–
	20	0.024	–	–	–
	30	−0.109	9.2	18.4	22
NEWS 1950	30	−0.312	3.2	6.5	17

[a] modulus measured at room temperature.
[b] $m_{sur} = -1/\text{slope of ln } \sigma \text{ versus ln } \phi$ plot.
[c] $m_{vol} = -2/\text{slope of ln } \sigma \text{ versus ln } \phi$ plot.

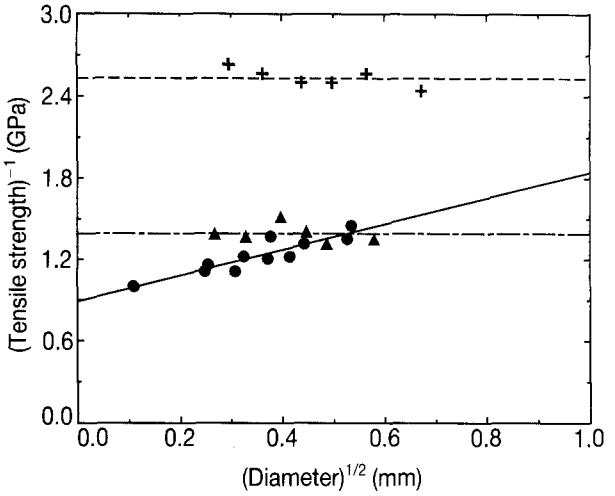

Figure 10 Reciprocal tensile strength versus square root of diameter of oriented SCLAIR 2909 fibres. (+) $E = 10$ GPa; (▲) $E = 20$ GPa; (○) $E = 30$ GPa.

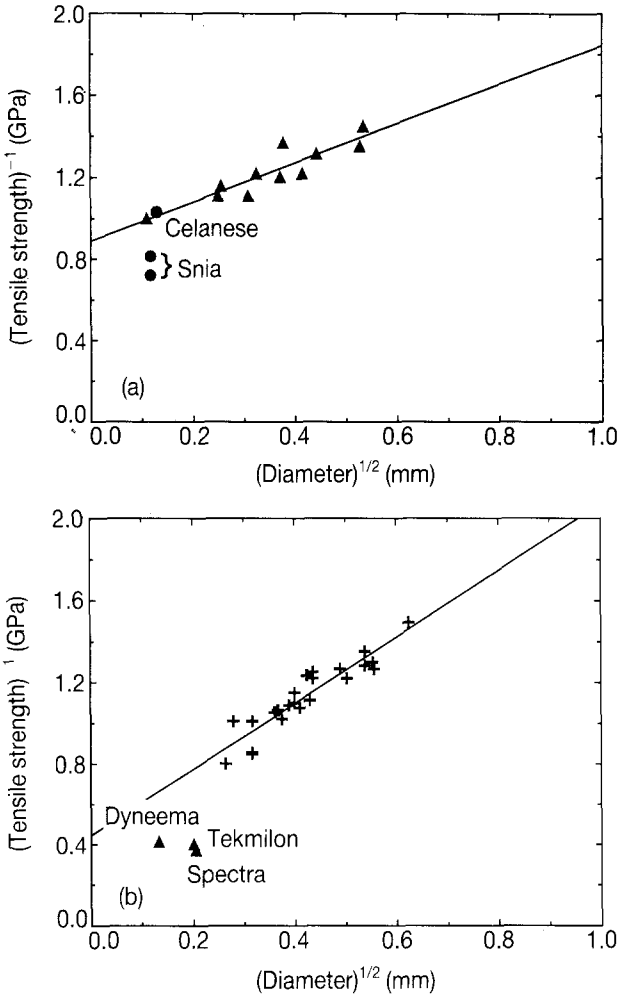

Figure 11 Reciprocal tensile strength versus square root of diameter of oriented polyethylene fibres. (a) (▲) 30 GPa SCLAIR 2909; (●) commercial fibres. (b) (+) 30 GPa NEWS 1950; (▲) commercial fibres.

These intrinsic strengths are far below the value of 19 GPa estimated for the theoretical strength of polyethylene [29] and are also much lower than those reported by Smook *et al.* [10]. In the latter case, the fibres were prepared by surface-growth/hot-drawn and gel-spun/hot-drawn methods and have a much

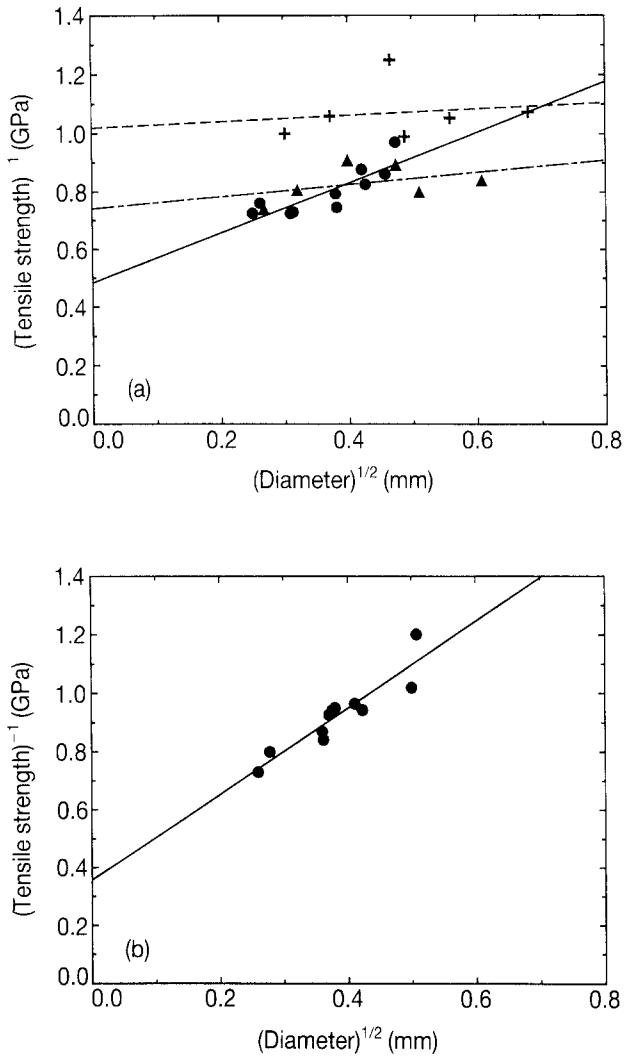

Figure 12 Reciprocal tensile strength, at $-55\,°C$, versus square root of diameter of oriented polyethylene fibres. (a) SCLAIR 2909; (+) $E = 10$ GPa; (▲) $E = 20$ GPa; (●) $E = 30$ GPa. (b) NEWS 1950; (●) $E = 30$ GPa.

TABLE V Low-temperature result

Polymer	Modulus[a] (GPa)	Slope of ln σ versus ln ϕ	m^b_{sur}	m^c_{vol}	m from Weibull plot
SCLAIR 2909	10	−0.031	32.3	64.5	27.6
	20	−0.064	15.6	31.2	–
	30	−0.175	5.7	11.4	18.4
NEWS 1950	30	−0.30	3.3	6.6	14.8

[a] modulus measured at room temperature.
[b] $m_{sur} = -1$/slope of ln σ versus ln ϕ plot.
[c] $m_{vol} = -2$/slope of ln σ versus ln ϕ plot.

TABLE VI Tensile strength of flawless fibres

Polymer	Modulus (GPa)	Tensile strength (GPa)	
		21 °C	−55 °C
SCLAIR 2909	10	0.397	0.98
	20	0.72	1.35
	30	1.13	2.07
NEWS 1950	30	2.24	2.81

higher modulus than the melt-spun fibres of this present study. They also vary considerably in modulus from the thickest fibres, which have a comparatively low modulus, to the thinnest, which have very high moduli, reaching 100 GPa. It would appear that the various diameter fibres studied by Smook *et al.* [10] were prepared by increasing the wind-up speed for both the solution-spun and gel-spun products. The spun fibres were then drawn to the maximum draw ratio for each wind-up speed, resulting in final fibres with a range of molecular structures. These fibres are not, therefore, comparable to those used in this present study which are drawn to a constant modulus. Applying Griffith theory to the present data gives values of the intrinsic strength which more nearly approach that reported by Smith and Lemstra [30] who obtained a maximum value for tensile strength of approximately 6 GPa by extrapolation of the strength/ modulus relationship to the maximum theoretical modulus for polyethylene. However, even in that investigation, the various moduli appear to have been achieved by varying the draw ratio of the initial spun fibre and hence the fibres are of different diameters.

As discussed above, the data on gel-spun fibres, with the exception of Bastiaansen [28], are derived from samples of variable modulus and cannot be directly compared with the melt-spun material where the modulus has been kept constant. The low strength of the apparent flawless melt-spun fibre that is derived from the Griffith approach is again a reflection of the flaws that develop in the fibre which arise from the deformation that it undergoes at drawing. In contrast, the gel-spun fibres, in spite of their very high draw ratio, are derived from a less entangled spun network and draw to a more homogeneous fibre.

6. Conclusion

We have considered the effect of filament diameter and molecular weight on the tensile strength and failure mechanisms of ultra-high-modulus polyethylene fibres. At low modulus, the tensile strength is invariant with diameter and is an intrinsic property of the fibre, determined primarily by its molecular weight and draw ratio. As the modulus increases to 30 GPa, the tensile strength depends on the diameter of the fibre and relates to the concentration of flaws in the fibre structure. At low molecular weight ($\bar{M}_w = 68\,000$), failure results from the linear growth of the major flaw in the sample but at higher molecular weight ($\bar{M}_w = 180\,000$–$300\,000$) there is a modification of the flaw growth, producing a greater dependence of tensile strength on the fibre diameter. At the higher molecular weights it appears that the linear flaw development is modified by a greater adhesion between the microfibrils of the fibre than at lower molecular weights, as shown by the higher force needed to split a fibre along its length. When we compare the results on melt-spun fibres with those of gel-spun from our limited study, and a comparison with reported data, it would appear that these revert to an intrinsic mechanism of failure. It is proposed that this

arises from a more mobile network in the undrawn gel-spun fibre which imposes less stress on the molecular structures when drawn to the high draw ratio producing a more homogeneous drawn fibre.

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