JOURNAL OF MATERIALS SCIENCE 21 (1986) 4199–4205

A study of the effect of molecular weight on the tensile strength of ultra-high modulus polyethylenes

M. A. HALLAM, D. L. M. CANSFIELD, I. M. WARD, G. POLLARD*
*Department of Physics, and *Department of Metallurgy, University of Leeds, Leeds LS2 9JT, UK*

In this paper the influence of molecular weight and molecular weight distribution on the tensile strength (tenacity) of melt spun and drawn linear polyethylene are investigated with the aim of outlining the requirements for a high strength fibre. The tenacity was investigated over the molecular weight average $\bar{M}_w$ range 60×10^3 to 330×10^3 with polydispersities $\bar{M}_w/\bar{M}_n$ ranging from 1.1 to 13.3. It was found that both molecular weight and its distribution affected tensile strength. The drawing conditions were also found to be important, a high draw temperature and a high draw ratio being needed for a high strength, high modulus fibre. By using a polymer of high $\bar{M}_w$ and low polydispersity, and drawing at the optimum conditions, strengths of 1.65 GPa and moduli of 85 GPa have been achieved for test temperatures of −55° C.

1. Introduction

The preparation of ultra high modulus polyethylene fibres by tensile drawing, by solution spinning and by drawing of gel-spun fibres is now well documented in the scientific and patent literature [1–6]. In addition to high modulus, these fibres possess comparatively high tensile strengths. Although this is also of considerable scientific interest, there is appreciably less understanding of the factors which determine strength than modulus. Smith and co-workers [7, 8] have compared the behaviour of gel spun and hot drawn fibres and shown distinct molecular weight effects. This was also indicated by Wu and Black [9], and is consistent with similar observations on conventional textile fibres, dating back to the pioneering work of Flory [10].

In the present paper, a detailed study is presented of the influence of molecular weight and molecular weight distribution on the tensile strength (tenacity) of melt spun and drawn linear polyethylene. Particular care has been taken to eliminate the influence of temperature and strain rate on the measured values of tenacity. In addition, the drawing process has also been varied to determine how sensitive the results are to optimisation in this respect.

2. Experimental details

2.1. Sample preparation

The samples were prepared from a series of twelve polyethylene homopolymers with a wide range of weight average and number average molecular weights. The values of $\bar{M}_w$ and $\bar{M}_n$ are shown in Table I, together with the grade identification of the polymer.

In the case of Alathon 7050 grade, multifilament yarn draw ratio (λ) of 45 prepared by melt spinning and drawing was supplied by the Celanese Research Company (CRC, Summit, New Jersey, USA). All the other polymer samples were processed into drawn monofilaments at Leeds University. First, an isotropic monofilament (the spun monofilament) was produced from the polymer granules or powder using a very small scale melt spinning machine of capacity ~3 g. In this machine the polymer was heated in a small pack and forced successively through a 200 mesh grid, a 50 mesh grid, a bridge plate with a 1.5 mm diameter hole and finally through a spinneret with a hole diameter of 0.4 mm. Continuous steady extrusion was maintained by driving a ram down the pack by means of a motor driven screw.

The spun filament was then drawn to the required draw ratio on a laboratory draw frame in a one stage operation. The nominal draw ratio was determined by the ratio of the circumferential speeds of the feed and draw rolls, the final drawing speed being between 3 and 6 m min^{-1}. The actual draw ratio was then ascertained by the weight ratio of a known length of undrawn and drawn material. A heated zone, 120 mm long, in which drawing took place was provided by a glycerol bath. Monofilaments produced by this process were between 0.06 and 0.10 mm diameter.

2.2. Dynamic mechanical measurements

Dynamic mechanical measurements were undertaken at different frequencies in the temperature range from room temperature to −160° C. These measurements were performed on apparatus described in a previous publication [11]. In this apparatus the sample, of length 50 mm, is subjected to a sinusoidal strain produced by an electromagnetic vibrator. The stress is measured by a non-bonded strain gauge transducer attached to the sample, and the strain by a similar transducer connected to the vibrator by a calibrated spring. The sample is enclosed in a polyurethane foam

0022–2461/86 $03.00 + .12

TABLE I Characterization and spinning conditions of polyethylenes

Ref. no.		Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Spinning temp. (° C)
1		Alathon 7050	22.0	59	2.7	150
2	Set I	Rigidex 50b	7.8	104	13.3	200
3		Rigidex 50a	12.3	101	8.2	200
4		Rigidex 25	13.0	100	7.7	200
5		BXP 10	16.8	94	5.6	200
6		Rigidex 006-60	19.0	120	6.3	200
7		Alathon 7030	28.0	115	4.1	200
8		NBS SRM 1484	110.0	120	1.1	210
9	Set II	BP 206	16.6	213	12.8	270
10		Unifos 2912	24.2	224	9.3	270
11		XGR 661	27.8	220	7.9	270
12		H020 65P	33.0	312	9.5	300

temperature chamber and the required temperature obtained by passing a stream of cold nitrogen gas, boiled from a dewar and heated to the required temperature by a wire heating element, through the chamber. The sample is first held under a constant dead load for a few seconds sufficient to produce a strain at room temperature greater than the strains to be imposed in the test. A sinusoidal strain increasing in set increments is applied about the static level. The signals from the stress and strain transducers are fed to a Solartron 1172 frequency response analyser and after further on-line computer processing the results are presented as storage and loss compliances over a range of temperatures and frequencies.

2.3. Tensile tests

To study the effects of temperature, strain rate, molecular weight and drawing temperature on tenacity, load–extension curves were obtained on an Instron 1026 tensile testing machine. Using a range of cross-head speeds it was possible to obtain a strain rate range of 8.3×10^{-6} to $33 \times 10^{-3}\,\text{sec}^{-1}$ for a fixed gauge length of 100 mm.

The testing machine was equipped with an environmental chamber, to enable temperatures from room temperatures to −70° C to be achieved by simultaneous use of carbon dioxide gas and a heating element. For lower temperatures liquid nitrogen was used in a similar system to that employed for cooling samples during dynamic mechanical testing.

The multifilament and monofilaments were held for testing between steel grips faced with either polyethylene or neoprene sheet. The facing was introduced to prevent premature failure of the fibre at the clamp. The clamps had a polyethylene lining for the temperature range between room temperature and 0° C, below 0° C neoprene was used.

The original cross-sectional area of each sample was calculated by weighing a known length of fibre and dividing by the assumed density of $965\,\text{kg}\,\text{m}^{-3}$. The tenacity and 1% secant modulus were computed from the nominal stress values using the original cross-sectional area and the load measured from the load–extension curve.

3. Results and discussion

3.1. Dynamic mechanical measurements

The temperature variation of the axial storage modulus, E', and the corresponding loss factor, $\tan \delta_E$ for the Alathon 7050 multifilament yarn (sample 1) are shown in Figs 1a and b. It can be seen that there is a steady rise in E' below − 100° C, due to the γ-relaxation process. With increasing draw ratio there is a slight broadening of this rise. Above − 50° C a rapid drop in E' with temperature can be observed due to the onset of the α-relaxation process. This process is shifted to

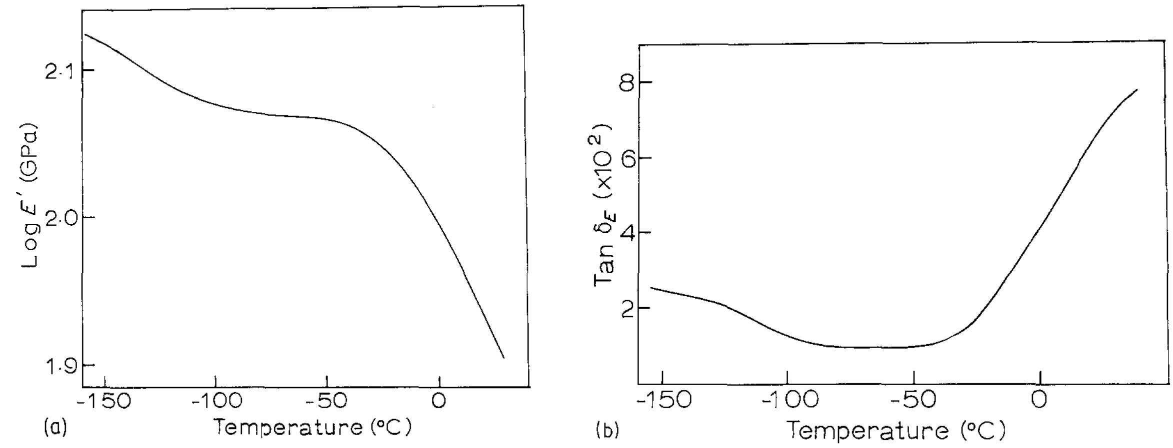

Figure 1 (a) The storage modulus, E', as a function of temperature for Alathon 7050 yarn drawn 45 times (supplied by CRC). (b) The mechanical loss factor, $\tan \delta_E$, corresponding to the data for Fig. 1a.

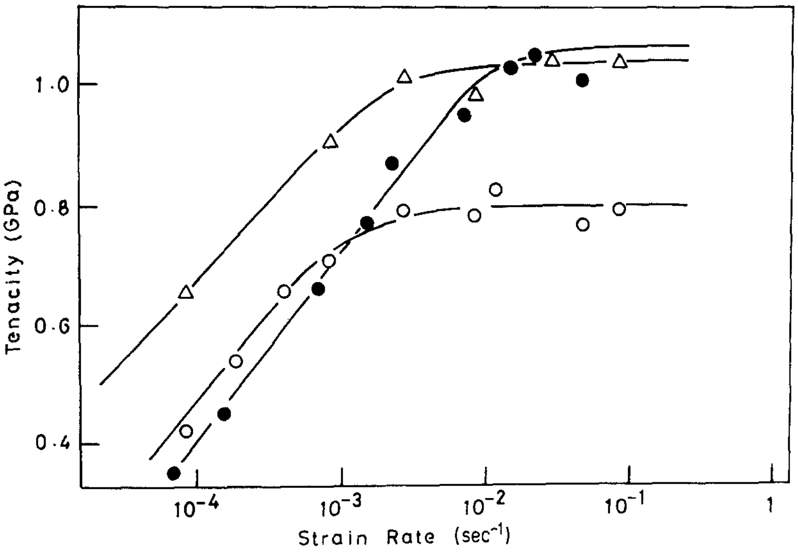

Figure 2 The effect of molecular weight on tenacity at varying strain rate for three molecular weight samples all drawn × 30 and tested at room temperature: (●) Alathon 7050; (○) Rigidex 50; (△) Unifos 2912.

lower temperatures and decreased in intensity with increase in draw ratio. In between the two relaxation processes a low temperature plateau region is present which is unaffected by draw ratio. The α and γ loss peaks in tan δ_E are shown in Fig. 1b.

These results confirm that there is a plateau in the modulus–temperature–frequency surface around $-55°$ C, free from any draw ratio dependent loss mechanism. This would make the temperature around $-55°$ C suitable to investigate molecular weight and draw temperature effects on the physical properties. There is excellent consistency with previous studies where the $-55°$ C plateau moduli were used to correlate with structural parameters [12].

3.2. Effect of strain rate on tenacity

Cansfield *et al.* [13] showed that strain rate has a marked effect on the tenacity of ultra high modulus polyethylene in the room temperature region. These results were obtained on a sample of low weight average molecular weight. In this investigation, a preliminary study of three different $\bar{M}_w$ samples, with a draw ratio of 30, tested at room temperature (Fig. 2) showed that tenacity is dependent on strain rate but to a varying extent for each molecular weight. It can be seen from Fig. 2 that all the curves exhibit a plateau region where the tenacity is independent of strain rate and the polymer fails in a brittle manner. As the strain rate is reduced the measured tenacity falls rapidly exhibiting a linear relationship between tenacity and strain rate, indicating a change in the failure mode from brittle to ductile behaviour. Draw ratio is also known to have an effect on the ductile–brittle transition temperature [14], T_B. On increasing the draw ratio at a constant temperature T_B moves to lower strain rates (alternatively at a constant strain rate increasing the draw ratio moves the ductile–brittle transition to higher temperatures).

For the present investigation it is desirable not to study the ductile region of failure because the effects of molecular weight and draw temperature on tenacity are then complicated by chain slippage and flow which are in turn affected by molecular weight and draw ratio. It is therefore necessary to find a temperature regime where tenacity is independent of strain rate. This means choosing a temperature at which the behaviour is not affected by relaxation processes, chain slippage or failure mode transitions. The dynamic mechanical results show $-55°$ C to be a temperature free of relaxation processes, suggesting a convenient region to search for tenacity values which will be strain rate independent.

Fig. 3 summarizes the results of a series of measurements showing tenacity as a function of strain rate and

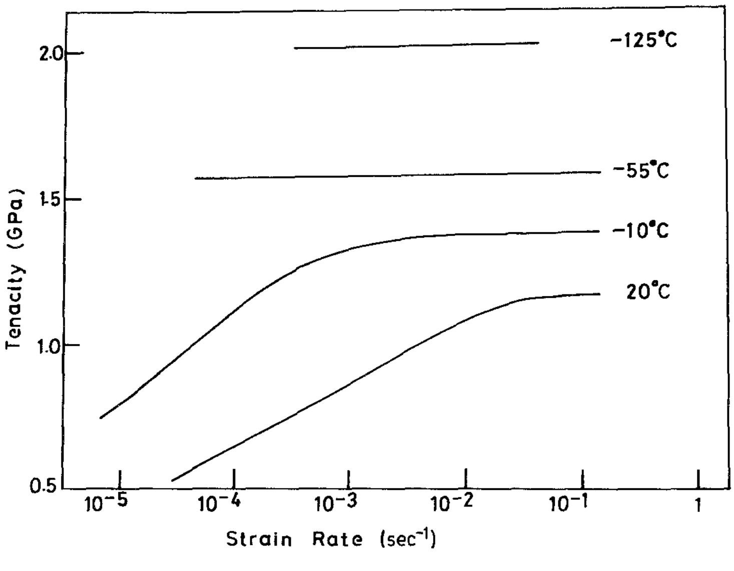

Figure 3 The effect of temperature and strain rate on yield/breaking stress for Alathon 7050, λ = 45 samples (CRC supplied).

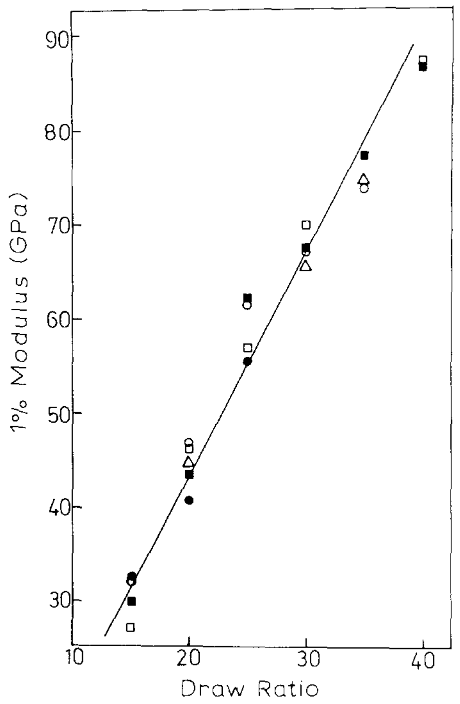

Figure 4 $-55°$ C 1% secant modulus as a function of draw ratio (λ) for two monofilament samples, Alathon 7030 and Unifos 2912, oriented at a number of different draw temperatures (λ_{DT}). Alathon 7030: (■) $\lambda_{DT} = 100°$ C; (□) $\lambda_{DT} = 115°$ C. Unifos 2912: (●) $\lambda_{DT} = 100°$ C; (○) $\lambda_{DT} = 115°$ C; (△) $\lambda_{DT} = 125°$ C.

temperature for the Alathon 7050 multifilament yarn ($\lambda = 45$). At room temperature and $-10°$ C the ductile–brittle transition is seen. On reducing the temperature from 20° C to $-10°$ C the transition point moves from 3×10^{-2} to $8 \times 10^{-4} \text{sec}^{-1}$. At $-55°$ C the ductile–brittle transition has moved to such a low strain rate that it can no longer be observed over the strain rate range 10^{-4} to 10^{-1}sec^{-1}. Over this strain rate range the tenacity is independent of strain rate. As expected no ductile–brittle transition is seen at $-125°$ C but the difficulties of working at this low temperature make it unsuitable for a lengthy series of tests.

In a strain rate independent region, the tenacity, 1% secant modulus and extension to break, can be determined from measurements at a single strain rate. On the basis of the measurements described above standard test conditions were set as a strain rate of 10^{-2}sec^{-1} (50mm min^{-1} for 100 mm gauge length) at $-55°$ C. For these conditions any effects due to molecular weight or draw temperature on tenacity can be clearly identified, and these will now be discussed in turn.

3.3. Effect of molecular weight on tenacity

The molecular weight characterization of the twelve samples selected for a study of the influence of molecular weight on tenacity are given in Table I. Two molecular weight average values, Set I with $\bar{M}_w$ 100 000 and Set II $\bar{M}_w$ 220 000, account for ten of the polymers. The other two polymers included in the study are a polymer of lower $\bar{M}_w$ (60 000) Alathon 7050, and a polymer of higher $\bar{M}_w$ (330 000) Rigidex, H020 54P.

The whole range of samples was drawn at a drawing temperature, λ_{DT}, of 100° C. It was necessary to show that the standard drawing conditions used produced effective drawing, and this was done by measuring the modulus.

Two polymers Alathon 7030 ($\bar{M}_w = 100 000$) and Unifos 2912 ($\bar{M}_w = 220 000$) were drawn to ratios between 15 and 40 times at different λ_{DT} values. The 1% secant modulus was determined for all samples and showed a linear relationship with draw ratio, λ (Fig. 4). This agrees with previously reported results [1–3, 15] that, provided the drawing process is effective, modulus is uniquely dependent on λ, and is unaffected by $\bar{M}_w$. The 1% secant modulus, for a sample of draw ratio 15 should typically be about 31 GPa and for draw ratio 20 about 43 GPa, at $-55°$ C.

Initially each of the twelve polymers was drawn to ratios of 15 and 20. These were chosen as draw ratios

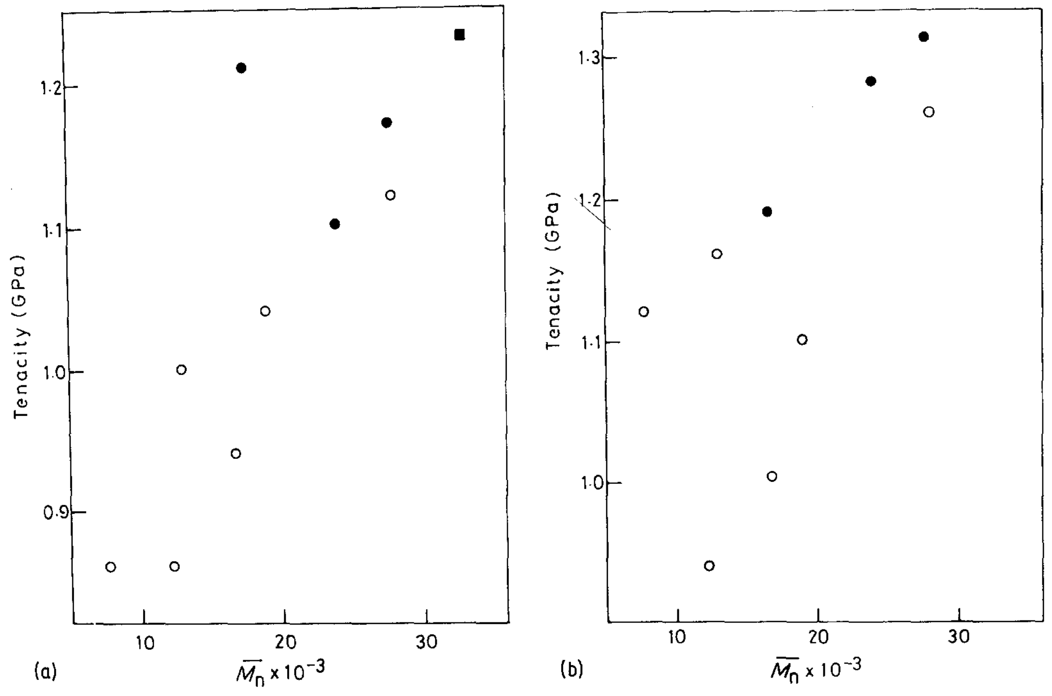

Figure 5 (a) The effect of molecular weight number average ($\bar{M}_n$) on tensile strength at $-55°$ C for different molecular weight averages ($\bar{M}_w$), draw ratio (λ) 15; (○) $\bar{M}_w = 100 000$ (●) $\bar{M}_w = 220 000$, (■) $\bar{M}_w = 330 000$. (b) $\lambda = 20$.

TABLE II Effect of molecular weight on the tensile properties of oriented polyethylenes at −55° C.
(a) Draw ratio of 15

Ref. no.		Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	σ (GPa)	E (GPa)
1		Alathon 7050	22.0	59	2.7	0.92	38.5
2	Set I	Rigidex 50b	7.8	104	13.3	0.86	32.2
3		Rigidex 50a	12.3	101	8.2	0.86	31.8
4		Rigidex 25	13.0	100	7.7	1.00	32.1
5		BXP 10	16.8	94	5.6	0.94	31.8
6		Rigidex 006-60	19.0	120	6.3	1.04	32.2
7		Alathon 7030	28.0	115	4.1	1.12	30.1
8		NBS SRM 1484	110.0	120	1.1	1.23	31.4
9	Set II	BP 206	16.6	213	12.8	1.21	33.6
10		Unifos 2912	24.2	224	9.3	1.11	32.2
11		XGR 661	27.8	220	7.9	1.17	31.4
12		H020 54P	33.0	312	9.5	1.23	36.6

(b) Draw ratio of 20

Ref. no.		Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	σ (GPa)	E (GPa)
1		Alathon 7050	22.0	59	2.7	1.13	43.2
2	Set I	Rigidex 50b	7.8	104	13.3	1.12	45.1
3		Rigidex 50a	12.3	101	8.2	0.94	43.8
4		Rigidex 25	13.0	100	7.7	1.16	46.6
5		BXP 10	16.8	94	5.6	1.03	42.9
6		Rigidex 006-60	19.0	120	6.3	1.11	42.0
7		Alathon 7030	28.0	115	4.1	1.26	43.7
8		NBS SRM 1484	110.0	120	1.1	–	–
9	Set II	BP 206	16.6	213	12.8	1.19	44.6
10		Unifos 2912	24.2	224	9.3	1.28	40.8
11		XGR 661	27.8	220	7.9	1.31	40.1
12		H020 54P	33.0	312	9.5	1.09	48.8

which could be expected to be achieved for the full range of $\bar{M}_w$ for a fixed draw temperature of 100° C. The values of 1% secant modulus, were in agreement with previously stated values and confirm that the drawing conditions were satisfactory.

The data presented in Tables IIa and b can be used to assess the effects of both $\bar{M}_w$ and $\bar{M}_n$ on tenacity. It can be seen that within a constant $\bar{M}_w$ set a polymer with a higher $\bar{M}_n$ value has a higher tenacity.

Consider also the effect of $\bar{M}_n$ on tenacity for the $\bar{M}_w = 100\,000$ set of polymers. A three-fold increase in $\bar{M}_n$ from 7000 to 28 000 produces a 0.25 GPa rise in tenacity at both draw ratios. A further increase in $\bar{M}_n$ from 28 000 to 110 000 increases the tenacity by a further 0.1 GPa, this result being only available for a draw ratio of 15.

For the three polymers with $\bar{M}_w$ of 220 000, the $\bar{M}_n$ range is not as large. Raising $\bar{M}_n$ from 16 600 to 27 800 produces little effect on tenacity at $\lambda = 15$ but there is an increase of 0.1 GPa at a draw ratio of 20. These results are shown in Figs 5a and b, where the increase in tenacity with increasing $\bar{M}_n$ is clearly visible.

Figs 5a and b also show the effect of $\bar{M}_w$ on tenacity, the higher $\bar{M}_w$ polymers being grouped together at higher values of tenacity, i.e. at constant $\bar{M}_n$ the polymer having the higher $\bar{M}_w$ has the greater tenacity. To illustrate this point three pairs of data, a, b and c with $\bar{M}_n$ values 16 800, 23 000 and 28 000, respectively, were selected from Tables IIa and b and are illustrated separately in Tables IIIa and b. At a draw ratio of 15, doubling $\bar{M}_w$ increases tenacity by approximately 0.15 GPa. This is also seen to be the case at a draw ratio of 20.

It will be concluded from all these results that neither $\bar{M}_w$ or $\bar{M}_n$ determine uniquely the breaking strength, but that both have a role to play confirming the findings of Smith *et al.* [8]. The combined effects of $\bar{M}_w$ and $\bar{M}_n$ can be best illustrated by plotting the molecular weight distribution, $\bar{M}_w/\bar{M}_n$, against tenacity, Figs 6a

TABLE III Selected data from Tables IIa and b to illustrate the effect of number average molecular weight ($\bar{M}_n$) on the tensile strength of oriented polyethylenes at −55° C
(a) Draw ratio of 15

	Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	σ (GPa)
Set a	BXP 10	16.8	94	0.94
	BP 206	16.6	213	1.21
Set b	Alathon 7050	22.0	60	0.92
	Unifos 2912	24.2	224	1.11
Set c	Alathon 7030	28.0	115	1.12
	XGR 661	27.8	220	1.17

(b) Draw ratio of 20

	Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	σ (GPa)
Set a	BXP 10	16.8	94	1.03
	BP 206	16.6	213	1.19
Set b	Alathon 7050	22.0	60	1.13
	Unifos 2912	24.2	224	1.28
Set c	Alathon 7030	28.0	115	1.26
	XGR 661	27.8	220	1.31

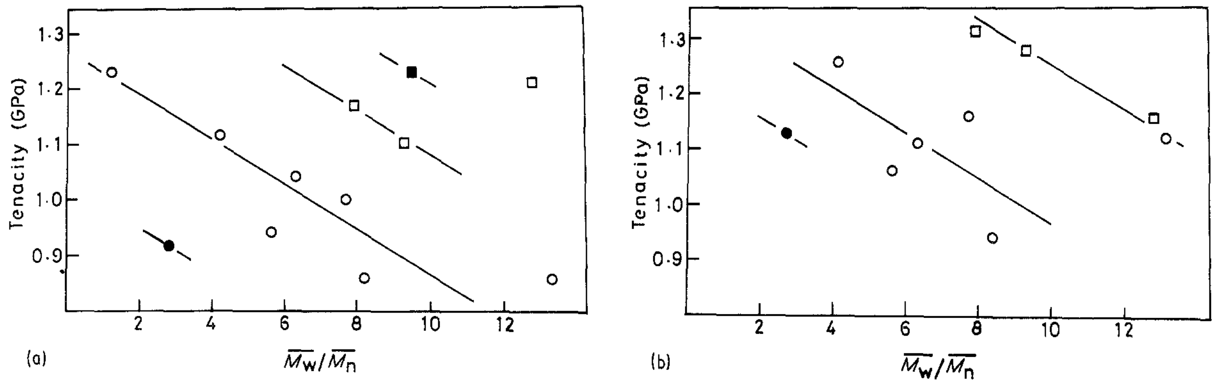

Figure 6 (a) The dependence of − 55° C tensile strength on molecular weight ratio ($\bar{M}_w/\bar{M}_n$), for a draw ratio (λ) of 15. The symbols indicating different $\bar{M}_w$ values; (●) 60 000, (○) 100 000, (□) 220 000, (■) 330 000. (b) $\lambda = 20$.

and b. In general the tenacity follows a linear relationship with $\bar{M}_w/\bar{M}_n$ at any particular $\bar{M}_w$ value, and increases as $\bar{M}_w/\bar{M}_n$ decreases.

3.4. Effect of draw temperatures on tenacity

As stated previously, the twelve polymers were all drawn under the same conditions of draw temperature and draw ratio. Previous workers [6] have shown that over such a range of molecular weight, although effective drawing will occur, it will not necessarily produce the optimum tensile properties in the final product. One polymer from each of the main $\bar{M}_w$ groups was therefore selected to investigate the effect of draw temperature, on drawability and tenacity. The polymers used were Alathon 7030 ($\bar{M}_w = 100\,000$) and Unifos 2912 ($\bar{M}_w = 220\,000$). The polymers were drawn to a series of draw ratios at draw temperatures of 100, 115, 120 and 125° C at a constant draw speed of 5.0 m min^{-1}. The results are shown in Figs 7a and b.

Fig. 7a refers to the polymer of lower $\bar{M}_w$ (Alathon 7030) and Fig. 7b to the polymer of higher $\bar{M}_w$ (Unifos 2912). For a fixed draw temperature it can be seen that as the draw ratio is increased the tenacity of the drawn product increases to a maximum and then declines. This maximum in the tenacity/draw ratio curve is clearly defined for Alathon 7030 drawn at 100° C and for Unifos 2912 drawn at 100 and 115° C. Further increases in the draw temperature to 120 and 125° C for Alathon 7030 and Unifos 2912, respectively, produce even higher tenacity values before a maximum in the curve can be reached. Any attempt to draw to higher draw ratios results in continual breaking of the fibre.

The reason for the decline in tenacity at high draw ratios is not clearly understood but appears to be connected with void formation. Filaments drawn to draw ratios above approximately 25 have an opaque appearance due to the presence of voids and fibrillation in their structure, which is associated with the lower rate of increase of tenacity with draw ratio, than that at lower draw ratios. In extending the draw process to these very high draw ratios, × 35 and above, if the draw temperature is low it appears that voids develop to such an extent that they significantly weaken the fibre structure. At draw ratios below about × 25 it is seen that for both polymers the tenacity is not affected by the draw temperature. It can also be noted that in both cases the actual maximum tenacity value achieved,

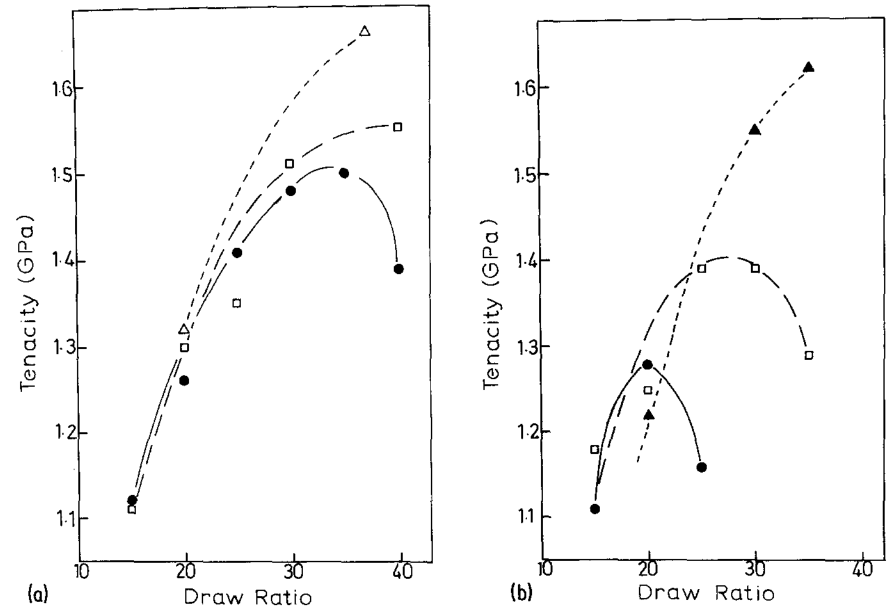

Figure 7 (a) The effect of draw ratio on −55° C tensile strength as a function of draw temperature (λ_{DT}), on samples of Alathon 7030 monofilament: (●) $\lambda_{DT} = 100°$ C; (□) $\lambda_{DT} = 115°$ C; (△) $\lambda_{DT} = 120°$ C. (b) On samples of Unifos 2912 monofilament: (●) $\lambda_{DT} = 100°$ C; (□) $\lambda_{DT} = 115°$ C; (▲) $\lambda_{DT} = 125°$ C.

irrespective of the difference in their molecular weights, is identical. If, however, we compare these results with the comparison of tenacity with $\bar{M}_w/\bar{M}_n$ ratio, for the two selected draw ratios (Figs 6a and b) it is seen that the enhancement of tenacity due to the high $\bar{M}_w$ value of Unifos 2912 is offset by its wide molecular weight distribution.

The polymers used in preparing the data for Figs 6a and b were not necessarily drawn at the optimum conditions for each particular polymer. These results for the determining of optimum draw temperature show that extremely high tenacities (1.65 GPa for example) can be obtained even from a polymer which has the intrinsic disadvantage of a wide molecular weight distribution. It would therefore appear that the selection of optimum drawing conditions is as important in obtaining maximum tensile properties as the correct choice of molecular weight and molecular weight distribution.

4. Conclusions

It has been shown that the problems involved in obtaining high strength, high modulus fibres from melt-extruded polymers by solid-state deformation are complex, due to the many variables involved in terms of the processing and the polymer characteristics.

Test conditions were established to evaluate molecular weight and drawing effects. A temperature of $-55°$ C and strain rate 10^{-2} sec^{-1} was selected because the measured modulus is then uniquely dependent on draw ratio and failure occurs in a brittle regime so that the fracture behaviour is independent of strain rate.

To obtain high strength and high modulus monofilaments it was found necessary to select: (a) high weight average molecular weight ($\bar{M}_w$); (b) either a monodispersed polymer or at least a polydispersity $\bar{M}_w/\bar{M}_n \leqslant 4$; (c) a high draw ratio; and (d) a high draw temperature.

References

1. G. CAPACCIO and I. M. WARD, *Nature Phys. Sci.* **243** (1973) 143.
2. *Idem*, Brit. Patent Appl. 10746 (filed 6 March 1973).
3. *Idem, Polymer* **15** (1974) 233.
4. A. ZWIJNENBERG and A. J. PENNINGS, *J. Polym. Sci. Polym. Lett. Ed.* **14** (1976) 339.
5. P. SMITH and P. J. LEMSTRA, *J. Mater. Sci.* **15** (1980) 505.
6. I. M. WARD, *Adv. Polym. Sci.* **70** (1985) 1.
7. P. SMITH and P. J. LEMSTRA, *J. Polym. Sci. Polym. Phys. Ed.* **19** (1981) 1007.
8. P. SMITH, P. J. LEMSTRA and J. P. L. PIJPERS, *ibid.* **20** (1982) 2229.
9. W. WU and W. B. BLACK, *Polym. Eng. Sci.* **19** (1979) 1163.
10. P. J. FLORY, *J. Amer. Chem. Soc.* **67** (1945) 2048.
11. J. B. SMITH, G. R. DAVIES and I. M. WARD, *J. Polym. Sci. Polym. Phys. Ed.* **13** (1975) 2331.
12. A. G. GIBSON, G. R. DAVIES and I. M. WARD, *Polymer* **19** (1978) 683.
13. D. L. M. CANSFIELD, I. M. WARD, D. W. WOODS, A. BUCKLEY, J. M. PIERCE and J. L. WESLEY, *Polymer Commun.* **24** (1983) 130.
14. P. L. CLARKE, PhD thesis, Leeds (1981).
15. G. CAPACCIO, T. A. CROMPTON and I. M. WARD, *J. Polym. Sci. Polym. Phys. Ed.* **14** (1976) 1641.

Received 9 January
and accepted 13 March 1986