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# Tensile Strength of Highly Oriented Polyethylene. II. Effect of Molecular Weight Distribution

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## Synopsis

The tensile strength of oriented polyethylene filaments is discussed in relation to molecular weight. Short-term tensile properties at room temperature were obtained in our laboratory and from the literature for polymer samples covering the molecular weight ( $\overline{M}_w$ ) range from  $54 \times 10^3$  to  $4 \times 10^6$ , and polydispersities ranging from 1.1 to 15.6, oriented by solid-state extrusion, melt spinning/drawing, solution spinning/drawing, and "surface growth." It was found that both the molecular weight and its distribution markedly affected tensile strength. The breaking stress  $\sigma$  of highly oriented fibers varied with molecular weight roughly as  $\sigma \propto M^{0.4}$ , at constant  $\overline{M}_w/\overline{M}_n$  over the entire range studied. Reduction of polydispersity from 8 to 1.1 by an increase of  $\overline{M}_n$  with  $\overline{M}_w$  approximately constant at  $10^5$  increased tensile strength of oriented polyethylene filaments by a factor of nearly 2.

## INTRODUCTION

A great many studies have been devoted to the influence of the molecular weight and its distribution on the mechanical properties of polymers.<sup>1-11</sup> These investigations are of utmost significance from both fundamental and technological points of view.

As long ago as 1945 Flory discussed the tensile strength in relation to molecular weight of high-molecular-weight polymers. On the basis of experimental data<sup>12</sup> on the tensile strength of cellulose acetate fractions and of butyl rubber vulcanizates he derived the relation

$$\sigma = A - B/\overline{M}_n \quad (1)$$

where  $\sigma$  is the tensile strength,  $A$  and  $B$  are constants, and  $\overline{M}_n$  is the number-average molecular weight. Equation (1) is, however, oversimplified. Time, temperature, and morphological and topological effects, which are known to determine the tensile properties of polymers to a large extent,<sup>13,14</sup> are exceedingly dependent on the distribution of chain lengths, rather than merely on the number of chain ends in a polymeric solid.

Up to now, only general and qualitative conclusions concerning the strength/molecular weight relation have been reached. Vincent<sup>1</sup> reported the flexural strength of polyethylene at  $-196^\circ\text{C}$  to depend markedly on the number-average molecular weight. In an extensive Russian study by Karasev et al.<sup>4</sup> it was found that the tensile strength of polyethylene at high temperatures ( $80$ – $100^\circ\text{C}$ ) depended to a considerable extent on the high-molecular-weight part of the distribution, and much less on the amount of low-molecular-weight fractions. At subzero temperatures not far from room temperature the me-

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chanical behavior of polyethylene was found to be largely determined by its content of low-molecular-weight material, which is in agreement with Vincent's findings. However, contradictory data have also been reported.<sup>9</sup>

The results quoted above were obtained for isotropic specimens. Now it is well established that molecular orientation introduces anisotropy of mechanical properties, and is accompanied by greatly improved tensile strength and Young's modulus in the axial direction.<sup>15-17</sup> Quantitative correlations between tensile strength of polyethylene and the molecular weight distribution are, however, lacking.

Difficulties in predicting, or even describing, the tensile properties of polymers having various molecular weights are intensified as a result of different responses to tensile tests of these materials. For example, isotropic high-molecular-weight polyethylene fractures at room temperature at a strain of about 400%, whereas material of lower molecular weight may exhibit plastic flow up to elongations of 1000% before failure occurs under identical testing conditions.<sup>4</sup> In the latter case the sample is subjected to chain extension and alignment, which is known to affect the number of chains which are stressed upon loading. Simply comparing the tensile strength or true stress at break of such different materials may give rise to incorrect interpretations. It would be of more significance to study the tensile properties as function of molecular weight for polymeric samples with the same degree of molecular orientation, particularly of highly oriented polyethylene, which is of direct technological interest. This amounts to comparison of polyethylene samples differing in molecular weights but having the same Young's modulus, which is thought to be strongly correlated with the degree of orientation of the macromolecules.<sup>18,19</sup> These highly oriented materials fail at relatively low strain (0.03-0.1),<sup>6,16</sup> and thus exhibit no major change in molecular orientation during the tensile test.

There are a number of techniques that can be employed to achieve orientation and extension of macromolecular chains, such as solid-state extrusion,<sup>6,7</sup> drawing,<sup>8,17,19</sup> and crystallization under stress.<sup>20-22</sup> Unfortunately, each of these methods has its optimum molecular weight range for processing. This is depicted schematically in Figure 1. Currently available equipment for solid-state deformation of polyethylene sets a limit at a weight-average molecular weight  $\bar{M}_w$  of about  $150 \times 10^3$ , owing to the rapid increase with molecular weight<sup>23</sup> of the forces required. (This upper limit can be increased by employing "disentangled," solution-crystallized high-molecular-weight polyethylene.) Drawing of melt-

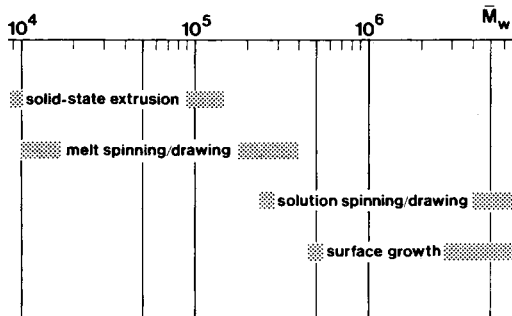


Fig. 1. Optimum (not necessarily exclusive) molecular weight ranges for various techniques of producing highly oriented/high-modulus polyethylene.

spun polyethylene filaments<sup>19</sup> becomes exceedingly difficult at molecular weights higher than ca.  $300 \times 10^3$ . This is due to the high density of trapped entanglements in these materials, which impedes the large deformations required for chain extension and alignment. This entanglement density can be drastically reduced by spinning from semidilute solution,<sup>17</sup> and the filaments obtained can then be drawn to very high draw ratios, despite the high molecular weight of the polymer. In the solution spinning/drawing technique a lower limit of  $\bar{M}_w \approx 300 \times 10^3$  is set by the poor spinnability of semidilute solutions of low-molecular-weight polyethylene. The "surface growth" method is primarily applicable to high-molecular-weight polyethylene<sup>20</sup>; as a matter of fact, linear polyethylene with  $\bar{M}_w = 500 \times 10^3$  and  $\bar{M}_n = 400 \times 10^3$  could not be processed successfully by this technique.<sup>24</sup>

Thus a straightforward investigation into the molecular weight dependence of the tensile strength of oriented polyethylene cannot be conducted over an appreciable molecular weight range using just one technique. In this study an attempt has been made to examine similarities between the various seemingly different orientation methods, and to compare tensile properties of polyethylene samples processed by these methods, covering a molecular weight range  $54 \times 10^3 < \bar{M}_w < 4 \times 10^6$  and polydispersities ranging from 1.1 to 15.6. The experimental results are in part taken from the literature and in part obtained in this work.

## EXPERIMENTAL

### Materials

Molecular characteristics of the various linear polyethylene samples used or quoted in this study are collected in Table I. Number- and weight-average molecular weights were obtained by gel permeation chromatography (GPC), or were provided by the manufacturers (Du Pont—Alathon; Phillips—Marlex; National Bureau of Standards—NBS SRM).

### Techniques

#### *Solid-State Extrusion*

Tensile properties of solid-state-extruded Alathon 7050 (sample 1) were taken from the extensive work of Porter et al.<sup>6,7</sup>

#### *Melt Spinning/Drawing*

Owing to the lack of reported data on the tensile strength of highly oriented melt-spun polyethylene, samples 2–6 were spun from the melt at 200°C at a takeup speed of about 15 m/min using small-scale laboratory spinning equipment. The monofilaments as spun had a diameter of ca. 0.3 mm. These fibers were subsequently drawn to various draw ratios up to ca. 30 under optimum conditions for effective drawing (given in Table I) at a strain rate of about 0.5 s<sup>-1</sup>. Additional results for sample 4 were taken from recent work by Wu and Black.<sup>8</sup>

TABLE I  
Characterization and Processing Conditions of Polyethylenes

Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$[\eta]_{\text{decalin}}^{\text{DSEC}}$ (dL/g)	Processing conditions	Reference
1 Alathon 7050	19	59	3.1	1.18	Solid-state extruded (data from Porter et al.)	6, 7
2 NBS SRM 1475	17	54	3.2	1.16	Melt spun; drawn at 75°C	
3 Marlex 6050	13	100	7.7	1.46	Melt spun; drawn at 75°C	
4 Alathon 7030	28	115	4.1	1.70	Melt spun/drawn (data from Wu and Black)	8
5 NBS SRM 1484	110	120	1.1	2.30	Melt spun; drawn at 80°C	
6 Marlex 6002	18	280	15.6	2.84	a) Melt-spun; drawn at 125°C b) Spun from 15% w/w solution; drawn at 95°C	
7 HDPE I <sup>a</sup>	120	800	6.7	9.0	Spun from 3% w/w solution; drawn at 110°C	25
8 HDPE II	150	1,100	7.3	11.2	Spun from 2% w/w solution; drawn at 120°C	26
9 Hostalen GUR	200	1,500	7.5	14.5	a) Surface grown (data from Zwijnenburg and Pennings) b) Spun from 2% w/w solution; drawn at 120°C (wet) c) Spun from 2% w/w solution; drawn at 130°C (dried)	20 17
10 HDPE III	>300	4,000	<13	25	Spun from 1% w/w solution; drawn at 125°C	25

<sup>a</sup> HDPE I-III are experimental DSM materials.

*Solution Spinning/Drawing*

Polyethylene samples 6–10 were spun from solution in decalin, quenched to form continuous gel fibers, and subsequently drawn according to procedures extensively described in previous papers.<sup>17,26</sup> Polymer concentrations of the spinning solutions were selected to ensure proper spinnability (indicated in Table I). The as-spun wet gel fibers were immediately drawn to various draw ratios at the temperatures given in Table I, unless stated otherwise.

*Surface Growth*

The tensile properties of “surface-grown” polyethylene filaments were taken from the work of Zwijnenburg and Pennings,<sup>20</sup> who employed the sample denoted 9 in Table I.

**Tensile Measurements**

Tensile properties of the various polyethylene filaments produced in this study were tested at room temperature at a strain rate of  $1 \text{ min}^{-1}$ . The initial sample length was 50 mm. It was found that changing the testing speed from 0.1 to  $1 \text{ min}^{-1}$  did not seriously affect the stress/strain behavior of the fibers. These testing conditions compare reasonably well with those employed by other authors, whose data are quoted in this paper. Accordingly, it is not expected that comparisons of the various data are invalid because of differences in experimental conditions. The moduli obtained in this work refer to the initial moduli. The cross-sectional area of all highly drawn filaments was found to be in the range  $(1-2) \times 10^{-3} \text{ mm}^2$  (determined from weight per unit length, assuming a crystal density of  $1 \text{ g cm}^{-3}$ ), except for the solid-state-extruded fibers, the cross section of which measured  $340 \times 10^{-3} \text{ mm}^2$ .

**RESULTS AND DISCUSSION**

It is not the purpose of this article to report on the effect of molecular weight and its distribution on the drawing behavior of polyethylene. This optic has been dealt with at length by a number of authors,<sup>16,27</sup> notably for melt-crystallized material. Accordingly, the tensile properties of the various polyethylene filaments will not be presented in the usual way as a function of the draw ratio. Our aim is to find a correlation between tensile strength and molecular weight for fibers having the same degree of orientation, which is reflected in the same value of the axial Young's modulus. Unlike the tensile strength, the modulus, as a small-strain quantity, is rather insensitive to the molecular weight.<sup>9,19,28</sup> Throughout we plot tensile strength versus Young's modulus of filaments having various molecular weights. It appears that experimental variables such as drawing temperature and rate do not affect tensile strength at constant modulus and molecular weight.

### Tensile Properties

Figure 2 shows the tensile strength–modulus relation for polyethylene samples 1 and 2 having nearly identical molecular weights but processed by solid-state extrusion<sup>6,7</sup> and melt spinning/drawing, respectively. Clearly, the melt-spun/drawn filaments exhibit higher tensile strength for all modulus values. Comparison of the tensile data obtained by Wu and Black<sup>8</sup> in melt spinning/drawing and by Kojima and Porter<sup>7</sup> in solid-state extrusion of Alathon 7040 ( $\bar{M}_n = 25 \times 10^3$ ;  $\bar{M}_w = 84 \times 10^3$ ) reveals the same tendency. The question arises whether the difference in mechanical properties is due to intrinsic dissimilarities between solid-state extrusion and drawing. This problem was discussed in a most interesting debate by Peterlin and Porter.<sup>29</sup> It was concluded that both techniques involve axial deformation of a macromolecular network leading to orientation and extension of the polymer chains. The major difference between solid-state extrusion and simple tensile drawing is the additional lateral stress in the former method. This is likely to result in differences in the lateral properties of the samples produced, but not in axial tensile characteristics.<sup>29</sup> Hence we attribute the lower tensile strength of the solid-state extruded samples to the significantly larger cross-sectional area of the final specimens in comparison with that of the melt-spun/drawn filaments (about a factor of 200, see Experimental). The effect of fiber dimensions on tensile properties is known to be rather strong, and this may very well explain the differences observed.<sup>30</sup>

In Figure 3, tensile strength–modulus data are presented for samples 3–5, which were spun from the melt and subsequently drawn. These polyethylenes had approximately the same weight-average molecular weight of ca.  $10^5$ , but widely different  $\bar{M}_n$  values. The results are discussed in detail below.

Sample 6 with medium molecular weight was spun both from the melt and from solution. The mechanical properties of the drawn filaments are given in Figure 4. This figure very clearly shows that filaments having a particular stiffness exhibit identical short-term tensile strength, whether they are oriented by melt spinning/drawing or by solution spinning/drawing. This is, in fact, not too surprising.

The results in Figure 5 seem less obvious. Here tensile data for high-molec-

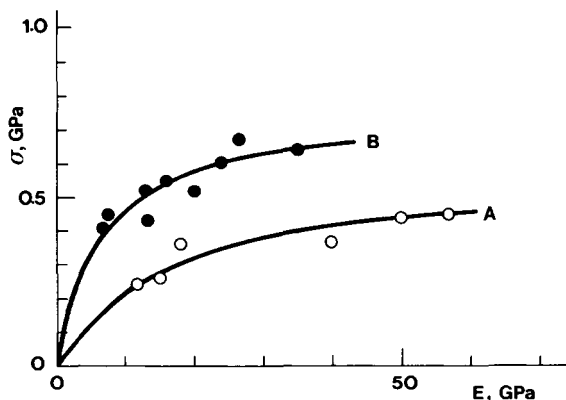


Fig. 2. Tensile strength vs. Young's modulus for various polyethylene filaments: (A) sample 1,  $\bar{M}_n = 19 \times 10^3$ ,  $\bar{M}_w = 59 \times 10^3$ , solid-state extruded (Porter et al.<sup>6,7</sup>); (B) sample 2,  $\bar{M}_n = 17 \times 10^3$ ,  $\bar{M}_w = 54 \times 10^3$ , melt spun/drawn.

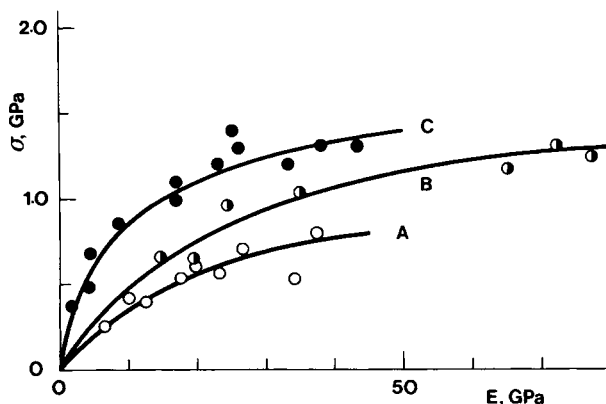


Fig. 3. Tensile strength vs. modulus for various melt-spun/drawn polyethylene fibers: (A) sample 3,  $\overline{M}_n = 13 \times 10^3$ ,  $\overline{M}_w = 100 \times 10^3$ ; (B) sample 4,  $\overline{M}_n = 28 \times 10^3$ ,  $\overline{M}_w = 115 \times 10^3$  (Wu and Black<sup>8</sup>); (C) sample 5,  $\overline{M}_n = 110 \times 10^3$ ,  $\overline{M}_w = 120 \times 10^3$ .

ular-weight polyethylene fibers produced at various temperatures by Zwijnenburg and Pennings employing the surface growth technique are plotted with results obtained for solution-spun/drawn filaments of the same polymer (sample no. 9, refs. 20 and 17). This plot clearly demonstrates that the tensile properties of the filaments virtually coincide, despite the fact that they were produced by seemingly different methods. There are two distinct ways of looking at this result. One way may be to conclude that the surface growth process entails drawing of polyethylene gels (as produced by solution spinning<sup>17</sup>) adhering to the surface of the rotor in the Couette apparatus in which the preparation is carried out. This view has been extensively discussed by Barham and Keller<sup>31,32</sup> and much less explicitly by Pennings.<sup>33</sup> On the basis of a number of well-chosen experiments, Barham et al.<sup>31</sup> arrived at the conclusion that the surface growth method amounts in fact to drawing of polyethylene gel structures. It should, however, be noted that filaments with identical mechanical properties were produced by drawing polyethylene gel fibers obtained by solution spinning that had been fully dried prior to stretching (refs. 26, 34; Fig. 5). The latter technique

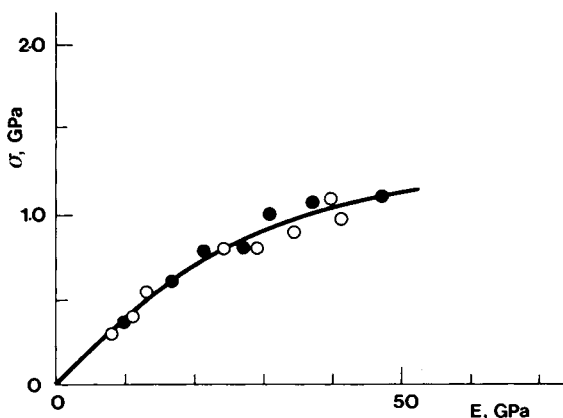


Fig. 4. Strength/modulus relation for polyethylene sample 6 ( $\overline{M}_n = 18 \times 10^3$ ,  $\overline{M}_w = 280 \times 10^3$ ): (O) melt spun/drawn; (●) solution spun/drawn.



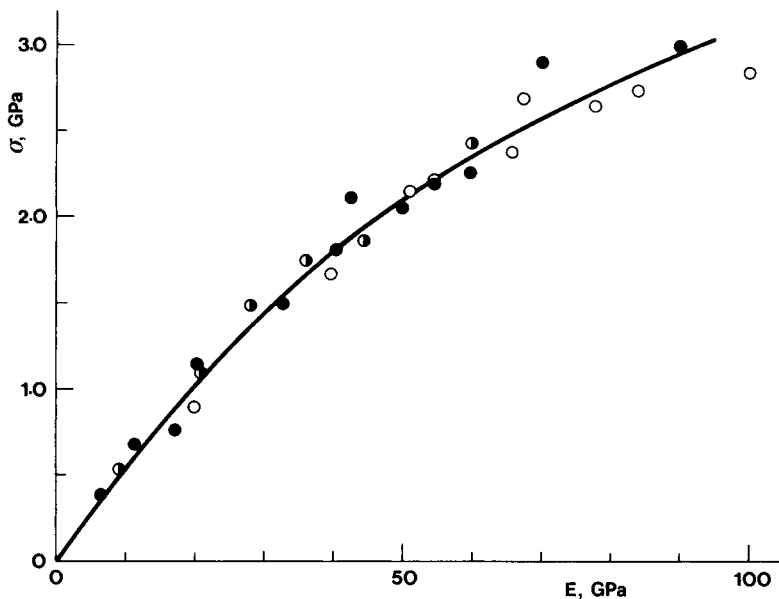


Fig. 5. Tensile strength vs. Young's modulus for high-molecular-weight polyethylene sample 9 ( $\bar{M}_n = 200 \times 10^3$ ,  $\bar{M}_w = 1.5 \times 10^6$ ): (O) surface grown (Zwijenburg and Pennings<sup>20</sup>); (●) solution spun/drawn wet; (●) solution spun/drawn dried. (For explanation see text.)

obviously cannot be termed "gel drawing," since no solvent was present in the drawing process, and, in fact, amounts to drawing of solution-spun high-molecular-weight polyethylene. The radically improved drawability of these solution-spun, dried fibers was explained previously<sup>34-36</sup> in terms of fixation of a low entanglement density in high-molecular-weight polyethylene crystallized from semidilute solution. At this point it would be more appropriate to conclude that surface growth and drawing of wet or dried gel fibers all involve the same macromolecular network deformation process as in drawing melt-crystallized polyethylene, the essential difference being the entanglement density (and accordingly the maximum draw ratio attained).

In Figure 6 the tensile strength is plotted versus Young's modulus for fibers produced by solution spinning/drawing of the high-molecular-weight samples 7, 8, and 10. This graph illustrates the need to employ high-molecular-weight polyethylene in order to produce high-strength filaments. The results are discussed in more detail in the next section.

It is known that with increasing orientation, the strain at break  $\epsilon$  rapidly decreases to approach asymptotically a constant value which is reached at a draw ratio of about 15 ( $E \approx 20$  GPa).<sup>6,17</sup> Concomitant with increased tensile strength for higher molecular weight is an increased strain at break at a particular Young's modulus, as already noted by other authors.<sup>6</sup> For highly oriented filaments  $\epsilon$  was found to increase monotonically with molecular weight from 0.03 to 0.08 for  $\bar{M}_w$  increasing from  $54 \times 10^3$  to  $4 \times 10^6$ .

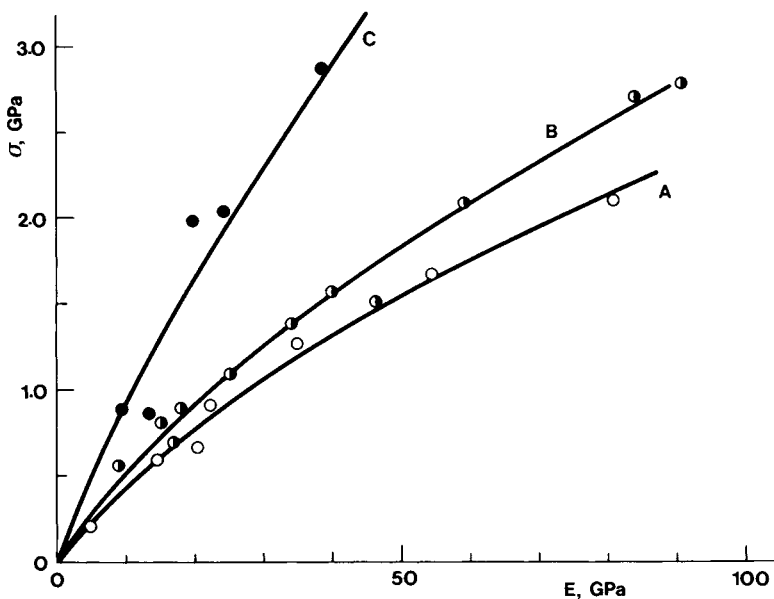


Fig. 6. Strength vs. modulus of solution-spun/drawn polyethylene filaments: (A) sample 7,  $\bar{M}_n = 120 \times 10^3$ ,  $\bar{M}_w = 800 \times 10^3$ ; (B) sample 8,  $\bar{M}_n = 150 \times 10^3$ ,  $\bar{M}_w = 1.1 \times 10^6$ ; (C) sample 10,  $\bar{M}_n = >300 \times 10^3$ ,  $\bar{M}_w = 4 \times 10^6$ .

### Effect of Molecular Weight

It is hard to envisage that just one particular moment of the distribution of chain lengths should uniquely determine the tensile strength. It is nevertheless useful to relate tensile strength to such commonly determined quantities as number- and weight-average molecular weight.

In Table II numerical results obtained for selected samples are grouped together in order to illustrate the influence of  $\bar{M}_n$  and  $\bar{M}_w$  on the tensile strength at a constant value of the Young's modulus. The latter values were interpolated from the experimental data plotted in Figures 2-6. The first set of results shows that at nearly constant  $\bar{M}_n$  [(13-18)  $\times 10^3$ ] tensile strength may differ widely for various values of  $\bar{M}_w$ : at  $E = 50$  GPa,  $\sigma$  is 0.68 and 1.10 GPa for samples with  $\bar{M}_w = 54 \times 10^3$  and  $280 \times 10^3$ , respectively. Similar results were obtained at different levels of axial order (i.e., at different Young's moduli), as is apparent

TABLE II  
Effect of Molecular Weight Distribution on Tensile Strength of Oriented Polyethylene

	Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\sigma$ at $E = 50$ GPa (GPa)
Set I	2	17	54	0.68
	3	13	100	0.75
	6	18	280	1.10
Set II	5	110	120	1.38
	7	120	800	1.55
Set III	3	13	100	0.75
	4	28	115	1.15
	5	110	120	1.38

from Figure 3. Obviously,  $\bar{M}_n$  does not uniquely determine the tensile strength at break. Set 2 in Table II confirms this conclusion for other values of  $\bar{M}_n$  and  $\bar{M}_w$ . These results indicate that eq. (1) is not valid for these materials. It is also concluded that fracture of oriented polyethylene is not preponderantly dependent on the number of defects caused by chain ends.

The third set of data in Table II demonstrates the effect of the number-average molecular weight when  $\bar{M}_w$  is nearly constant at  $1.0 \times 10^5$  to  $2 \times 10^5$ . An increase in  $\bar{M}_n$  from  $13 \times 10^3$  to  $110 \times 10^3$  (i.e., a reduction of polydispersity by a factor of about 8) caused the tensile strength to increase drastically from 0.75 to 1.38 GPa at  $E = 50$  GPa. Obviously neither  $\bar{M}_n$  nor  $\bar{M}_w$  uniquely determines the tenacity but both the molecular weight and its distribution strongly influence the room-temperature tensile strength of oriented polyethylene. In Figure 7 the breaking stress of filaments having a modulus of  $E = 50$  GPa is plotted against weight-average molecular weight on a logarithmic scale.  $\bar{M}_w$  was selected rather than  $\bar{M}_n$  because the former quantity is obtained more readily and more accurately, particularly in the high-molecular-weight range studied. Quite similar results are, however, obtained by plotting against  $\bar{M}_n$ . A surprisingly smooth dependence is found between  $\bar{M}_w$  and  $\sigma$ , at  $\bar{M}_w/\bar{M}_n \geq 7$ , over the complete range from  $54 \times 10^3$  to  $4 \times 10^6$ , suggesting the correlation:

$$\sigma \propto \bar{M}_w^p \quad (2)$$

with  $p \approx 0.4$ . The limiting behavior of relation (2) (for  $\bar{M}_w = 0$ ,  $\sigma = 0$ ;  $\bar{M}_w = \infty$ ,  $\sigma = \infty$ ) shows that this equation cannot hold at extremely high molecular weights ( $>4 \times 10^6$ ). The stress at break of a single polyethylene chain was calculated to be 19 GPa with  $E = 300$  GPa.<sup>37</sup> Accordingly,  $\sigma_{\text{max}}$  of a fiber with  $M = \infty$  and  $E$  of only 50 GPa should be considerably lower than 19 GPa (see also ref. 25), rather than infinity as suggested by relation (2). Despite the intrinsic misconception in this equation, it provides an empirical correlation between tensile strength and molecular weight over the complete range of commercially available linear polyethylenes, and as such it may be useful.

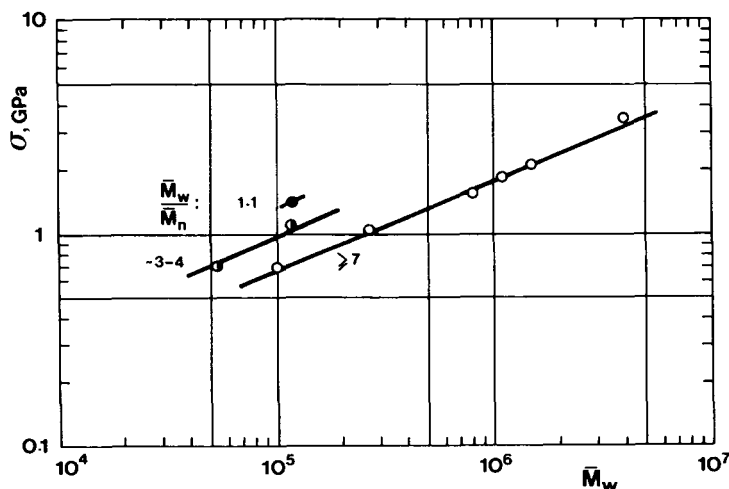


Fig. 7. Tensile strength of highly oriented polyethylene with  $E = 50$  GPa vs. weight-average molecular weight for the polydispersities indicated.

It appears that variation of  $\bar{M}_w/\bar{M}_n$  from 7 to 15.6 does not produce significant scatter in tensile strength versus  $\bar{M}_w$ . Reduction of polydispersity from 7 to 3 or 4, or rather an increase of  $\bar{M}_n$  by a factor of 2 at constant  $\bar{M}_w$  (samples 2, 4), on the other hand, consistently increased the breaking stress at  $E = 50$  GPa by a factor of about 1.5 (see Fig. 7). Further reduction of  $\bar{M}_w/\bar{M}_n$  to 1.1 caused  $\sigma$  to increase by another factor 1.3. Although very limited experimental data are at present available to substantiate the suggestion, it may very well be that at constant polydispersity, tensile strength varies with  $\bar{M}_w$  (and thus with  $\bar{M}_n$ ) according to relation (2) over a wide range of molecular weight.

Tensile data are discussed above at constant Young's modulus  $E = 50$  GPa, a value which was, in fact, chosen quite arbitrarily. Very similar observations were made at other degrees of orientation, i.e., other values of  $E$ , except in the very low range of 0–10 GPa. Here it was found that perhaps the most interesting sample in this study, specimen 5 with  $\bar{M}_w/\bar{M}_n = 1.1$ , already exhibited high strength at low draw ratios of ca. 10, thus at low modulus, as is illustrated numerically in Table III. As a matter of fact, the stress at break (at  $E = 10$  GPa) of sample 5 with  $\bar{M}_w = 120 \times 10^3$  compares favorably with that of filaments of the very high-molecular-weight sample 10 with  $\bar{M}_w = 4 \times 10^6$ . This observation may be explained as follows. Upon drawing of low-polydispersity samples most macromolecules are likely to deform uniformly and to the same extent. Hence the load-bearing tie molecules that bridge defects in the oriented fibrillar structure produced are probably distributed more evenly in the nearly monodisperse specimen, giving rise to higher strength. This effect vanished, however, at higher draw ratios, as becomes apparent from Figures 3 and 6.

It should be noted that high-modulus polyethylene can also be produced by using a technique developed by Odell et al.,<sup>22</sup> referred to as the "blocked-plug" method, yielding an intrinsically oriented lamellar structure. This method involves chain alignment only and hardly any extension of the macromolecules, as was revealed by neutron scattering.<sup>38</sup> The materials produced exhibit high modulus (up to 50 GPa), but have a low tensile strength and strain at break, despite the medium molecular weight of the polymer used. These results obviously do not compare with the present data, which were obtained with samples subjected to both chain extension and orientation. As is clearly explained by Peterlin's model for drawing of polymers,<sup>18,28</sup> upon extension of macromolecules the number of tie molecules bridging interruptions in the oriented structure is drastically increased, resulting in a higher breaking stress. Thus the degree of chain extension affects the tensile strength markedly, although it is not necessary for attainment of high modulus.

TABLE III  
Tensile Strength of Polyethylene Filaments (Young's Modulus 10 GPa)

Sample	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\sigma$ at $E = 10$ GPa (GPa)
3	13	100	0.40
5	110	120	0.88
6	18	280	0.40
8	150	1,100	0.51
10	>300	4,000	0.95

## CONCLUDING REMARKS

In this study the tensile strength of oriented polyethylene fibers is discussed in relation to molecular weight. It was concluded that the entire chain length distribution affects the breaking stress, rather than a particular moment, of the distribution. Time and temperature effects, however, were not examined. In particular, tensile properties at high temperatures and long loading times are expected to depend increasingly on the residual number of trapped entanglements in the oriented polymeric solid, and are thus thought to be dominated more by  $\overline{M}_w$  than  $\overline{M}_n$ . Experiments have yet to be performed to establish relationships at temperatures other than room temperature and for time scales other than the short-term range (1–10 s).

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