

## Tensile strength of highly oriented polyethylene

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# NOTES

## Tensile Strength of Highly Oriented Polyethylene

In the past decade the production of ultrahigh-modulus polyethylene through drawing or solid-state extrusion has become a topic of increasing interest.<sup>1</sup> More recently<sup>2-5</sup> attempts have been made to generate polyethylene structures having not only high modulus (ca. 100 GPa), but also high strength (2-4 GPa).

Theoretical estimates of the ultimate tensile strength of polyethylene range from 3.7 to 19 GPa.<sup>3,6-8</sup> The lower value of 3.7 GPa is based on the assumption that tensile failure of polyethylene is merely a creep process involving chain slippage.<sup>3</sup> The maximum value of 19 GPa, by contrast, reflects the ultimate breaking strength of a polyethylene chain.<sup>6</sup> The fracture mechanism of oriented polyethylene is still a matter of controversy, but it is well documented that generally the actual tensile strength of polymeric materials depends on molecular weight and its distribution,<sup>9,10</sup> morphology, and molecular orientation,<sup>5,11-13</sup> and on testing variables, such as temperature, time or strain rate, sample dimensions, etc. (see, e.g., ref. 14).

As long ago as 1945, Flory<sup>15</sup> predicted the tensile strength  $\sigma$  of isotropic polymers to depend on the number-average molecular weight  $\bar{M}_n$  as

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

where  $A$  and  $B$  are constants. Intuitively one can argue that the tensile strength should decrease with increasing number of chain ends, but this picture is oversimplified. It was extensively discussed by Peterlin<sup>11</sup> that morphology plays a dominant role in fracture of oriented polymers, and that the tensile strength is largely determined by defects of the microfibrillar structure. This view is strongly supported by microcrack nucleation and growth during extension of these materials, as revealed by small-angle x-ray scattering.<sup>16</sup>

Obviously, it is a formidable task to construct a unifying theory that predicts the actual and ultimate axial tensile strength of oriented polymers.

In this paper we explore empirically the relation between the room-temperature short-term (1-10 sec) tensile strength and the Young's modulus of highly oriented polyethylene filaments. Extrapolation to the theoretical axial modulus, which is reasonably well established to be 250-300 GPa (see, e.g., a compilation in ref. 14), allows us to make an estimate of the maximum tensile strength of oriented polyethylene.

Highly oriented filaments were produced by solution spinning of high-molecular-weight polyethylene and subsequent hot drawing to various draw ratios (for details see refs. 5 and 17). Molecular weights of the polymer samples used are given in Table I. Room-temperature tensile properties of the filaments were tested with an Instron tensile tester. The initial specimen length was 15 cm and the cross-head speed was 10 cm/min.

In Figure 1 the tensile strength is plotted against the Young's modulus of solution spun/drawn polyethylene filaments (sample B). Data were partly taken from our previous work.<sup>5</sup> The results presented in Figure 1 suggest a linear dependence between  $\log \sigma$  and  $\log E$ , which can be rewritten

$$\sigma = mE^n \quad (2)$$

Here  $E$  refers to the Young's modulus, and  $m$  and  $n$  are constants, which have values of 0.105 and 0.77, respectively, for this particular polyethylene sample.

TABLE I  
Molecular Weights of Polyethylene Samples, Constants in Eq. (2) and Maximum Tensile Strength Calculated with Theoretical Modulus of 250 GPa

Sample	$\bar{M}_w$ (kg/kmole)	$\bar{M}_n$ (kg/kmole)	constants eq. (2)		strength at $E = 250$ GPa (GPa)
			$m$	$n$	
A	$4 \times 10^6$	$>3 \times 10^5$	0.153	0.80	12.7
B	$1.5 \times 10^6$	$2 \times 10^5$	0.105	0.77	7.4
C	$8 \times 10^5$	$1.2 \times 10^5$	0.082	0.75	5.2

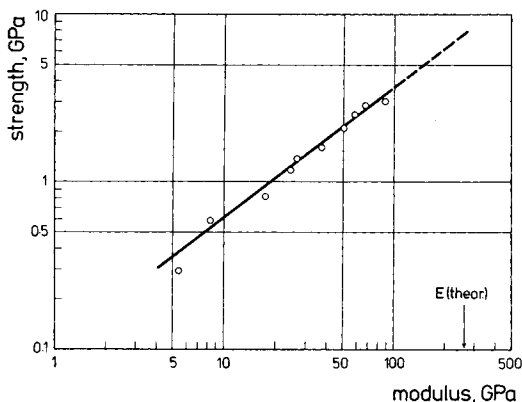


Fig. 1. Tensile strength vs. Young's modulus of solution spun/drawn filaments of high molecular weight polyethylene (sample B). The broken line extrapolates to maximum strength at the theoretical modulus (250–300 GPa).

Extrapolation to the theoretical Young's modulus of 250–300 GPa leads to a maximum tensile strength in the range of 7.4 to 8.5 GPa for polyethylene with  $\bar{M}_w = 1.5 \times 10^6$  and  $\bar{M}_n = 2 \times 10^5$ .

In Figure 2,  $\sigma$  vs.  $E$  is plotted for solution spun/drawn fibers of polyethylene having various molecular weights. This graph shows clearly the strong molecular weight dependence of the tensile strength of oriented polyethylene structures at constant Young's modulus. From Figure 2 the necessity to employ high molecular weight polyethylene in order to produce high strength filaments becomes quite apparent. The solid lines in Figure 2 were calculated with Eq. (2). The values of the constants  $m$  and  $n$ , and the maximum tensile strength obtained by substitution of  $E(\text{theor.}) = 250$  GPa are given in Table I.

The present data are not decisive on the influence of the molecular weight distribution on the tensile strength; nor do they allow us to make a sensible extrapolation to infinite molecular weight. This topic will be dealt with in a subsequent paper.

The rather simple correlation between the tensile strength and Young's modulus which emerges from Figures 1 and 2 demands some further exploration. Although the values of the constants  $m$  and  $n$  in eq. (2) cannot be derived with great accuracy from the experimental data, it seems that  $m$  increases with increasing molecular weight (see Table I). This can readily be understood, since  $m$  is likely to be related to, although not equal to, the strain at break, which is known to increase with

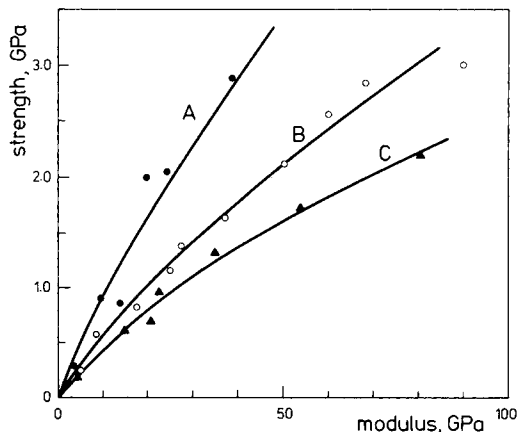


Fig. 2. Tensile strength vs. Young's modulus of solution spun/drawn polyethylene filaments having various molecular weights  $\bar{M}_w$ : (A)  $4 \times 10^6$ , (B)  $1.5 \times 10^6$ , and (C)  $8 \times 10^5$ . Solid lines were calculated according to eq. (2). Values of constants  $m$  and  $n$  are given in Table I.

molecular weight (e.g., ref. 10). The exponent  $n$  in eq. (2) has a value in the range from 0.75 to 0.80. A number of years ago, van Krevelen<sup>18</sup> suggested, virtually on an empirical basis, that the brittle strength of isotropic polymers was related to the Young's modulus as

$$\sigma = \text{const.} \times E^n \quad (3)$$

where  $n \approx 0.8$ , which is in surprising accord with our present findings.

Purely elastic or Hookean materials fail in brittle fashion, which is usually described in terms of the flaw theory of fracture, originally developed by Griffith.<sup>19</sup> According to this theory the tensile strength of brittle solids is governed by cracks, which are assumed to have an elliptical shape (diameter  $2c$ ), and is given by

$$\sigma = (2\nu E/\pi c)^{1/2} \quad (4)$$

Here  $\nu$  is the surface free energy per unit area of surface, or, more generally,<sup>20</sup> the surface work parameter, which was introduced to account for energy dissipation in viscoelastic and flow processes. A Griffith-type approach was employed successfully to describe fracture of polymeric glasses<sup>21</sup> and rubbers.<sup>22</sup> Despite the observation that highly drawn polyethylene filaments seem to fail in a brittle way (see for example stress/strain curves in refs. 2 and 5), the simple Griffith relation does not produce the observed dependence of tensile strength on Young's modulus. It is known, however, that fracture of fibrillar polyethylene structures is accompanied and preceded by slippage of microfibrils,<sup>11</sup> which would result in a meaningless high value of  $\nu$ , and most likely, departure from the square-root dependence between strength and modulus.

The question can be raised whether or not the present empirical relation (2) between the tensile strength and Young's modulus is uniquely restricted to the mechanical properties of highly oriented polyethylene filaments produced by solution spinning/drawing. It appears, by inspection of Figures 4 and 5 in ref. 2, that the tensile properties of "surface grown" filaments of polyethylene (having the same molecular weight as sample B) produced at various temperatures, fit curve B in Figure 2 exactly. This suggests a wider applicability for the present treatment.

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