

# Effect of Propylene Comonomer on the Modulus of Oriented Ultra-High Molecular Weight Polyethylene

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## Introduction

A well-known problem associated with melt-<sup>1,2</sup> and gel-spun<sup>3</sup> high-modulus polyethylene fibers is their poor long-term, or creep, performance. Several publications (e.g., refs 4-6) have alluded to the fact that the long-term properties of these fibers may be improved either through the introduction of a small degree of branching (through copolymerization) and/or by cross-linking the polymer. Often, comonomers, such as propylene or butene, are used in the synthesis of the polyethylene to reduce creep under static loading and to increase the yield stress at low strain rates. However, as was shown in previous studies,<sup>6,7</sup> these gains are made at the expense of reductions of the short-term properties, such as the maximum attainable draw ratio and the Young's modulus and the tensile strength of the drawn fibers.

This paper describes a brief study of the room-temperature Young's modulus of solution-spun/drawn ultra-high molecular weight polyethylene samples (UHMW PE) that contain minor amounts of the comonomer propylene. In particular, the applicability is discussed of an earlier model for the stiffness of oriented polymers<sup>8,9</sup> to the current systems. A simple modification of this theory is presented which enables the calculation of the tensile modulus as a function of the comonomer concentration at high draw ratios ( $\lambda > 30$ ).

## Experimental Section

Samples of UHMW PE were supplied by DSM Research, Geleen, The Netherlands. The molecular characteristics of the various grades are collected in Table I. The materials were carefully selected to ensure virtually identical weight-average molecular weights and polydispersities, which are known to significantly affect the tensile deformation behavior. Solutions containing 4% w/w of the various UHMW PE samples were prepared in decalin at 160 °C. The polymer solutions were stabilized with 2% w/w of the antioxidant dibutyl-*p*-cresol. Gel fibers of 0.5-mm diameter were spun at 160 °C with a laboratory extrusion device, quenched to room temperature, and subsequently dried at ambient conditions (cf. ref 3).

The dried UHMW PE fibers were drawn at 115 °C in the heated chamber of an Instron tensile tester (Model 1122). This relatively low deformation temperature was chosen in order to prevent nonaffine deformation, particularly of the copolymers with high propylene content. The cross-head speed typically was 100%/min based on the original fiber length. The draw ratios were determined through measurements of the weight of the fibers before and after the drawing process and from thermal shrinkage measurements.

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Table I  
Characteristics of UHMW PE Grades

sample	[CH <sub>3</sub> ] (mole fraction × 10 <sup>2</sup> )	$M_w \times 10^{-3}$	$M_w/M_n$
1	0.05	2000	8
2	0.28	2300	8
3	0.63	1900	10
4	1.35	2100	11

The mechanical properties of the drawn fibers were tested at room temperature. The gauge length was 20 mm and the rate of elongation 100%/min.

## Results and Discussion

Figure 1 shows the familiar plot of the room-temperature Young's modulus ( $E$ ) versus draw ratio ( $\lambda$ ) for the various UHMW PE samples. At a constant draw ratio, the values of  $E$  were found to decrease at increasing comonomer concentration, an effect that was more pronounced at increasing draw ratio.

Here, we will analyze this reduction of  $E$  by employing a previously presented theory, which describes the development of the axial Young's modulus  $E$  with draw ratio  $\lambda$  of flexible chain (linear) polymers.<sup>8,9</sup> In the original theory a partially oriented fiber is considered to be comprised of two types of elastic elements, i.e., "helix", elements that are perfectly oriented about the draw axis (denoted by suffix h) and "coil" elements that are unoriented (denoted by c). The fraction of the helix element ( $f_h$ ) is obtained as a function of the draw ratio from classical rubber elasticity:

$$f_h = \frac{3\lambda^3}{2(\lambda^3 - 1)} [1 - (\lambda^3 - 1)^{-1/2} \tan^{-1} \{(\lambda^3 - 1)^{1/2}\}] - \frac{1}{2} \quad (1)$$

Following Ward and co-workers,<sup>10</sup> the model assumes a uniform stress distribution in the helix and coil elements, which are characterized by their respective moduli  $E_h$  and  $E_c$  (the designation  $E_c$  deviates from the previously<sup>8,9</sup> employed notation  $E_u$ , to ensure more consistent subscripts); thus

$$E = [f_h E_h^{-1} + (1 - f_h) E_c^{-1}]^{-1} \quad (2)$$

From eqs 1 and 2 the functionality between the modulus ( $E$ ) and the draw ratio ( $\lambda$ ) for flexible, linear polymers becomes

$$E = \left[ E_c^{-1} - \left[ \frac{3\lambda^3}{2(\lambda^3 - 1)} [1 - (\lambda^3 - 1)^{-1/2} \times \tan^{-1} \{(\lambda^3 - 1)^{1/2}\}] - \frac{1}{2} \right] (E_c^{-1} - E_h^{-1}) \right]^{-1} \quad (3)$$

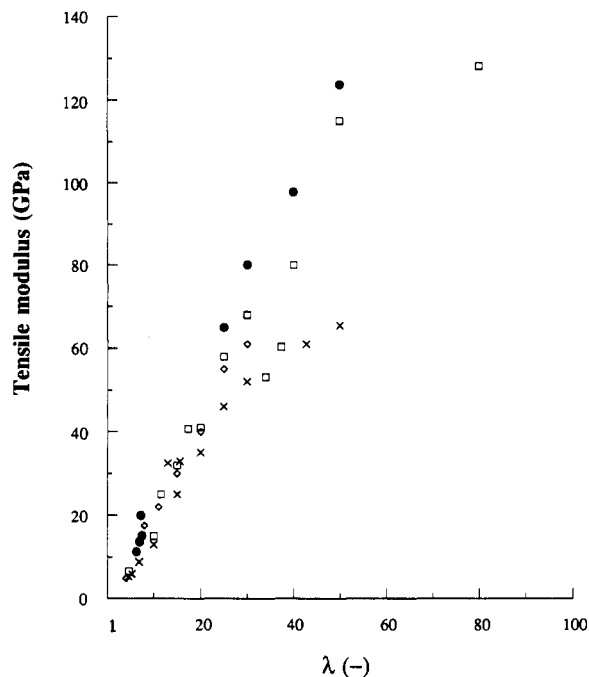
which, for  $\lambda > 5$ , to a good approximation reduces to

$$E = [E_h^{-1} + (E_c^{-1} - E_h^{-1})(3\pi/4)\lambda^{-3/2}]^{-1} \quad (4)$$

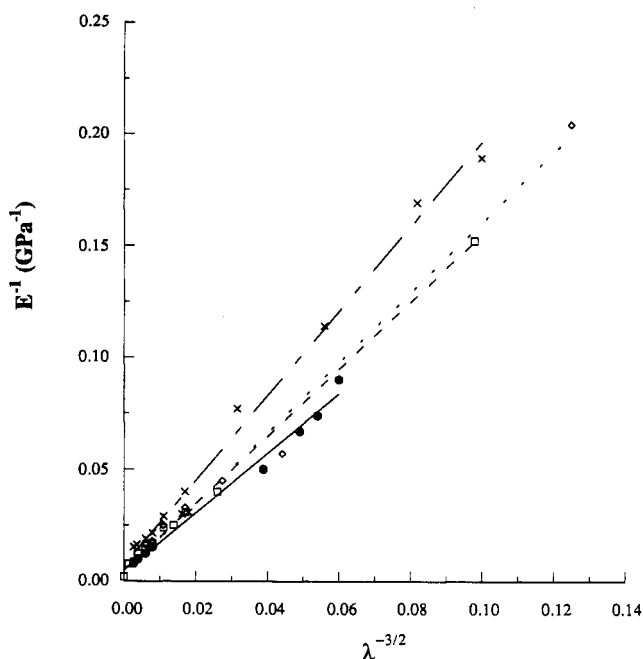
Note that a plot of  $E^{-1}$  against  $\lambda^{-3/2}$  is predicted to yield a straight line with an intercept at  $1/E_h$ ; the value of the  $E_c$  is derived from the slope.

Within the unmodified, simple mathematical framework of the above theory, one may attempt to describe the observed reduction in  $E$  at increased comonomer content, in principle, by variation of the values of  $E_h$ ,  $E_c$ , or both.

Figure 2 displays a  $E^{-1}$  vs  $\lambda^{-3/2}$  plot of the data in Figure 1. In this, strictly empirical, approach it is implicitly assumed that both the values of  $E_h$  and  $E_c$  are affected by the presence of the comonomer. Figure 3 displays these modulus values (derived from Figure 2) as a function of comonomer content.  $E_h$  (Figure 3A) is seen to decrease with an increase in the fraction of CH<sub>3</sub> side groups, with



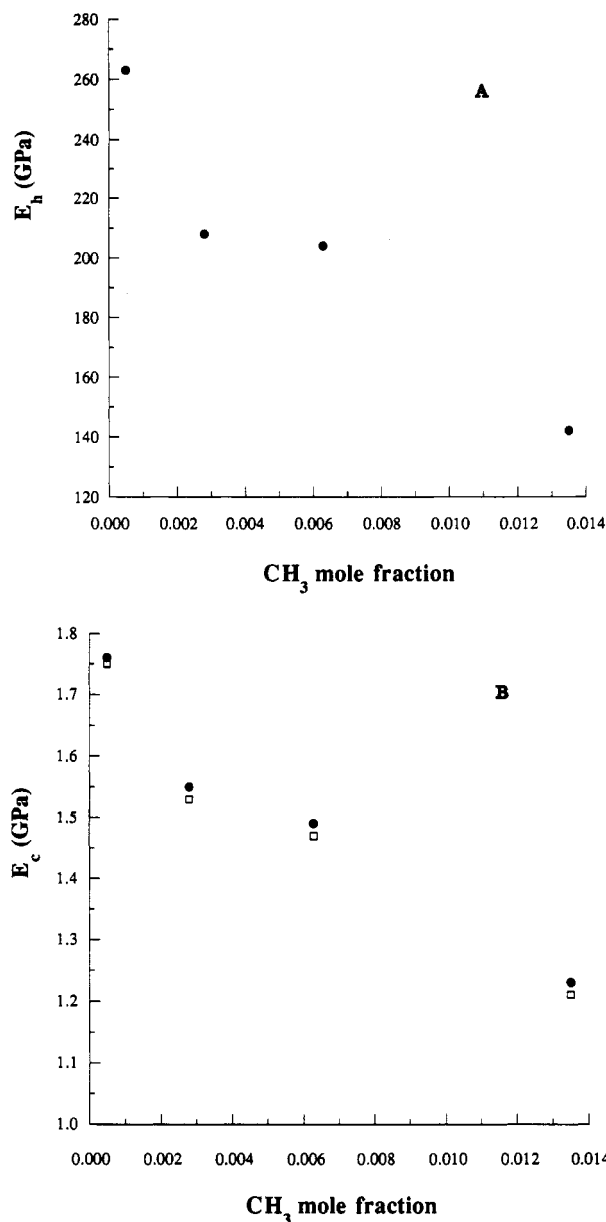
**Figure 1.** Effect of propylene comonomer content and draw ratio on the tensile modulus of gel-spun UHMW PE fibers: (●) 0.05 mol %; (□) 0.28 mol %; (◇) 0.63 mol %; (×) 1.35 mol %.



**Figure 2.** Plot of  $E^{-1}$  versus  $\lambda^{-3/2}$ : (●) 0.05 mol %; (□) 0.28 mol %; (◇) 0.63 mol %; (×) 1.35 mol %.

the value for grade 1 being close to the theoretical modulus of  $\sim 300$  GPa.<sup>9,12</sup> Like  $E_h$ ,  $E_c$  also is seen to decrease with an increase in the number of methyl side groups (Figure 3B). The value of  $E_c$  for sample 1, calculated to be 1.76 GPa, is within the range of 1.6–2.4 GPa quoted earlier<sup>8</sup> for the homopolymer.

Obviously, this straightforward application of eq 4, although temptingly simple, lacks a fundamental base; and, as a matter of fact, it yields results that are in conflict with notions regarding the variables that affect  $E_h$  and  $E_c$ . Evidently, the well-documented improved creep properties of the propylene-containing polyethylene fibers derive from increased resistance to (shear) flow. Previously, the value of  $E_c$  has been shown to be closely related, if not equal, to the crystal shear modulus.<sup>9</sup> Thus, if a significant



**Figure 3.** Calculated values of moduli as a function of  $\text{CH}_3$  mole fraction: (A)  $E_h$  of the helix (oriented) segments; (B)  $E_c$  of the coil (unoriented) segments. (●) Experimental; (□) calculated using  $E_h = 300$  GPa (see text).

change were to occur, a slight increase is expected in  $E_c$  with increased propylene content, which, of course, is opposite to the trend seen in Figure 3B. Also, it is difficult to envisage that even 1.35% of propylene would reduce the theoretical axial chain modulus,  $E_h$ , by as much as 50%. More likely, the value of  $E_h$  is unaffected in this low comonomer content regime. Following the latter argument, i.e., that  $E_h$  is a constant (300 GPa), and analyzing the data of Figure 1 with relation 4 and a variable value of  $E_c$  yield, of course, a similar (and unrealistic) decrease in  $E_c$  with increased comonomer content. Analogously, introduction of a constant value of  $E_c$  into relation 4 results in erroneously low values for  $E_h$ .

A more sensible analysis of the stiffness data of Figure 1, in our opinion, derives from the recognition that even in perfectly oriented structures, i.e., those obtained at  $\lambda = \infty$ , where  $f_c$  should reach the value zero, off-axis coil elements persist. This is due to the presence of the comonomer units in the chain molecules that cause strains and defects in the crystalline unit cell of the linear ho-

mopolymer. Within the above theory, the fraction of these permanently present off-axis segments may be represented by  $f_c^*$ . Thus, for the copolymers

$$f_h' + f_c' = 1 \quad (5)$$

where  $f_h'$  and  $f_c'$  are the new fractions of helix and coil elements in the stretched copolymer such that

$$f_h' = f_{h_0} - f_c^* \text{ and } f_c' = f_{c_0} + f_c^*$$

Here, the suffix 0 refers to the homopolymer. Thus, eq 2 may be rewritten as

$$\frac{1}{E} = \frac{f_{h_0} - f_c^*}{E_h} + \frac{f_{c_0} + f_c^*}{E_c} \quad (6)$$

and subsequently

$$\frac{1}{E} = \frac{1}{E_0} + f_c^* \left\{ \frac{1}{E_c} - \frac{1}{E_h} \right\} \quad (7)$$

$E_0$  refers to the draw ratio dependent modulus of the homopolymer according to relations 3 or 4. The value of  $f_c^*$ , of course, is expected to depend on the comonomer concentration. If all the present  $\text{CH}_3$  groups are assumed to be similarly effective in yielding off-axis coil segments, and not to interact with each other, the following relationship may be written

$$f_c^* = K[\text{CH}_3] \quad (8)$$

where  $[\text{CH}_3]$  is the mole fraction of the methyl side groups and  $K$  is a functionality factor. Combining eqs 7 and 8 yields

$$\frac{1}{E} = \frac{1}{E_0} + K[\text{CH}_3] \left\{ \frac{1}{E_c} - \frac{1}{E_h} \right\} \quad (9)$$

Substitution of relation 4 for  $E_0$  as a function of the draw ratio in eq 9, finally, yields

$$\frac{1}{E} = \frac{1}{E_h} + [(3\pi/4)\lambda^{-3/2} + K[\text{CH}_3]] \left\{ \frac{1}{E_c} - \frac{1}{E_h} \right\} \quad (10)$$

Based on the above considerations regarding  $E_h$  and  $E_c$ , it is assumed that for the present polyethylenes of low comonomer content both the axial chain modulus and the shear modulus essentially are constant and equal to the corresponding values of the homopolymer ( $E_h = 300 \text{ GPa}$ ,  $E_c = 1.6 \text{ GPa}^{9,12}$ ).

Figure 4 is a plot of  $1/E$  against the  $\text{CH}_3$  mole fraction for various draw ratios. This figure shows a linear dependence between these two parameters, which indicates that the relationship in eq 8 is, in fact, valid for the present series of polyethylenes. The slope of each line in Figure 4 represents the dependence of  $K$  on the draw ratio. Table II presents the values of  $K$ , calculated from the slope of the lines in Figure 4, as a function of draw ratio. Also included in Table II are the uncertainties in  $K$  resulting from the scatter in the modulus data. Particularly at relatively low draw ratios ( $\lambda \leq 10$ ), the possible error involved in the calculation of  $K$  is comparatively large. Nevertheless, the results in Table II clearly reveal that the functionality factor increases up to  $\lambda \approx 30$  and then remains practically constant for  $\lambda > 30$  at approximately  $K = 1$ . The initial increase of  $K$  with draw ratio indicates that the methyl side groups become increasingly effective in creating defects with properties of coil segments. Interestingly, it can be inferred from the limiting value of  $K = 1$ , reached at  $\lambda \sim 30$ , that, in highly drawn samples, each methyl side group introduces into the oriented structure only one effective, low modulus defect. Thus, with  $K$  reaching a constant value, it appears possible to

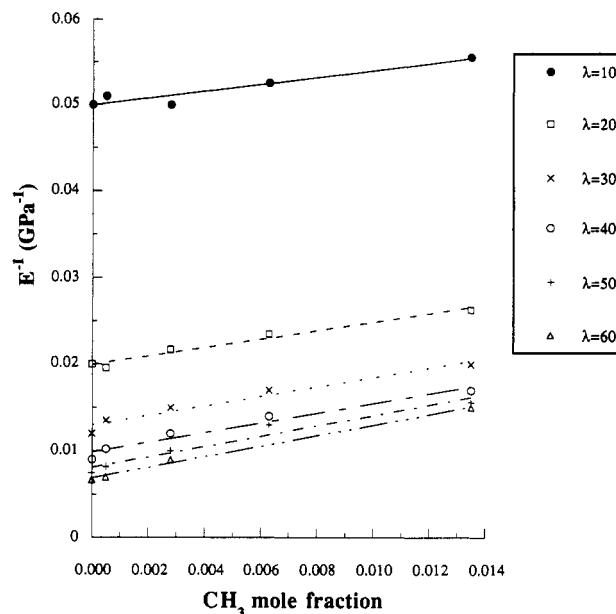


Figure 4. Plot of the inverse experimental tensile modulus,  $E^{-1}$ , as a function of  $\text{CH}_3$  mole fraction at various draw ratios.

Table II  
Parameter  $K$  as a Function of Draw Ratio

draw ratio, $\lambda$	parameter $K$	draw ratio, $\lambda$	parameter $K$
10	$0.5 \pm 0.3$	40	$0.9 \pm 0.1$
20	$0.78 \pm 0.15$	50	$0.95 \pm 0.08$
30	$0.9 \pm 0.1$	60	$1 \pm 0.08$

predict the tensile modulus of highly drawn copolymers (draw ratios  $> 30$ )<sup>11</sup> using the appropriate parameter values in the simple eq 9.

In summary, we presented a brief study of the room-temperature Young's modulus of oriented UHMW PE/PP copolymers of low comonomer content. A simple model was derived which enables the prediction of the modulus at  $\lambda > 30$ . It is anticipated, however, that, for materials of comonomer contents much higher than those examined here, the model may not be appropriate because eq 9 may no longer hold true, due to "interactions" of the defects created by the comonomers.

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## References and Notes

- (1) Capaccio, G.; Ward, I. M. *Polym. Eng. Sci.* 1975, 15, 219.
- (2) Peterlin, A. *Polym. Eng. Sci.* 1977, 17, 183.
- (3) Smith, P.; Lemstra, P. J. *J. Mater. Sci.* 1980, 15, 505.
- (4) Wilding, M. A.; Ward, I. M. *Polymer* 1981, 22, 870.
- (5) Capaccio, G.; Ward, I. M. *J. Polym. Sci., Polym. Phys. Ed.* 1984, 22, 475.
- (6) Seguela, R.; Rietsch, F. *Polymer* 1986, 27, 532.
- (7) Glenz, W.; Morosoff, N.; Peterlin, A. *J. Polym. Sci., Polym. Lett. Ed.* 1971, 9, 211.
- (8) Irvine, P. A.; Smith, P. *Macromolecules* 1986, 19, 240.
- (9) Postema, A. R.; Smith, P. *Macromolecules* 1990, 23, 3296.
- (10) Hadley, D. W.; Pinnock, P. R.; Ward, I. M. *J. Mater. Sci.* 1969, 4, 152.
- (11) High-strength/high-modulus UHMW PE fibers are usually produced at draw ratios exceeding 30.
- (12) Prasad, K.; Grubb, D. T. *J. Polym. Sci., Polym. Phys. Ed.* 1990, 28, 2199.

**Registry No.** PE/PP (copolymer), 9010-79-1.