Notes

Development of the Axial Young's Modulus with Draw Ratio of Flexible-Chain Polymers

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The maximum extension ratio λ_{max} of an unperturbed polymer chain depends on its stiffness and overall length as

$$\lambda_{max} = (l_p/l)(n/C_\infty)^{1/2} \quad (1)$$

Here n is the number of chain segments having a length l and a projected length l_p in the chain direction and C_∞ is the characteristic ratio.[1] An important consequence of this equation is that short molecules reach full extension at low draw ratios, whereas very long chains comprising hundreds of thousands of units may require draw ratios of well in excess of 100 before complete chain extension is achieved.[2,3] One might be tempted to conclude on this basis, therefore, that low molecular weight polymers are more readily drawn into extended-chain materials and supposedly with accompanying high axial moduli. This conclusion is, in fact, at variance with the experimental observations of Ward and co-workers[4] as well as other authors (cf. ref 5). Now it is firmly established that the axial Young's modulus of flexible polymers, drawn under experimental conditions of optimum efficiency where there is little or no chain slippage, is independent of molecular weight and determined only by the absolute draw ratio.[4] In this paper we set out to explore a possible theoretical framework underlying this experimental observation.

Molecular Model of Tensile Drawing

We restricted our attention to fibers derived from flexible polymers. In its initial state prior to drawing a fiber is considered to comprise polymer chains in their normal unperturbed random coil configurations. Chain entanglements present are envisaged to act as permanent cross-links on the time scale of deformation. Complicating influences of of crystallites are ignored.[3] We assume that the chain vectors $\mathbf{R}_e^0$ that join adjacent entanglement points along chains are affine in the macroscopic strain. Accordingly, following tensile drawing through draw ratio λ a chain vector $\mathbf{R}_e^0$ is transformed to $\mathbf{R}_e = \lambda\mathbf{R}_e^0$, where

$$\lambda = \text{diag}\ (\lambda, \lambda^{-1/2}, \lambda^{-1/2}) \quad (2)$$

and uniaxial symmetry is assumed about the draw axis. Thus, the present model for tensile drawing is identical with that for stretching a cross-linked rubber.[6]

An appropriate measure of molecular orientation following deformation λ is the angle ψ subtended by a chain vector about the draw axis

$$\psi = \cos^{-1}\ [\lambda\mathbf{R}_e^0\mathbf{i}/(\mathbf{R}_e^0\lambda\lambda\mathbf{R}_e^0)^{1/2}] \quad (3)$$

where $\mathbf{i}$ is a unit vector along the draw axis. The distribution of such orientations $P(\psi)$ is well-known[7] and is given by

$$P(\psi) = \lambda^3(\cos^2\psi + \lambda^3\sin^2\psi)^{-3/2} \quad (4)$$

From eq 4 it follows that

$$\langle\cos^2\psi\rangle = \frac{\lambda^3}{\lambda^3 - 1}[1 - (\lambda^3 - 1)^{-1/2}\tan^{-1}\{(\lambda^3 - 1)^{1/2}\}] \quad (5)$$

and perfect orientation is only achieved as $\lambda \to \infty$.

Axial Tensile Modulus

A partially oriented fiber is considered to comprise two types of elastic elements: "helix" elements that are perfectly oriented about the draw axis, and "coil" elements that are completely unoriented. The effect of tensile drawing is understood to increase the fraction of helix f_h at the expense of coil $(1 - f_h)$; initially, $f_h = 0$. The designations "helix" and "coil" should not be interpreted too literally, however, and tensile drawing should not be confused with the helix–coil transitions observed in, e.g., biopolymeric systems. The division of chains into helix and coil segments is a device to describe the development of uniaxial orientation in the fiber direction and reduce the number of elastic constants required for computation of the modulus.

The orientational distribution function for the helix–coil ensemble may be written

$$g(\mathbf{n},\mathbf{n}') = f_h\delta(\mathbf{n} - \mathbf{n}') + (1 - f_h)/4\pi \quad (6)$$

where $\mathbf{n}$ is a unit vector along the draw axis and $\mathbf{n}'$ is a unit vector that specifies orientation of an element. It follows that

$$\langle\cos^2\psi\rangle = \int(\mathbf{n}\cdot\mathbf{n}')^2 g(\mathbf{n},\mathbf{n}')\,d\mathbf{n}' = (1/3)(1 + 2f_h) \quad (7)$$

Connection between f_h and λ is established by requiring the $\langle\cos^2\psi\rangle$ be identical for the two distributions $P(\psi) = g(\mathbf{n},\mathbf{n}')$. This operation essentially replaces the predicted distribution by a "two-state distribution". From eq 5 and 7 we obtain the result[8]

$$f_h = \frac{3\lambda^3}{2(\lambda^3 - 1)}[1 - (\lambda^3 - 1)^{-1/2}\tan^{-1}\{(\lambda^3 - 1)^{1/2}\}] - \frac{1}{2} \quad (8)$$

Note $f_h \to 1$ as $\lambda \to \infty$.

Following Ward and co-workers,[9] we assume a uniform distribution of stress in our helix and coil elements.[10] The axial tensile modulus E is then given by the expression

$$E = [f_hE_h^{-1} + (1 - f_h)E_u^{-1}]^{-1} \quad (9)$$

where E_h and E_u are the respective tensile moduli of the perfectly oriented and unoriented polymer. Substitution of eq 8 in eq 9 yields

$$E = \left(E_u^{-1} - \left[\frac{3\lambda^3}{2(\lambda^3 - 1)}[1 - (\lambda^3 - 1)^{-1/2}\tan^{-1}\{(\lambda^3 - 1)^{1/2}\}] - \frac{1}{2}\right](E_u^{-1} - E_h^{-1})\right)^{-1} \quad (10)$$

for the dependence of E on the draw ratio λ. For $\lambda \gtrsim 5$ this expression reduces to good approximation to

$$E = [E_h^{-1} + (E_u^{-1} - E_h^{-1})(3\pi/4)\lambda^{-3/2}]^{-1} \quad (11)$$

Note that a plot of E^{-1} vs. $\lambda^{-3/2}$ is predicted to yield a straight line with slope $(E_u^{-1} - E_h^{-1})3\pi/4$ and intercept E_h^{-1} at $\lambda = \infty$. From eq 10 it follows that the axial modulus E is a unique function of the draw ratio λ and, moreover, reaches its ultimate value E_h only as the draw ratio approaches infinity.

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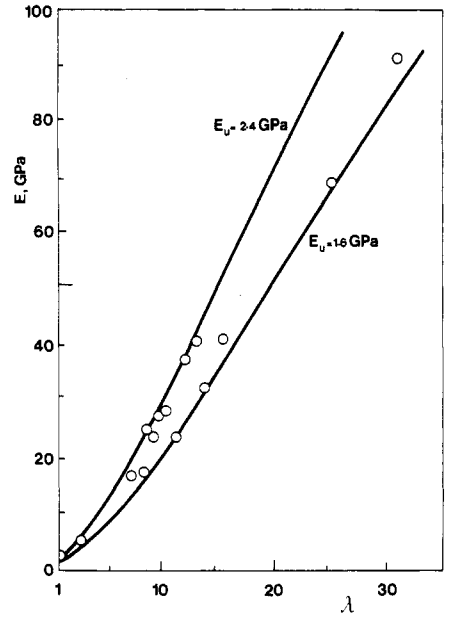

Figure 1. Development of the axial Young's modulus E with draw ratio λ computed for polyethylene from eq 10 with E_h = 300 GPa and E_u = 1.6 or 2.4 GPa. Experimental data points for gel-spun/drawn high molecular weight ($\bar{M}_w = 1.5 \times 10^6$) filaments are taken from ref 13.

Maximum Draw Ratio

In practice, infinite (effective) draw ratios are not realized. The actual maximum draw ratios of polyethylene samples drawn at elevated temperatures, for example, are known to be limited by chain entanglements (cf. ref 3). We now address the effect of such entanglement constraints on attainable draw ratios.

Consider for example a chain vector $\mathbf{R}_e^0$ of magnitude R_e^0 prior to deformation and let L_e represent the chain length between its apices (adjacent entanglement points). Following deformation λ its new magnitude is

$$R_e = R_e^0[\lambda^2 \cos^2 \psi + \lambda^{-1} \sin^2 \psi]^{1/2} \qquad (12)$$

where we have averaged over azimuthal orientations ϕ. When $R_e = L_e$ this particular subchain is fully stretched and incapable of accommodating further strain.

Rigorous extension of the foregoing arguments to an ensemble of subchains allowing for the distribution of ψ (eq 4), R_e^0, and L_e is a formidable task well beyond the scope and intent of this paper. For the present purposes we implement a "preaveraging" approximation, whereby the mean values for R_e^0 and L_e are assigned to all chains and eq 12 is replaced by

$$\langle R_e \rangle = R_e^0[\lambda^2 \langle \cos^2 \psi \rangle + \lambda^{-1} \langle \sin^2 \psi \rangle]^{1/2} \qquad (13)$$

with $\langle \cos^2 \psi \rangle$ given by eq 5. The condition $\langle R_e \rangle = L_e$ defines a maximum (preaveraged) attainable draw ratio λ_{max} *for the network*, given to good approximation by eq 1 with L_e replacing the chain length nl_p. At this juncture, subchains in the network are fully stretched and their orientations are "frozen". Further deformation will lead to fracture of the network. Of course, under particular experimental conditions, such as high drawing temperatures, fracture may be averted through chain disentanglement.

If very few entanglements are present in the macromolecular network, such as semidilute solutions and solids derived thereform,[3,11] L_e will approach the overall chain length and λ_{max} is governed directly by eq 1.

Results

We now proceed to test our theoretical model against experiment. The system best suited for this purpose is linear polyethylene, for which a wealth of data is available. Estimates for the axial modulus E_h reported in the literature fall in the range 240–340 GPa,[12] the consensus being ~300 GPa. The modulus E_u for the completely unoriented polymer will be regarded as an adjustable parameter, bound sensibly by the experimental values reported (1–3 GPa at room temperature[12]).

The development of the axial Young's modulus with draw ratio predicted according to eq 10 is shown in Figure 1 together with experimental data previously obtained at room temperature for gel-spun/drawn high molecular weight ($\bar{M}_w = 1.5 \times 10^6$) polyethylene filaments.[13] Excellent agreement between theory and experiment is obtained with E_u = 1.6 GPa. Figure 2 shows the results for a more complete set of data recently reported by Russian authors.[14] Although not displayed here, the extensive body of data obtained by Ward and co-workers[4] on melt-crystallized/drawn polyethylene of various (lower) molecular weights are similarly well reproduced by our calculations.

The experimental results cited above for polyethylene support the conclusion that the axial modulus is uniquely dependent on the draw ratio. We have noted, however, that there is an upper limit to the attainable draw ratio for a given molecular weight (eq 1). This implies that the highest achievable modulus of materials produced *through tensile deformation*[15] is ultimately dictated by the molecular weight of the polymer used. From the relations (1) and (10) this molecule weight dependent maximum modulus can readily be computed. Results for polyethylene (C_∞ = 6.7; l_p/l = 0.8)[1] are presented in Figure 3. Also shown in this figure are the experimental maximum (room temperature) axial Young's moduli reported by various authors for drawn linear polyethylene specimens spanning a wide range of molecular weights. The outstanding agreement between predicted and experimental maximum achievable modulus obtained by plotting against the weight-average molecular weight suggests that this particular moment is pertinent for polydisperse systems.

It was remarked earlier that when λ reaches λ_{max} the molecular network is fully stretched and the orientations of chains are "frozen". Further drawing would then lead to failure (or possible chain slippage); i.e., no further orientation would develop. Gratifyingly, the data plotted in Figure 3 reveal no further improvement of the modulus beyond draw ratio ~120, the calculated value of λ_{max} for the polyethylene of molecular weight ($\bar{M}_w$) 2.0 × 10^6 used.[14]

Discussion

In this paper we have presented a simple model for the development of the axial modulus during tensile drawing of polymers. It was assumed that the maximum draw ratio of the macromolecular network is dictated by chain entanglements, crystallites being ignored altogether. A more precise statement regarding the contributions of crystals in the deformation process would be that, at temperatures where the macromolecules readily slip through the crystalline lattice, the crystallites do not act as physical cross-links. They merely provide a highly "viscous" medium preventing relaxation and recoiling of the deforming chains. Strong evidence that the crystals play such a role was previously inferred from experiments.[3]

The assumption that deformation is affine is reasonable only at temperatures well below the melting point of the polymer. When the drawing temperature approaches the melting temperature, increasing chain disentangling and

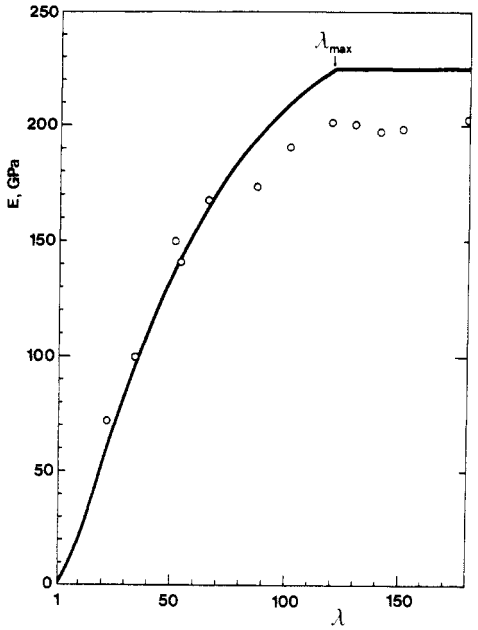

Figure 2. Young's modulus of gel-spun/drawn polyethylene ($\bar{M}_w = 2 \times 10^6$) filaments taken from ref 15. Solid line calculated according to eq 10 with $E_0 = 1.6$ GPa and $E_h = 300$ GPa. "Cutoff" at $\lambda = 120$ corresponds to maximum draw ratio for polyethylene of molecular weight 2×10^6 (see text).

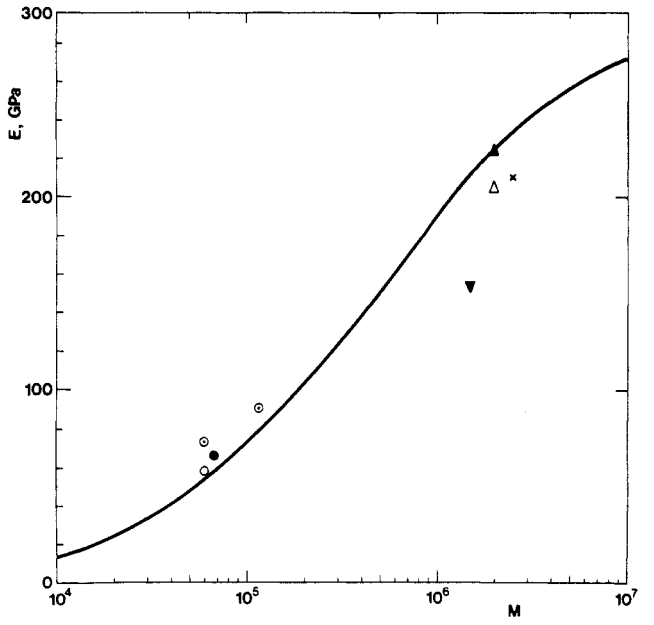

Figure 3. Predicted maximum axial Young's modulus achieavable through tensile drawing as function of molecular weight, calculated for polyethylene with eq 1 and 10. Also plotted are the reported maximum moduli for samples of various molecular weights: (●) ref 5; (○) ref 16; (△) ref 14; (⊙) Wu, W.; Black, W. B. *Polym. Eng. Sci.* **1979**, *19*, 1163. (▲) Kanamoto, T. Tsuruta, A.; Tanaka, K.; Takeda, M.; Porter, R. S. *Polym. J. (Tokyo)* **1983**, *15*, 327; (×) Kavesh, S.; Prevorsek, D. C. U. S. Patent 4 413 110, 1983; (▼) Barham, P. J.; Keller, A. *J. Mater. Sci.* **1980**, *15*, 2229.

recoiling occur, resulting in reduced efficiency of the drawing process. This is manifest experimentally as a decreasing slope of the modulus/draw ratio curve with increasing draw temperature.[16-18] Under such experimental conditions the affine approximation clearly is no longer valid, and the predicted moduli are inevitably too high.

The calculation of the modulus acknowledged only two types of elastic elements, i.e., helix and coil, which obviously is an oversimplified description of the actual structure of drawn polymers. We consider this, however, to be one of the major merits of the presented treatment. In contrast to our theory, other models[19-21] assume a more detailed fiber morphology, characterized typically by a number of structural parameters. These parameters, often not readily accessible, must be determined before computation of the modulus is possible. The "aggregate" model of Ward and co-workers[9] from which the present mechanical model is essentially derived, is, according to the authors, of limited applicability "because of the complex changes in morphology and molecular mobility which occur on drawing". It would appear from our work that these complex changes underlying the development of the modulus with draw ratio are adequately reflected in a simple helix-coil representation.

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Theory of the Helix-Coil Transition in Singly Cross-Linked, Two-Chain Coiled Coils. 2. Role of Mismatched States

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