A Simple Relation to Estimate the Maximum Tensile Modulus of Drawn Polymer Fibers

A. BONDI, *Shell Development Company, Emeryville, California*

Synopsis

The partial unfolding of folded lamellae crystals is taken as point of departure for the development of a model to describe the elastic properties of cold-drawn polymer filaments. The resulting relation sums the van der Waals tensile compliance and the spectroscopic tensile compliance of the polymer backbone chain in proportion to the length of folded and unfolded crystal lamellae, respectively, in the drawn filament. Many reported tensile moduli of drawn filaments of semicrystalline polymers are substantially below the predicted value. However, specially careful drawing experiments are rewarded with tensile moduli which closely approach the magnitude predicted by the relation presented here.

Purpose and Scope

The effect of the draw ratio on the high frequency tensile modulus of cold-drawn polymer filaments is often expressed as a function of the orientation angle θ between the symmetry axis of the polarizable unit (e.g., the polymer molecule) and the filament axis.[1,2] Samuels' recent correlation of this elastic orientation function with optical properties has given further strong support to the soundness of this view.[3] However, at the high draw ratios used in practice the orientation function approach encounters a serious limitation. The experimental measurement of the orientation angle θ (by any technique) becomes quite inaccurate in a region where the orientation function $\sin^2 \theta$ (which, according to the theory, determines the tensile modulus) changes extremely rapidly. ˙ It appears then, that the orientation function ceases to help our understanding of the elastic properties of cold-drawn filaments at draw ratios in excess of about 6, which may also be the end point of the affine deformation of spherulites.

The purpose of the present exploratory analysis is therefore to relate the high frequency modulus of highly (cold) drawn filaments to the intrinsic elastic properties of the polymer and to the draw ratio through an alternate model. The very large difference between the tensile moduli parallel and normal to the molecule axis suggested that a fairly primitive analysis would suffice to assess the validity of a particular model for the structure of drawn filament. Hence no attempt was made to refine either the model or the mathematical treatment once an estimate had been produced for the curve relating the maximum attainable modulus to the draw ratio.

The reason for stopping at that point is twofold: agreement with experiment is as good as can be expected, and further analysis is hardly justified until a better picture of the crystal structure of oriented filaments has been produced.

The Model

Current information[3-5] on the microscopic events during the drawing of (semi)crystalline filaments suggests that the lamellae of the spherulites align in parallel with the draw direction during the early part of the process (to a draw ratio of 1.5–2) so that the axes of most folded chain molecules align normal to the draw direction. Hence, on this model the well-known initial decrease of the extension modulus during the draw process is just the difference $\bar{E}_c - E_\perp$, where E_c is the Young's modulus of the unoriented polymer and $E_\perp$ is the modulus normal to the fully oriented filament. A simple analysis suggests that as a rule $(\bar{E}_c - E_\perp)/\bar{E}_c$ is of the order $^1/_3$. Pinnock and Ward's measurements of $\bar{E}_c$ and $E_\perp$ on unoriented and fully drawn poly(ethylene terephthalate) fibers[5] yield $(\bar{E}_c - E_\perp)/E_c \approx 0.38$. Such strain-induced reduction of the extension modulus has been recognized as a necessary condition for necking to occur.[6]

Further extension of the filament at $T \ll T_m$ leads to partial unfolding of the lamellae in the draw direction. If all the new length of a fiber derives from the chain unfolded in the draw direction, then at ~100% crystallinity before and after drawing

$$\frac{1}{E_F} = \frac{l_0}{l}\left[\left(\frac{l}{l_0} - 1\right)\frac{1}{E_p} + \frac{1}{E_\perp}\right] \tag{1}$$

where E_p is the Young's modulus of the extended molecule calculated from molecular structure and spectroscopic data (see Table I) and $E_\perp$, the modulus normal to the polymer chain, which can be taken as equal to $^2/_3$ of the modulus of the isotropic crystal.

Equation (1) will overestimate E if crystallinity decreases during the drawing process or underestimate if there is partial orientation in the "amorphous" regions of the fiber. An implicit assumption in eq. (1) is that the drawn part of the molecule parallels the fiber axis. Should this extended molecule make an angle θ with the fiber axis, E_p^{-1} in eq. (1) must be multiplied with $\cos^2\theta$:[1]

$$\frac{1}{E_F} = \frac{l_0}{l}\left[\left(\frac{l}{l_0} - 1\right)\right]\frac{\cos^2\theta}{E_p} + \frac{1}{E_\perp} \tag{2}$$

This expression should also be corrected for the shear at the interface between the elongated regions and adjacent folded chain crystallites. However, since the shear modulus of the latter is small, that is probably a negligible second-order correction. Far less negligible is the correction for the presence of noncrystalline components of the system.

If one assumes that the fully oriented crystalline domains of a fiber form

TABLE I
Spectroscopic Elastic (Young's) Modulus E_p of Various Polymer Molecules

Polymer	$E_p \times 10^{10}$, dyne/cm.^{2}	
	Calc.[a]	Obs.[b]
Polyethylene	182[c]–340	260
Polytetrafluoroethylene	160	—
Poly(vinyl chloride) (syndiotactic)	160 (or 230?)	—
Poly(vinylidene chloride)	—	41.5
Polyoxymethylene	220	54
Polyisobutylene	70–84	—
Polypropylene (isotactic)	49	42
Polystyrene	—	12
Poly(vinyl alcohol)	—	255
Poly(ethylene terephthalate)	122[c]–146[d]	76[d]
Nylon 66	196[c]–157[e]	—
Cellulose I	—	137
Cellulose II	—	90
Poly(ethylene glycol) (M → ∞)	4.8	—
Poly-3,3-bis(fluoromethyl)oxacyclobutane	110	—
Poly-3,3-bis(chloromethyl)oxacyclobutane	100	—
Poly-3,3-bis(bromomethyl)oxacyclobutane	92	—
Poly-3,3-bis(iodomethyl)oxacyclobutane	77	—

[a] From the spectroscopic force constants of Asahina et al.[7]
[b] By x-ray diffraction analysis of crystallite extension; data of Sakurada et al.[8]
[c] Data of Treloar.[9]
[d] Dalmage and Contois[10] find 140×10^{10} dyne/cm.^{2} by the same technique.
[e] Data of Lyons.[11]

a continuous network with pores of amorphous domains, then in the temperature range where $E_c \gtrsim 10^2 E_a$, and where $\phi_c \gtrsim 0.5$, one might expect

$$E \approx \phi_c E_c$$
$$G \approx \phi_c G_c \tag{3}$$

This crude approximation may be valid over most of the temperature range of interest, namely, that within which $E_c > 10^9$ dyne/cm.^{2}, rubber elasticity E_a never exceeding 10^7 dyne/cm.^{2} The most probable area of validity of eq. (3) is that of cold-drawn fibers, where ϕ_c is a measure of the cross-sectional area occupied by the crystalline phase and combination of eqs. (1) and (3) yields

$$\frac{1}{E_F} = \frac{l_0}{\phi_c l} \left[\left(\frac{l}{l_0} - 1 \right) \frac{1}{E_p} + \frac{1}{E_\perp} \right] \tag{4}$$

Neglect of the rubber elasticity contribution at high values of l/l_0 might lead to an underestimate of E_F by means of eq. (4).

Comparison with Experiment

Experimental tests of eqs. (1) and (4) at high draw ratios have been assembled in Table II. In all cases calculation overestimates the modulus

TABLE II
Room Temperature Tensile Modulus of Drawn Filaments

Filament	Conventional draw process			Special draw process		
	l/l_0	E_F(calc.)[a] $\times 10^{10}$, dyne/cm.[2a]	E_F(obs.) $\times 10^{10}$, dyne/cm.[2]	l/l_0	E_F(calc.) $\times 10^{10}$, dyne/cm.[2a]	E_F(obs.) $\times 10^{10}$, dyne/cm.[2]
Polyethylene[b]	10	20	4.4[c]	12	23	16[d]
				16	64[e]	61[f]
Polypropylene[b]	12	20	6.4[c]	34	32.6 (18.9)[g]	9.0[h]
				60	38.4	25.6[i]
Poly(ethylene terephthalate)	8	11.3[j]	12.5[k]	—	—	—

[a] Calculated by means of eq. (1) and (4), taking E_p from Table I.

[b] Estimate of $E_\perp$ from Bondi.[12]

[c] From *Fibre Data Handbook*.[13]

[d] From Higgins and Bryant;[14] these authors used highest modulus obtained at l/l_0 corresponding to their cold draw ratio.

[e] Calculated from $\varphi_c = 0.80$; E_F calc. for $\varphi_c = 1.0$ is 79×10^{10} dyne/cm.[2].

[f] At 103°K.; filament drawn at 1.25 cm./min. at 100°C.; Data of Vincent.[15]

[g] Value in parentheses is corrected for decrease in φ_c during drawing.

[h] From Sheehan and Cole;[16] drawn at 135°C.

[i] Drawn on a special draw bench by G. Lopatin.[17]

[j] Calculated with $E_p = 140 \times 10^{10}$ dyne/cm.[2]; $E_p = 76 \times 10^{10}$ dyne/cm.[2] yields $E_F = 10.7 \times 10^{10}$ dyne/cm.[2].

[k] Data of Pinnock and Ward.[5]

of the drawn fiber. The extent of the overestimate is quite instructive, however. Where special precautions were taken in the drawing process to attain filaments of high modulus, the experimental observations closely approach the theoretical prediction. The approach would probably have been even closer had the calculated modulus been corrected for the well-known decrease in crystallinity during high extension drawing. Conventional drawing techniques, on the other hand, yield polyolefin filaments with moduli far below those of the theoretical prediction. The excellent agreement between calculated and observed moduli of poly(ethylene terephthalate) filaments suggests that achievement of the theoretical maximum modulus is not equally difficult for all kinds of fibers. The very preliminary evaluation of the present primitive theory is sufficiently encouraging to consider its predictions as upper limits for the achievable tensile modulus of polymer filaments.

The tensile modulus normal to the draw axis should be dominated by van der Waals interactions to the extent that the one parallel to the draw axis is dominated by E_p. It should therefore be predictable from the behavior of crystals of small molecules.[12] Several measurements indicating the correctness of this conclusion have been assembled in Table III. It is also borne out by the small magnitude of the torsion modulus of drawn filaments obtained by Wakelin et al.,[22] as compared to the torsion modulus of the unoriented bulk polymer.

TABLE III

Transverse Moduli $E_\perp$ ($= S_{11}^{-1}$) of Semicrystalline drawn Monofilaments and Films[a]

	Filament		Film		
Polymer	l/l_0	$E_\perp \times 10^{10}$, dyne/cm.[2]	l/l_0	$E_\perp \times 10^{10}$, dyne/cm.[2]	$2/3\ \bar{E}_c \times 10^{10}$ dyne/cm.[2]
Polypropylene		0.78	7.7	1.0	1.1[b]
Poly(ethylene					1.6[c]
terephthalate)		1.14	4.5	1.5	1.8[c]
					2.1[c]
Nylon		0.6	—	—	23[d]

[a] Data of D. W. Hadley et al.[18]
[b] Based on data of Baccaredda and Butta[19] for polypropylene, $\rho = 0.902$.
[c] Based on data of Kawaguchi[20] for $\varphi_c = 0.02, 0.12$, and 0.41, respectively.
[d] Based on data of Woodward et al.[21] for $\varphi_c = 0.54$. The discrepancy between E_c and $2/3\ \bar{E}_c$ may be due to creep in the experiments of Hadley et al.[18]

Comparison with Other Work

The relation of the present work to the models based on polymer orientation has been touched on in the introduction. The analysis of elastic anisotropy of oriented polymers by Kao and Hsiao[23] does not contain the differentiation between spectroscopic and the van der Waals moduli explicitly, but, on the contrary, tries to relate all elastic moduli of the fiber in the different directions to a single elastic constant, which then constitutes an empirical correlating parameter rather than a physical property. Repetition of this type of analysis with a more realistic model might be very instructive. The oriented, partly unravelled lamellae proposed by Hansen and Rusnock[24] is probably a very realistic model, but it has not yet been formulated in a way that would permit an experimental test of its validity.

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Résumé

On prend comme point de départ d'un modèle destiné à décrire les propriétés élastiques de filaments de polymères étirés à froid, le déplissage partiels de lamelles cristallines plissées. La relation qui en résulte additionne le fluage dû aux tensions plissées des forces de van der Waals à celui dû aux tensions détectées spectroscopiquement concernant le squelette polymérique, cela en rapport avec la longueur des lamelles respectivement plissées et non plissées du filament étiré. Une grande partie des modules des filaments étirés de polymères semicristallins rapportées dans la littérature est notablement en-dessous de la valeur prédite. Cependant, lorsque l'on procède à des expériences d'étirages avec grand soin, on obtient un module de Young qui se rapproche très fort de la valeur prédite par la relation présentée ici.

Zusammenfassung

Die teilweise Auffaltung gefalteter Lamellenkristalle wird als Ausgangspunkt für die Entwicklung eines Modells zur Beschreibung der ebenierlieu Eigenshaften kaltgereckter Polymerfäden gewählt. Die erhaltene Beziehung summiert die Van der Waals-Zugnachgiebigkeit und die spektroskopische Nachgiebigkeit der Polymerhauptkette im Verhältnis der Länge der gefalteten bzw. der ungefalteten Kristallamellen im gereckten Faden. Viele der mitgeteilten Zugmoduln der gereckten Fäden aus semikristallinen Polymeren liegen wesentlich unterhalb der theoretischen Werte. Besonders sorgfältige Reckungsversuche werden jedoch mit Zugmoduln belohnt, welche sich eng der durch die hier angegebene Beziehung vorausgesagten Grösse nähern.