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A random distribution (spectrum) of mechanical relaxation/retardation rate constants and its influence on tensile strength of imperfect (real, visco-elastic) polymer fibers in constant strain-rate extension[☆]

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Abstract

A random distribution of relaxation/retardation rate constants is derived and incorporated into the thermodynamic theory of strength of imperfect (real) polymer fibers, which is used to analyze empirical polyethylene (fiber) strength data. The results, weighted equally with previous results, give for the perfect polyethylene fiber — the only unique reference state — at 25°C: σ_c(strength) ≈ 7.5 GPa, K_c(modulus) ≈ 325 GPa, ε_c(strain) ≈ 0.023, and W_c(failure work) ≈ 0.087 GPa. These numbers represent the best currently available for the characterization constants of a perfect fibrilliform single crystal of finite molecular weight polyethylene. The widths of uncertainty are ca. 15%. Also, these numbers are exactly those calculated with the thermodynamic theory of failure based on stress-induced fusion with a constant heat of fusion. Such figures indicate the general strength of the fusion theory. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fiber strength; Failure work; Modulus

1. Introduction

The failure point of crystalline fibers composed of ultra high molecular weight polymers of finite molecular weight recently has been interpreted as a thermodynamic first-order crystal-melt phase transition [1,2]. Reversible tensile deformations reduce the fiber crystalline melting temperature in a predictable fashion, allowing the stressed fiber to melt and fail by molecular flow (slippage) and/or rupture. The theory appears to handle brittle fracture quantitatively, but ductile properties remain in a qualitative realm. Perhaps the difference is determined by temperature–viscosity behavior. High internal viscosities at lower temperatures might precipitate brittle fracture by allowing fiber strain to outrun molecular slippage. But higher temperatures diminish viscosity, generating long range ‘liquid’ like ductile behavior, which also may be replicated at low temperatures by slow deformations. The viscosity referred to is that of the polymer melt. Both stress and fracture can produce a few chemical bond scissions [3], but they are merely incidental to the fracture process and play but a minor role, certainly not one as initiator unless polymer molecular weight is infinite [2].

The ‘melt’ phase generated by tensile stress might not materialize completely as a randomly oriented amorphous melt. Randomization of an ordered fibrilliform configuration of long, non-crystalline extended polymer molecules should be hampered by a necessity to maintain requisite interunit non-bonded contacts. This requires cooperative conformational motions of several molecules until a gradual randomization is achieved, a process that may require a great deal of time. In no sense does a true random amorphous phase appear in the short time allowed before molecular slip in the tensile direction occurs. Once slip is possible stress is diminished, and even a minute diminution below the critical fusion level regenerates crystallization in a relaxed state. However, if the critical stress is maintained molecular slip along the fiber axis continues until fracture, which may be early (brittle) or late (ductile) depending upon stretching conditions and temperature.

Fusion is initiated when the chemical potential of a crystalline unit equals that of a similar amorphous unit in the melt at the same temperature and pressure. A crystal supporting a *c*-axis stress of the right magnitude fulfills this requirement. Consequently, under this condition the extended, oriented polymer molecules are not rigid rods but capable of amorphous flexibility if an opportunity avails itself. This is evident in axial flow (slip) under critical stress. Slip generates internal pores of high interfacial energy within rigid arrays. But conformational flexibility allows neighboring segments to fill such voids or prohibit their

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formation altogether, resulting in a reduced fiber cross-section. Without this 'melt' flexibility a constant Gibbs energy density could not be maintained. It certainly appears that the most thermodynamically efficient way to mobilize crystalline molecules is via a first-order phase transition, in this case a solid-melt transition.

The last word on this is to be found in empirical data. Does experiment agree with theory in a convincing fashion? This article focuses on two quantities that appear relevant to this question: the tensile work W^* required to induce fusion, and the ratio of the strength σ^* to the strain at break ε^*. W^* is important because of its theoretical simplicity and unambiguous relationship to classical thermodynamic qualities. It is central to the theory of perfect (ideal) fibers [2]. The ratio σ^*/ε^* is found to be

$$\frac{\sigma^*}{\varepsilon^*} = \gamma K_\mathrm{i}, \tag{1}$$

where K_i is the initial modulus and γ is a theoretical constant determined by the particular test procedure and the distribution of relaxation/retardation times [4]. The validity of Eq. (1) is central to the entire theory of imperfect (real) fibers [4]. If the distribution of relaxation times is monodisperse, $\gamma = 0.613$ in creep and 0.632 for constant strain-rate deformations [4]. An extensive study of polythylene fibers [5] determined $\gamma = 0.69$ for the latter, but some literature data [6] indicate 0.64, close to the monodisperse value [4]. An error of this size also will manifest itself in the tensile work.

To pursue this further we require a distribution function of relaxation times. The gamut would seem to span from monodisperse to random. We already have the monodisperse. We derive in Appendix A the random and draw upon those results in the body of this report as needed.

As all of this work is recent and original, a very brief overview is desirable at this point. The thermodynamic theory of polymer fibers divides into two parts: the perfect (ideal) fiber [1,2] and the imperfect (real) fiber [4]. The two are inseparable. The perfect fiber, being ideal and nonexistent, can be characterized only by analysis of the real imperfect fiber [5]. However, the real fiber cannot be analyzed without the rigorous theory of the ideal fiber [2], and even so some approximations are required that fortunately decrease in importance as near perfection attains [4].

The perfect fiber [1] is completely crystalline, oriented, and uniform. Its constituent polymer, however, is real with a finite molecular weight that prohibits the melt phase from supporting an equilibrium stress. The completely crystalline fiber is perfectly elastic, i.e. reversibly Hookean in its tensile behavior until failure at the critical melting stress σ^*, which is the maximum stress the fiber can support at a given temperature and pressure. The thermodynamics of the perfect fiber have been extensively developed [2], including the fusional transition with regard to temperature T and pressure P, the tensile work of fusion (failure), the variation of fiber (crystal) modulus with T and P, and the variations of volume, enthalpy, entropy, Poisson's ratio, etc. with tensile stress. The results are, in general, rigorous and often simple [2].

The imperfect fiber, especially a nearly perfect one, is visco-elastic, non-Hookean, and incompletely crystalline and oriented [4]. Its crystalline phase behaves in complete accord with the perfect fiber under similar conditions. The origin of visco-elasticity of highly crystalline fibers might arise principally from a heterogeneous stress distribution that melts over-stressed crystalline regions, allowing stress relaxation and recrystallization [4], hardly an original proposal in its general form. But a new twist appears to add substance to the idea [4]. The breaking time t_B of a fiber supporting a constant tensile load has been interpreted [4] as the particular retardation time of creep failure $\tau^* \equiv t_\mathrm{B}$, which is the sole principle or condition that produces Eq. (1). The breaking time traces to an activation energy of fracture of polythylene equal to the heat of fusion of about 31 methylene units [4] — the approximate size of the Krausz–Eyring kinetic unit of molten polymer flow [7] (of polyethylene) at room temperature. Thus, the activation volume should be that of a methylene unit, $1.4 \times 10^{-5}\,\mathrm{m^3/mol}$, which compares favorably with the experimental value of ca. $1.6 \times 10^{-5}\,\mathrm{m^3/mol}^4$. It was shown [4] that the failure condition $\tau^* = t_\mathrm{B}$ also applies to constant strain-rate deformations.

Overall, such figures indicate support for a connection between localized, stress-induced melting and the visco-elastic behavior of real, imperfect fibers, which therefore implies support for the entire concept of stress-induced melting as apparently manifest in fiber failure and perhaps cold drawing as well. A possible influence of a relaxational distribution function is important to explore.

2. Constant strain-rate deformations

A highly drawn semi-crystalline fiber exhibits visco-elastic behavior upon tensile deformation at a constant rate of strain. The appropriate simulant is a parallel array of Maxwell elements with a random distribution of relaxation constants $k_j = jk_1$ given by Eq. (A6) in Appendix A

$$N_j = N(\mathrm{e}^{\beta} - 1)\mathrm{e}^{-j\beta}, \qquad j = 1, 2, 3, \ldots, \infty,$$

where $\mathrm{e}^{\beta} - 1 = (\langle j \rangle - 1)^{-1}$, $\langle j \rangle$ is the average value of j and expected to be large so that $\beta \approx \langle j \rangle^{-1}$. N_j is the number of elements of j and N is the total systemic elements. The stress σ_j on one of the N_j elements of relaxation rate constant $k_j = jk_1$ at time t is

$$\sigma_j = \frac{\langle K \rangle \dot{\varepsilon}}{jk_1}[1 - \mathrm{e}^{-jk_1 t}], \tag{2}$$

and $\langle \mathrm{K} \rangle$ is the average modulus, k_1 the fundamental or smallest rate constant in the system, and $\dot{\varepsilon}$ the rate of strain, $\dot{\varepsilon} = \varepsilon/t$. Eq. (2) is identical to eq. (11) in [4].

We have then for the total stress

$$\sigma = \sum_{1}^{\infty} \sigma_j N_j = \frac{K_\mathrm{i}\dot{\varepsilon}}{k_1}(\mathrm{e}^{\beta} - 1)\ln\left[\frac{1 - \mathrm{e}^{-q}}{1 - \mathrm{e}^{-\beta}}\right], \tag{3}$$

where $K_\mathrm{i} = N\langle K\rangle$ is the array's (fiber's) initial modulus or the total springs' moduli, q is given by

$$q = k_1 t + \beta = \frac{\langle k\rangle t}{\langle j\rangle} + \beta \tag{4}$$

with $\langle k\rangle = \langle j\rangle k_1$, representing the average relaxation rate constant. The reciprocal of $\langle k\rangle$ often will be written as a relaxation time τ^* of failure, equal to the time of break t_B. This follows from our earlier report demonstrating that $\tau^* k = 1$ if the distribution is monodisperse. Polydispersity then clearly requires $\tau^*\langle k\rangle = 1$ as a general condition of failure. Because $\langle j\rangle$ is large, perhaps two or three orders of magnitude, or even more, this condition of failure limits q to very small values in all situations and permits an excellent simplification of Eq. (3) to

$$\sigma = \frac{K_\mathrm{i}\dot{\varepsilon}}{\langle k\rangle}\ln[1 + \langle k\rangle t]. \tag{5}$$

Corresponding deformational work W is easily found with Eq. (5) to be

$$W = \int_0^{\varepsilon} \sigma\,\mathrm{d}\varepsilon = K_\mathrm{i}\left(\frac{\dot{\varepsilon}}{\langle k\rangle}\right)^2 [x(\ln x - 1) + 1], \tag{6}$$

with $x = 1 + \langle k\rangle t$ and $\varepsilon = \dot{\varepsilon}t$.

Both Eqs. (5) and (6) are highly accurate for all situations in which $\langle j\rangle \gg 1$, so accurate, in fact, that they are written as equalities rather than approximations. Using an asterisk to signify the fiber failure (fusion) point, we have from Eq. (5) and the failure condition $\langle k\rangle t = 1$ the failure strength σ^* at failure strain ε^*

$$\sigma^* = K_\mathrm{i}\varepsilon^* \ln(2) = 0.693 K_\mathrm{i}\varepsilon^*, \tag{7}$$

thus $\gamma = \ln(2) = 0.693$.

If we let $\varepsilon^* \ln(2) = \varepsilon_\mathrm{i}$, a strain, then

$$\sigma^* = K_\mathrm{i}\varepsilon_\mathrm{i} = \sigma_\mathrm{i}, \tag{8}$$

which represents a Hookean, reversible fiber that fails at strength σ_i equal to the actual strength of the real fiber σ^* at a failure strain $\varepsilon_\mathrm{i} = \gamma\varepsilon^*$ and a modulus equal to the initial modulus (the spring modulus) of the actual fiber. This imaginary fiber is the equivalent Hookean fiber earlier defined [4] that behaves as a perfect fiber of the same melting temperature, heat of fusion, and entropy of fusion as the actual fiber. It is the link between the equilibrium thermodynamics of the perfect (ideal) fiber and the viscous kinetics of the imperfect (real) fiber, although not without approximations. Fortunately, approximations decrease in importance in the realm of nearly perfect fibers of high crystallinity. It is not an overstatement to say that at this time the equivalent perfect fiber is the only tool available for meaningful analyses of real, visco-elastic, imperfect fibers.

By Eq. (6) the work to failure W^* becomes

$$W^* = K_\mathrm{i}\varepsilon^{*2}[2\ln(2) - 1] = 0.386 K_\mathrm{i}\varepsilon^{*2}, \tag{9}$$

and the failure work of the equivalent fiber W_i is

$$W_\mathrm{i} = \frac{K_\mathrm{i}\varepsilon_\mathrm{i}^2}{2} = \frac{[\ln(2)]^2}{2[2\ln(2) - 1]} W^* = 0.622 W^*, \tag{10}$$

which is reversible, Hookean work approximated by fusion theory [2] as

$$W_\mathrm{i} \approx \omega\Delta H_\mathrm{v}(1 - T/T_0) = \omega W_\mathrm{c}, \tag{11}$$

where ω is the degree of crystallinity, T_0 the unstretched fiber's melting point and ΔH_v is the heat of fusion of the perfect fiber.

Picking up Eq. (7), writing it in the form of Eq. (1) gives

$$\frac{\sigma^*}{\varepsilon^*} = \gamma K_\mathrm{i} = \frac{\gamma\sigma_\mathrm{i}^2}{2W_\mathrm{i}},$$

or

$$\sigma_\mathrm{i} = \left[\frac{2}{\gamma}\left(\frac{\sigma^*}{\varepsilon^*}\right)W_\mathrm{i}\right]^{1/2} \approx \left[\frac{2}{\gamma}\left(\frac{\sigma^*}{\varepsilon^*}\right)\omega W_\mathrm{c}\right]^{1/2}. \tag{12}$$

This form is preferred because it emphasizes the ratio (σ^*/ε^*) rather than σ^*, ε^* separately. In the case as hand the emphasis is of no importance. There is only one stress and one strain at failure. No other possibilities exist. However, the form of Eq. (12) is general for several experimental techniques, including creep. With creep there are multiple breaking stresses and strains for a given fiber, but according to theory there is only one ratio (σ^*/ε^*) and it is this ratio that must connect with the equivalent fiber. In creep $\sigma_\mathrm{i} \neq \sigma^*$, $\varepsilon_\mathrm{i} \neq \varepsilon^*$, but

$$\frac{\sigma_\mathrm{i}}{\varepsilon_\mathrm{i}} = \frac{\sigma^*}{\gamma\varepsilon^*} = K_\mathrm{i}$$

in all cases.

3. Dimensional creep under constant tensile load

A constant strain-rate deformation inherently is a thermodynamically reversible procedure, provided the strain-rate is not excessive. By this we mean that a reversible fiber, devoid of all tendencies toward stress relaxation, performs reversibly at reasonable rates of strain. But practically all polymer fibers are mechanically irreversible and perform as such in this procedure, a fault of the fiber and not of the experimental technique. None of this is so for a classical creep procedure. Creep is a tensile deformation by a constant load, a dead load. It is a perfect example of a single step, irreversible procedure in which irreversibility attains regardless of the fundamental properties of the fiber itself. Irreversibility inherent to the fiber compounds the situation further. The reader is reminded that a thermodynamic *reversible* transformation is one for which both system (fiber) and surroundings are reversible. For classical creep (constant load) the surroundings are never reversible even if the fiber is reversible. It must not be forgotten that the deformational work in creep is always irreversible; there is no such thing as a reversible deformation path in classical creep. Creep deformational work is unrelated to equilibrium fiber thermodynamics. Therefore, such work, though in principle easily and accurately determined, is of no consequence for our equilibrium (reversible) thermodynamic theory of fibers. Only deformational work along a reversible path is appropriate.

As a result, creep obscures the equivalent fiber that is so readily constructed if strain-rate is constant. Because the equivalent fiber is necessary in order to characterize the perfect crystalline fiber, which is the sole, unambiguous reference state of a polymer fiber, creep is hardly an experimental technique of first priority.

An analysis of creep quickly stalls for want of additional information. The random distribution gives for creep

$$\varepsilon = \frac{\sigma}{K_{\mathrm{i}}}\left[1 - \left(\frac{\mathrm{e}^{\beta} - 1}{\mathrm{e}^{q} - 1}\right) + \langle k\rangle t\right]. \tag{13}$$

For $\langle j\rangle \gg 1$, this approximates to

$$\varepsilon = \frac{\sigma}{K_{\mathrm{i}}}\left[1 - \frac{1}{1 + \langle k\rangle t} + \langle k\rangle t\right]. \tag{14}$$

Invoking the fracture condition $\langle k\rangle t \longrightarrow 1$, we have

$$\sigma^* = \frac{2}{3}K_{\mathrm{i}}\varepsilon^* \tag{15}$$

or

$$\frac{\sigma^*}{\gamma\varepsilon^*} = K_{\mathrm{i}} = \frac{\sigma_{\mathrm{i}}}{\varepsilon_{\mathrm{i}}} = \frac{\sigma_{\mathrm{i}}^2}{2W_{\mathrm{i}}}.$$

Then

$$\sigma_{\mathrm{i}} = \left[\frac{2}{\gamma}\left(\frac{\sigma^*}{\varepsilon^*}\right)W_{\mathrm{i}}\right]^{1/2} \approx \left[\frac{2}{\gamma}\left(\frac{\sigma^*}{\varepsilon^*}\right)\omega W_{\mathrm{c}}\right]^{1/2}, \tag{16}$$

where $\gamma = 2/3$, and W_{i} (the reversible work of fusion of the equivalent fiber) is approximately equal to the work of the perfect fiber W_{c} reduced by the crystallization, $W_{\mathrm{i}} \approx \omega W_{\mathrm{c}}$.

The difficulty is Eq. (16), which traces back to Eq. (15). We have no independent means of ascertaining the stress experienced by the equivalent fiber, σ_{i}. An analysis is possible for a constant strain-rate deformation in which $\sigma_{\mathrm{i}} \equiv \sigma^*$ but not for creep where $\sigma_{\mathrm{i}} \neq \sigma^*$. It is here emphasized that the asterisk symbolizes a failure or fracture condition of the actual fiber. It does not represent a thermodynamic characterization constant unless the fracture condition refers to a perfect fiber, i.e., $\sigma^* \equiv \sigma_{\mathrm{c}}$, etc. At constant strain-rate, the asterisk can also denote a characterization constant of the equivalent fiber since $\sigma^* \equiv \sigma_{\mathrm{i}}$, but that denotation perhaps should be avoided here because an equivalent fiber, being so emeshed in crystallinity and morphology, may be impossible to define uniquely, contrary to the perfect fiber.

According to the fusion theory recipe, Eq. (15) should represent a valid result capable of verification. In a creep experiment the load ($\sigma = \sigma^*$) is arbitrary. For various loads (on identical fibers), is the ratio σ^*/ε^* constant? And does it equal γK_{i}? These questions appear to be quite important, but whatever the answers, without a means of extracting from the creep experiment a value of σ_{i}, further progress in not possible.

4. Results and discussion

Analyzing a real imperfect (visco-elastic) polymer fiber requires construction of a corresponding equivalent perfect (reversible) fiber [4] to which the thermodynamic fusion theory of perfect fibers [2] can be applied [5]. This hypothetical perfect fiber must devolve directly from the empirical process employed, without extraneous help, if the process is to stand-alone. Both creep and stress relaxation fail on this account. But constant strain-rate deformation easily qualifies: the equivalent perfect fiber is readily deduced from the experimental stress–strain behavior [4]. The equivalent fiber is an imaginary perfect fiber identical to the actual real fiber in all aspects except reversibility. The real fiber is visco-elastic, the equivalent fiber is perfectly elastic (i.e. reversible) and, therefore, subject to thermodynamical analysis.

We hypothesized a cause-effect link of melting to mobility [1,4]. Irreversible visco-elasticity in a high crystalline, high molecular weight fiber wherein individual molecules pass through many crystalline–amorphous domains should be slight unless some melting frees up sub-molecules for stress generated rearrangements, perhaps followed by recrystallization in a more relaxed condition. The group of relaxation times or relaxation rates reflects various local conditions impinging upon crystallites or portions thereof. As the solid-melt transition is of necessity a cooperative phenomenon it is doubtful that relaxation times pertaining to molecules or submolecules are of much import directly on melting. Rather, they might contribute in a local aggregate to produce an effective time pertinent to a particular crystalline element, if they contribute at all.

The equivalent perfect fiber, however, stretches in a reversible, Hookean fashion up to the point of failure in exact accord with a perfect fiber [4]. Melting and recrystallization does not occur en route, only at the critical fusion point, at which the equivalent breaking stress σ_{i} is the same as the actual breaking stress σ^*, but equivalent breaking strain ε_{i} equals $\gamma\varepsilon^*$. Real fiber data bubbles up the equivalent perfect fiber so easily as to be obvious [4]. Consequent thermodynamic analysis is straightforward.

The equivalent fiber, if it is reversible, must be independent of strain-rate $\dot{\varepsilon}$. At failure $t \longrightarrow \tau^*$ and $\tau^*\dot{\varepsilon} = \varepsilon^*(P,T)$ which reveals how τ^* depends upon strain-rate at constant

Table 1
Recalculated polyethylene fiber data [5] using the random distribution of rate constants $\varepsilon' = 0.693\varepsilon^*$, $K' = \sigma^*/\varepsilon'$

σ^* (GPa)	ε^*	ε'	K' (GPa)	ω	$(\omega K')^{1/2}$	$(\omega/K')^{1/2}$
0.97	0.072	0.050	19.44	0.705	3.70	0.190
2.07	0.088	0.061	33.93	0.757	5.07	0.149
2.54	0.071	0.049	51.63	0.864	6.68	0.129
3.12	0.065	0.045	69.33	0.916	7.97	0.115
3.22	0.069	0.048	67.36	0.831	7.48	0.111
3.38	0.067	0.046	72.84	0.816	7.71	0.106
4.65	0.040	0.028	167.87	0.875	12.12	0.072
4.67	0.052	0.036	129.72	0.864	10.59	0.082
4.90	0.051	0.035	138.81	0.880	11.05	0.080
5.88	0.058	0.040	146.27	0.925	11.63	0.080
6.37	0.042	0.029	218.90	0.956	14.47	0.066
6.83	0.060	0.042	164.18	0.964	12.58	0.077
7.15	0.034	0.024	302.98	0.984	17.27	0.057

pressure P and temperature T under reversible conditions — slower rates of strain. Therefore, fiber strength is also independent of strain-rate so long as the region of reversibility is not abandoned, which will gradually occur if $\dot{\varepsilon}$ is promoted to higher rates that permit stress to lead strain. Such irreversibility eventually displays a strength noticeably in excess of the thermodynamic equilibrium amount. In short, a classical irreversible condition produces higher irreversible strength, and, it should be added, higher failure work.

Our polyethylene (PE) data published earlier [5] is herewith subjected to re-analysis based on the random distribution of rate constants. The principal study involved high strength fibers of Himont 1900 PE. A much smaller sampling of GUR 412 PE was also mentioned. Both materials are listed in Table 1–3 of Ref. [5]. The Himont data (Tables 2 and 3) consisted of 177 test samples from 40 separate fibers. Each fiber yielded either four or five samples. Plotting fracture data in accord with Eq. (7) reveals $\gamma = 0.69$. GUR fibers [5] (Table 1), limited to only 17 fibers, gave $\gamma = 0.71$. The theoretical value employing the random distribution is $\gamma = 0.693$, and for a monodisperse distribution [4] $\gamma = 0.632$. Analysis [4] of 15 PE samples reported in the literature [6] gave $\gamma = 0.64$. On balance, these figures favor the random distribution simply because of the great number of tests executed. But some reservations persist. For example, thirteen of the Himont fibers were also included in a further analysis involving crystallization, modulus, and work of failure. These fibers, consisting of 58 test samples, displayed $\gamma = 0.66$ [5].

The 13 Himont fibers mentioned also are herewith analyzed anew in the fashion shown in Ref. [5] but with $\gamma = 0.693$, or $\varepsilon_i \equiv \varepsilon' = 0.693\varepsilon^*$ and $K' = \sigma^*/\varepsilon'$. A plot of σ^* vs $(\omega K')^{1/2}$ gives for the perfect crystalline polyethylene fiber work of failure (fusion) $W'_c = 0.094$ GPa. Equally valid is a plot of ε' vs $(\omega/K')^{1/2}$, from which $W'_c = 0.082$ GPa. The average $W'_c = 0.088$ GPa and the determined value $\sigma_c = 7.5$ GPa produce $K' = 320$ GPa and $\varepsilon'_c = 0.023$. A subscript c denotes the perfect crystalline fiber. Table 1 provides the recalculated data (ε', K'). W'_c may be obtained from the slopes of the mentioned plots using Eq. (12) with $\sigma_i, = \sigma^* = [2\omega K' W'_c]^{1/2}$ and with $\varepsilon' = [2\omega W'_c/K']^{1/2}$. Alternatively, the appropriate columns may be averaged and W'_c calculated directly.

The results of one ($\sigma^* = 0.97$ GPa, see Figs. 4 and 7 of Ref. [5]) of the 13 fibers appear erroneous in the same manner as reported earlier [5]. Eliminating it, the remaining 12 yield for the respective plots (above) $W'_c = 0.097$ and 0.092 GPa, for an average of $W'_c = 0.095$ GPa. Therefore, $\sigma_c = 7.5$ GPa, $K'_c = 296$ GPa, and $\varepsilon'_c = 0.025$.

Both results above seem less attractive than former results [5] exclusively because W'_c is climbing higher than can be justified easily. The value of γ seems right and the value of W'_c seems wrong, so our data neither supports nor rejects the random distribution of relaxation rates. Perhaps, the true situation lies somewhere between the extremes of monodisperse and random rates. Then we should include these with the former mix [5] of analytical results based on $\gamma = 0.632$, and on the empirical (graphical) determination of ε_i and K_i as opposed to calculated (ε', K'). Thus, we have $\sigma_c = 7.5$ GPa in all cases, and

$$0.081 < W_c < 0.095 \text{ GPa},$$

$$296 < K_c < 347 \text{ GPa},$$

$$0.022 < \varepsilon_c < 0.025.$$

To the extent that the value $\sigma_c \approx 7.5$ GPa is correct, or reasonably correct, these windows should be reliable. Almost certainly the perfect fiber (crystal) modulus K_c is somewhere between ~300 and ~350 GPa.

The fiber tests [5] were performed at 25°C and atmospheric pressure. Consequently, the figures are characteristic of the perfect crystalline fiber — a perfect fibrilliform single crystal of finite molecular weight polyethylene — under essentially standard state conditions, i.e. unit activity. If forced to select a number for each quantity, it would be an average over all six sets of analyses weighted equally:

$\sigma_c \approx 7.5$ GPa,

$W_c \approx 0.087$ GPa,

$K_c \approx 325$ GPa,

$\varepsilon_c \approx 0.023$.

Of course, other choices are available. We could count the graphical results as one-half instead of one-third, but the numbers barely change.

The earlier analysis without the random distribution gave $\sigma_c \approx 7.5$ GPa, $W_c \approx 0.084 \pm 0.003$ GPa, $K_c \approx 335 \pm 12$ GPa, and $\varepsilon_c \approx 0.0225 \pm 0.0005$. Including the random distribution increases the upper limit of W_c, and decreases the lower limit of K_c to ca. 300 GPa.

These new results are interesting. They are essentially identical to the 12-fiber results — both graphically determined and calculated via $\gamma = 0.632$ (monodisperse distribution) — reported earlier [5].

The thermodynamics of perfect fibers [2] provide a rigorous method of calculating the tensile fusional work required to destroy a fiber. This work is identified with W_c, the failure work. For our calculation it is necessary to defer to an approximation of constant heat of fusion $\Delta H_v = 0.293$ GPa to obtain

$$W_c \approx \Delta H_v(1 - T/T_0) = 0.0867 \approx 0.087 \text{ GPa},$$

where T_0 is the unstressed fiber melting point (423 K) and T is the ambient temperature (298 K). With $\sigma_c = 7.5$ GPa, we have $K_c \approx 325$ GPa and $\varepsilon_c \approx 0.023$.

Of course, this is too good to be true, and it is not. The problem is that ΔH_v is not a constant. Its value must decrease as temperature decreases, which lowers W_c also, so that $W_c < 0.0867$ GPa is mandatory, although we cannot now say how much less it is. Note that a lower W_c gives a higher K_c for the same strength σ_c. A first-order fusional transition under reversible tensile conditions requires the least (minimum) work on the fiber to transform the perfect crystal to the random melt, a transition of maximum breadth from maximum to minimum order. This work cannot be exceeded in a reversible transition, not even if it is punctuated with an intervening transition or transitions. Any such intervening transition must lie within the crystal-melt transition, dividing it into a two-step affair, each of less heat and entropy of transition than the crystal-melt quantities. Consequently, if the polyethylene transition observed (failure) is not that of crystal → melt but rather an intervening transition of perhaps crystal (form 1) → crystal (form 2) this tensile work of transition must be less than the fusional work W_c calculated above. Situations, for which failure work, under reversible conditions, exceeds fusional work, as apparently is the case with polyethylene, cannot be explained by an intervening transition. A previous publication [8] on solid–solid phase transitions may be of interest here.

However, this does draw the question of how it is possible for experimental failure work to exceed tensile fusional work if fusion is the mechanism of failure? Two explanations readily come to mind. Either the empirical data is contaminated with a small systemic error, or the strain-rate (0.00667 s^{-1} herein) is insufficiently slow to replicate thermodynamic (reversible) conditions. A third explanation, perhaps a partial explanation only, is incomplete *c*-axis crystallite orientation along the fiber axis. Incomplete orientation has not yet been factored into the theory.

A more likely explanation, however, involves the approximation $W_i \approx \omega W_c$, Eq. (11). Actually, W_i must exceed ωW_c by a small amount, depending upon the degree of fiber imperfection, because deformational work of amorphous regions is neglected. Thus, because $W_i > \omega W_c$

$$\sigma^* = [2K_i W_i]^{1/2} > [2\omega K_i W_c]^{1/2}.$$

The slope of σ^* vs $(\omega K_i)^{1/2}$ therefore produces an apparent value of W_c that exceeds its true value. Consequently, our experimental value of the apparent W_c is expected to be a little larger than the rigorous theoretical value of the perfect fiber, and in general a confliction with the laws of thermodynamics is not manifest. Empirical results appear in accord with the theoretical expectations. This is a strong argument weighing heavily in favor of the random distribution of relaxation rates, which encourages retention of that distribution as a competitive theoretical factor. However, our data do not supply a conclusive result at this time. Tentatively it appears that the monodisperse function may suffice, as we earlier surmised [4], but this is subject to revision as additional studies may warrant.

Appendix A

The traditional description of polymer visco-elasticity is based on phenomenological rather than molecular concepts. To be sure, molecular theories are important and often employed, but their applicability is essentially limited to the region where the constituent molecules are elastically rubber-like: that is, the polymer molecules and sub-chains thereof behave in accord with the kinetic theory of elasticity under the time–temperature conditions imposed. Anterior phenomenological concepts constructed about hypothetical idealized springs and dashpots also have various limitations, principally an absence of a general analytical expression for a necessary spectrum, or distribution, of mechanical relaxation/retardation times. Such a spectrum is inferred from the failure of a single relaxation/retardation time to replicate adequately empirical visco-elastic data.

The phenomenological version of visco-elasticity substitutes for the real polymer material an artificial, hypothetical array of viscous dashpots and elastic springs appropriately configured to accommodate either stress relaxation or dimensional creep. The springs and dashpots are not real, merely imaginary artifices capable of simulating visco-elastic behavior if appropriately arrayed.

Stress relaxation is the sudden imposition of an initial strain ε_0, remaining constant thereafter, by a stress σ_0 that degenerates with time as viscous flow (i.e. slipping and sliding of molecules and submolecules irreversibly past one another) diminishes the initial elastic response of the material. It is well established that this procedure behaves in a manner similar to a spring and dashpot connected in series (a Maxwell element) if the polymer is uncross-linked — that is, if the individual polymer molecules are unencumbered in their individual motions by chemical means so as to yield an equilibrium stress $\sigma_\infty = 0$ at large times. The relaxation time τ is the time $t = \tau$ necessary for the element to relax its stress σ to σ_0/e at constant strain ε_0 A single Maxwell element, thus a single relaxation time, is inadequate for good results. Instead an array of Maxwell elements aligned in parallel, each with its own characteristic relaxation time reflecting somewhat more or less local variations of elastic moduli and viscosities within the actual material, seems capable of accurate simulations of relaxation data if the distribution of relaxation times (also called a spectrum) is known. Note that the total stress on the array is the sum over all elemental contributions, and each Maxwell unit is equally strained, ε_0.

If the stretched polymer is a lightly cross-linked network, it must of necessity have a finite equilibrium stress at very long times. Simulation of this material is accomplished by connecting an additional spring in parallel with each Maxwell element, providing a basic modified three-unit Maxwell element, all of which are arrayed in parallel also.

Deformable parallel elements respond independently to an applied stress. All are equally strained, and stress relaxations occur independently at various rates as determined by the individual relaxation times τ. Consequently, the spectrum (or distribution) of relaxation times τ must be generated by a random distribution of the τs among the elements. Fortunately, as shown herein, this is a straightforward calculation.

Dimensional creep occurs if a constant load is attached to the polymer, causing continued strain elongation along the load direction. This behavior is similar to that of a Voigt element, which is an elastic spring paralleled with a viscous dashpot. Refined simulation requires an array of Voigt elements connected in series, but this array is only applicable to cross-linked polymers. Uncross-linked material requires an additional dashpot joined in series to each Voigt element — a modified, three-unit Voigt element. Such modified Voigt elements are also connected in series. In creep simulations, all elements experience the same, identical load, but each must elongate independently as determined by its particular retardation time τ. The retardation times are randomly distributed among the elements in exactly the same manner as relaxation times.

Our purpose is to inquire about the random distribution, or spectrum, of τ as required by the Maxwell/Voigt arrays, which are the least complicated simulants of polymer visco-elasticity. However, the inquiry actually is directed to the random distribution of the visco-elastic relaxation/retardation rate constants k, which are the reciprocals of τ. This alteration is insubstantive, merely a manipulative mathematical convenience. Consequently, the distribution is rapidly and easily developed. Of immediate interest and import is an incorporation of the distribution into the fusion theory of strength of imperfect (real) fibers of finite molecular weight crystalline polymers. However, its applicability to visco-elastic polymers in general, while unexplored, is not unnoticed. It appears to be the only distribution or spectrum that transcends the entire range of times τ from very short to very long. A single example (viscosity) is offered in the following section.

A.1. A random, most probable distribution

Our treatment is phenomenological and statistical; molecular and sub-molecular analogs are not introduced, except perhaps as wide generalizations in the sense that both viscous and elastic behaviors must devolve from inter and intramolecular characteristics of the polymer molecules.

Stress relaxation and dimensional creep are simulated by visco-elastic arrays consisting of elastic springs and dashpots. A relaxation time τ is defined as the quotient of viscosity η by spring modulus K, and relaxation (rate) constant $k = \tau^{-1} = K/\eta$. Such constants vary throughout the system according to local conditions, which are simulated by appropriate Maxwell elements. What then is the probability that an element has a rate constant of a particular value? Such a probability may well be a smooth, continuous variation from one value to another, but we resort to the common technique of introducing a discontinuous variable initially and move to a continuous function if needed. Let ρ represent the probability that a rate constant is of unit value (to be defined) and ρ^2 one of two units value, and of j units value ρ^j, denoted as P_j. Thus

$$P_j = \rho^j = e^{-jg}, \tag{A1}$$

where $g = -\ln \rho$ and $\rho < 1$.

The probability P_j is the probability a Maxwell (or Voigt) element has a mechanical rate constant k_j. Within a specified system there are N_j such elements, the sum over all j being the total number N of elements in the simulation system, i.e.

$$\sum N_j = N, \qquad j = 1, 2, 3, \dots, \infty. \tag{A2}$$

The average value of j in the system is $\langle j \rangle$, which is

$$\sum jN_j = N\langle j \rangle, \qquad j = 1, 2, 3, \dots, \infty \tag{A3}$$

and the rate constant $k_j = jk_1$ where k_1 is the smallest constant and serves to define the unit value previously mentioned. The relaxation time $\tau_1 = k_1^{-1}$ is therefore the largest in the system. The average rate constant is $\langle k \rangle = \langle j \rangle k_1$, the reciprocal of which is denoted τ^*, which turns out to be the time of failure or fracture $t_B \equiv \tau^* = \langle k\rangle^{-1}$. The summations above exclude $j = 0$ because a zero rate constant means no relaxation at all. At the other extreme j is extended to infinity because $N_j \to 0$ as $j \to \infty$.

We now determine N_j for a random distribution as required by the simulation arrays. The probability of a particular assignment of ks is

$$\Pi_j P_j^{N_j}. \tag{A4}$$

But all possible arrangements or assignments are equally probable. Since the total number of arrangements (complexions or ways) is $N!/\Pi_j N_j!$, the total probability P is the product with Eq. (A4), i.e.

$$P = \frac{N!}{\Pi_j N_j!}\Pi_j P_j^{N_j}. \tag{A5}$$

Following standard procedures in statistical mechanics the set of N_js for which P is a maximum, subject to conditions (A2) and (A3), is the desired distribution, which is

$$N_j = N(\mathrm{e}^{\beta} - 1)\,\mathrm{e}^{-j\beta}, \qquad j = 1, 2, 3, \ldots, \infty, \tag{A6}$$

where

$$\mathrm{e}^{-\alpha} = N(\mathrm{e}^{\beta} - 1), \tag{A7}$$

$$\mathrm{e}^{-\beta} = 1 - \frac{1}{\langle j\rangle}.$$

The Lagrangian multipliers α and β are associated with, respectively, Eqs. (A2) and (A3) [9].

A single distribution is usually inadequate to simulate amorphous polymer systems over many decades of time. For example, it is widely believed that intermolecular entanglements necessitate a separate, additional distribution at long times. To the extent that all such distributions are functionally identical, they can be treated by the distribution, Eq. (A6). Consider viscosity. Let relaxations within a molecule be represented by a prime ($'$) and intermolecular entanglement relaxations by double prime ($''$). If viscosity is the dependent variable, modulus and rate constant are independent. Thus the moduli in a given distribution can be replaced by the distribution average $\langle K'\rangle$, and we have

$$\eta = \frac{\langle K'\rangle}{k'_1}\sum_1^{\infty}\frac{N'_j}{j} + \frac{\langle K''\rangle}{k''_1}\sum_1^{\infty}\frac{N''_j}{j},$$

$$= \left[\frac{N'\langle K'\rangle}{k'_1} + \frac{N''\langle K''\rangle}{k''_1}\right]\left(\frac{1}{\langle j\rangle - 1}\right)\ln\langle j\rangle, \tag{A8}$$

$$\approx \left[\frac{K'}{\langle k'\rangle} + \frac{K''}{\langle k''\rangle}\right]\ln\langle j\rangle, \tag{A9}$$

where $N'\langle K'\rangle = K'$ and $N''\langle K''\rangle = K''$.

Eq. (A9) may be written as $\eta = K\langle\tau\rangle$ or

$$\eta = K'\langle\tau'\rangle + K''\langle\tau''\rangle = K\langle\tau\rangle, \tag{A10}$$

where K is the average system modulus and $\langle\tau\rangle$ is the average relaxation time. Note that $\langle\tau\rangle\langle k\rangle = \ln\langle j\rangle$, $\langle\tau'\rangle\langle k'\rangle = \ln\langle j\rangle$, etc., if $\langle j\rangle \gg 1$.

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