polymer

The breaking strength of imperfect (real) polymer fibers

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Abstract

The thermodynamic fusion theory of strength of perfect polymer fibers of finite molecular weight is extended to include imperfect (i.e. real) fibers of incomplete crystallinity and orientation. Approximate equations for failure strength, strain, and work of failure are derived by extracting from the real visco-elastic fiber an equivalent reversible component suitable for thermodynamic analysis. This is facilitated by an explicit relationship between fiber breaking stress, σ_*, and breaking strain, ε_*, which is shown to be $\sigma_* = 0.632 K \varepsilon_*$ (K = modulus) for constant strain-rate deformations. It is shown that fiber breaking time is equivalent to the fiber visco-elastic mechanical relaxation time. Experimental data shows that the activation energy of rupture of polyethylene fibers is not the activation energy of covalent bond rupture. Instead it agrees with the activation energy expected of crystal melting in accordance with the fusion theory of rupture. The activation volume of the polyethylene fibers also agrees with the value expected from this theory. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ultimate mechanical properties of *perfect* polymeric fibers composed of *finite molecular weight* polymers were successfully calculated via elementary phase equilibrium thermodynamics six years ago [1]. A *perfect* fiber is a fibrilliform single crystal of complete orientation and 100% crystallinity. It is a hypothetical entity that establishes behavioral limits for real fibers, and these limits are easily calculated because of the simplicity of the single crystal concept. However, real fibers are imperfect or, at best, nearly perfect. The nearly perfect fiber is a little short of 100% crystallinity and contains a small amount of disoriented (amorphous) material. To a first approximation, the thermodynamic theory also applies to the nearly perfect, real fiber with increasing accuracy as crystallinity approaches 100%. The quantities of interest are the breaking strength, σ_*, breaking strain, ε_*, and work to break, W_*.

It is necessary to emphasize that the perfect fiber concept pertains to *finite molecular weight* polymers only. Fibers composed of molecules of infinite molecular weight, wherein unbroken, continuous chains of covalent bonds transcend the entire fiber length might require a different theoretical approach. At present, this does not constitute a meaningful restriction because real polymers are of limited

contour lengths. It is exactly this feature alone that insures that fiber strength is determined by intermolecular cohesive forces and not by stress-induced scissions of the polymer backbone covalent bonds [1]. Crystalline intermolecular forces, of course, translate into fusional energies or enthalpies. Noting that fusion energy per bond unit is nearly two orders of magnitude lower than covalent bond strengths, it is axiomatic that bond scissions play no role in initiating failure of the *perfect* fiber. In fact, empirical evidence suggest that scission in a stressed fiber is confined mainly to the amorphous regions and in amounts too small to influence fiber rupture [2,3].

Intermolecular crystalline forces within the perfect fiber resist external deformational forces. Clearly, a tensile force attempts to pull the fiber (crystal) apart by sliding molecules past one another, but molecules within a crystal do not have an easy mobility. Estimates [4] of the molar internal cohesive energy of a molecule approximately 1000 Å in contour length (a molecular weight of ~11 100, if polyethylene) range from ~3 to 10 times the –C–C– bond energy (80 kcal/mol), the lower number pertaining to hydrocarbons and the higher to hydrogen bonded polymers. A fully extended polymer molecule 10 or 100 times larger in a perfect fiber (crystal) is without doubt completely immobilized, which prompts the usual conclusion that molecular slippage is not feasible; rupture therefore must occur by stress-induced bond scission [4]. Such a conclusion is completely invalid. Indeed, polymer molecules cannot and

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do not slip and slide throughout the crystal. Molecular slippage and crystallization are antithetical concepts, actually mutually exclusive, excepting the less stringent constraints endowed to liquid crystals. What seems to have been persistently overlooked, or perhaps misunderstood, is the possibility of a solid–melt phase transition, wherein a rigid, hard, solid crystal abruptly changes at a particular temperature and pressure into a liquid of mobile molecules. The crystal lattice collapses at a single point. Before the collapse molecules are immobilized within the crystal, afterwards they are mobile. The cost of mobilization is energetically cheap.

A tensile force can induce the crystal–melt phase transition [1,5]. Since the *crystalline* polymer molecules cannot slip, the load acts effectively against intermolecular crystalline forces, destabilizing the fiber (crystal) and lowering its melting temperature. If the tensile load is sufficient to reduce the melting point to ambient temperature, the fiber melts with concomitant slippage of molecules. Molecular slippage constitutes fiber failure [1,5]. But it is unexpected to see overall flow or telltale signs of melting such as rounded edges on fracture faces, etc. The slightest diminution of stress below the critical level instantly regenerates the crystal. Only an ephemeral, microscopic slip bridges the gap between an intact crystalline fiber and its fractured crystalline pieces. Transitional slip is instantaneous and momentary.

All this is standard thermodynamics, so irrefutable that only a wholesale repudiation of elementary thermodynamics can nullify it. A crystalline fiber of finite molecular weight molecules cannot exist as an intact fiber under a tensile load in excess of that required for the phase transition [1]. At this load the fiber ceases to be a fiber. In accordance with thermodynamics, it will not support a greater load. But it is possible for fracture to occur at a lesser load should an alternative failure mechanism exist. We do not know of one, and the close concordance of theoretical and experimental strength of nearly perfect fibers of polyethylene and polypropylene leaves but little doubt that fiber strength is determined by the critical fusion load [1].

The theory [1] yields for the perfect fiber of finite molecular weight molecules:

$$W_* = \Delta H_\mathrm{v} \ln (T_\mathrm{o}/T),$$

$$\sigma_* = [2K_\mathrm{c}\Delta H_\mathrm{v} \ln (T_\mathrm{o}/T)]^{1/2},$$

$$\varepsilon_* = \left[\frac{2\Delta H_\mathrm{v}}{K_\mathrm{c}} \ln(T_\mathrm{o}/T) \right]^{1/2},$$

where ΔH_v is the heat of fusion per unit volume, K_c, the crystal axial modulus, T_o, the melting temperature of the unstressed fiber, and T, the melting temperature of the stressed fiber (i.e. ambient temperature). Some of the symbols are changed from the original paper to facilitate clarity. A recent reinvestigation [5] of the theory of perfect fibers shows that $\ln(T_\mathrm{o}/T)$ must be replaced by $(1 - T/T_\mathrm{o})$.

This is because the earlier work omitted the variation of the heat of fusion with tensile force. Accordingly, the preceding equations must be replaced by

$$W_* = \Delta H_\mathrm{v}(1 - T/T_\mathrm{o}), \tag{1}$$

$$\sigma_* = \left[2K_\mathrm{c}\Delta H_\mathrm{v}(1 - T/T_\mathrm{o})\right]^{1/2}, \tag{2}$$

$$\varepsilon_* = \left[\frac{2\Delta H_\mathrm{v}}{K_\mathrm{c}}(1 - T/T_\mathrm{o}) \right]^{1/2} \tag{3}$$

These results are predicated upon reversible, linear elasticity, i.e. Hookean elastic behavior. Of the three, the work to rupture, W_*, is the most fundamental and the least ambiguous. It is determined by only two quantities, the unstressed fiber (crystal) melting point and its heat of fusion, both of which are drawn from data pools completely separate from mechanical behavior. There are no adjustable parameters here. As such, a close agreement between the work predicted by Eq. (1) and the measured mechanical work of rupture would constitute a strong confirmation of the fusion theory of fiber failure. Both the breaking stress, σ_*, and the breaking strain, ε_*, are contained within the work, W_*, as factors thereof, but they cannot be extracted without introduction of a third quantity, the Young's modulus, K_c. Since the crystalline modulus is currently problematic, both the stress and the strain are mildly ambiguous compared to the rigid certainty of W_*.

We have to work with real fibers that are imperfect: crystallization is less than complete, stress distribution within the fiber is likely to be inhomogeneous, time and irreversibility are consequential, visco-elasticity is prominent, and reversible thermodynamics plays a lesser role. To the extent that all such deviations from the perfect fiber are small, the equations of the perfect fiber can be adapted to the imperfect fiber by replacing K_c and ΔH_v with the actual experimental values of the real fiber, K'' and $\Delta H_\mathrm{v}'' \approx \omega\Delta H_\mathrm{v}$, where ω represents the degree of fiber crystallinity. This gives

$$W_* \approx \omega\Delta H_\mathrm{v}(1 - T/T_\mathrm{o}), \tag{4}$$

$$\sigma_* \approx [2\omega K''\Delta H_\mathrm{v}(1 - T/T_\mathrm{o})]^{1/2}, \tag{5}$$

$$\varepsilon_* \approx \left[\frac{2\omega\Delta H_\mathrm{v}}{K''}(1 - T/T_\mathrm{o}) \right]^{1/2}. \tag{6}$$

These are results previously given [1] and subsequently corrected [5].

In this paper, we concentrate on the imperfect fiber and the proper application thereto of Eqs. (4)–(6), which are grounded in reversible thermodynamics yet contain irreversible components. We seek to amend the equations and/or clarify their constraints of applicability in order to improve our understanding of the imperfect fiber. To do this properly, we first consider the role of time on ultimate mechanical properties.

2. Time, strength, and visco-elasticity

Zhurkov [6–9] and several collaborators made an important contribution to fracture mechanics. They established for a variety of materials—metals, alloys, crystals, and polymers—an empirical equation relating the fracture time (lifetime), t_B, to the tensile breaking stress, σ_*, of a standard creep experiment:

$$t_B = t_o \exp[(U_c^{\neq} - V_c^{\neq} \sigma_*)/RT], \qquad (7)$$

where $U_c^{\neq}$, $V_c^{\neq}$ are material constants and t_o is a universal time of $\smile 10^{-13}$ s. The form of the equation is that of a rate process in which $U_c^{\neq}$ constitutes the activation energy of fracture and $V_c^{\neq}$ is the corresponding activation volume. Both quantities were experimentally determined for each material. For polymers, $U_c^{\neq}$ showed a close correspondence to activation energies of thermal destruction, which led Zhurkov to conclude that the process of polymer rupture is determined by the "energy of breaking chemical bonds." This view has exerted powerful sway for more than 25 years, yet the weight of evidence in its favor is slight.

To begin, some of Zhurkov's results are not, in fact, as he claims. For example, his reported value of $U_c^{\neq}$ for poly(methyl methacrylate) is 54 kcal/mol, which is exactly that cited to be the activation energy of thermal destruction of PMMA. But one cannot obtain 54 kcal/mol from the data of Zhurkov, rather the correct result is ~30 kcal/mol. The difference is significant. Concerning other polymers, a close agreement between Zhurkov's measured energies and the activation energies of thermal degradation can be problematic. Data compiled by T. He [10] reveal for poly-vinylchloride 95 kcal/mol versus Zhurkov's 35 kcal/mol. What about polyethylene? Zhurkov [7] found 113 kJ/mol for $U_c^{\neq}$ for this material, and in this study we find 107 kJ/mol (26 kcal/mol) as opposed to the bond energy of 80 kcal/mol, or to the activation energy of thermal degradation, 72 kcal/mol [10].

If $U_c^{\neq}$ is not the activation energy of bond scission, what might it be? The general answer to this question is obvious. The experiment in question is creep, which is the response of a visco-elastic element to a constant tensile load. Eq. (7), therefore, pertains to visco-elastic creep. As such, $U_c^{\neq}$ and $V_c^{\neq}$ are the corresponding activation quantities for creep. Keep in mind that rupture is an irreversible process that cannot occur without some degree, however small, of molecular slip or flow (i.e. a visco-elastic response). Hence, the mechanism of fracture must be identical to the mechanism of visco-elastic flow. We prove this rather easily in the following sections.

It is universally agreed that Eq. (7) is of the form of a rate equation. The reciprocal of a mechanical rate constant is a relaxation or retardation time. Therefore, the time to break, t_B, (lifetime) is a particular retardation time, to wit, that of fracture. The creep deformation ε (strain) attributable to a particular retardation time τ of a Voigt–Kelvin visco-elastic element supporting a constant stress σ is

$$\varepsilon = \frac{\sigma}{K}\left[(1 - e^{-t/\tau}) + \frac{t}{\tau}\right], \qquad (8)$$

where K is the spring modulus and τ, the retardation time of both dashpots, taken to be identical. Our condition of fracture is $t \to t_B \equiv \tau$. Thus, from Eq. (8) ε, $\sigma \to \varepsilon_*$, σ_* as $t \to \tau$; i.e.

$$\varepsilon_* = \frac{\sigma_*}{K}\left(2 - \frac{1}{e}\right)$$

or

$$\sigma_* = \left(\frac{e}{2e - 1}\right)K\varepsilon_* = 0.613 K\varepsilon_*. \qquad (9)$$

We now have a unique correlation of σ_* with ε_* that is subject to rigorous verification. However, we move on to a more convenient visco-elastic experiment—that of constant rate of strain.

Forced deformation at a constant rate of strain, $\dot{\varepsilon}$,

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{\varepsilon}{t} = \text{constant} \qquad (10)$$

is fundamentally stress relaxation. Two advantages are associated with it. First, the experiment is easily performed on an Instron, whereby τ and ε_* are related by Eq. (10). Second, the appropriate visco-elastic model is the simple Maxwell unit consisting of a single spring and dashpot connected in series. A single relaxation time τ renders it unambiguous. The stress σ and deformational work W are well known for this situation:

$$\sigma = \tau K\dot{\varepsilon}(1 - e^{-t/\tau}), \qquad (11)$$

$$W = \tau\dot{\varepsilon}K\varepsilon - (\tau\dot{\varepsilon})^2 K(1 - e^{-t/\tau}), \qquad (12)$$

where K is the spring modulus or *initial* modulus. Our condition of fracture must also apply to this situation. Thus, the rupture condition $t \to t_B \equiv \tau$ and Eq. (10) yield from Eqs. (11) and (12) the following *visco-elastic* results

$$\sigma_* = \left(1 - \frac{1}{e}\right)K\varepsilon_* = 0.632 K\varepsilon_*, \qquad (13)$$

$$W_* = \frac{K\varepsilon_*^2}{e} = 0.368 K\varepsilon_*^2. \qquad (14)$$

An *experimental* confirmation that the fracture principle does apply to constant strain rate experiments, and an *experimental* validation of the visco-elastic result Eq. (13) constitute the necessary proof that the mechanism of fracture is indeed identical to the mechanism of visco-elastic flow, the proofs of which are shown in Sections 3 and 4.

3. Experimental proof I

We show that $\ln(t_B)$ is linear with σ_* in a constant rate of strain deformation for a set of non-identical fibers of the

Table 1
Activation energy $U^{\neq}$ and volume $V^{\neq}$ of polyethylene fibers

Reference	$U^{\neq}$ (kJ/mol)	$V^{\neq} \times 10^5$ (m³/mol)
[7]	113	1.06
[7]	117	2.42
[15]	119	1.24
[16]	110	—
This work	107	2.35
This work	107	1.92
This work	107	1.76
This work	107	1.52
This work	107	1.15
This work	107	0.93

same species. First, it is necessary to establish for a creep deformation the values of $U_c^{\neq}$ and $V_c^{\neq}$ for high strength polyethylene fibers. The literature reveals variations in both quantities, as shown in Table 1. Only the values of $V_c^{\neq}$ are problematic as it is generally thought to be structure sensitive. We made six determinations via creep at 25°C of GUR 412 polyethylene fibers prepared by gel spinning in the manner described in the following paper [11], reported in Table 1. Differing units of $V_c^{\neq}$ are converted to m³/mol. The results reported in Ref. [15] are obtained by plotting the reported data from Fig. 6 at 25°C as ln (t_B) versus σ_*. Our six determinations gave $U_c^{\neq} = 107$ kJ/mol and an average $V_c^{\neq} = 1.6 \times 10^{-5}$ m³/mol. The results of $V_c^{\neq}$ are reported here as an average simply to indicate an order of magnitude. Averaging all data in Table 1 gives $U_c^{\neq} = 110$ kJ/mol and $V_c^{\neq} = 1.59 \times 10^{-5}$ m³/mol.

Since our value $U_c^{\neq} = 107$ kJ/mol (26 kcal/mol) is certainly not the activation energy of C–C bond rupture (335 kJ/mol or 80 kcal/mol), we conclude without doubt that polyethylene fibers do not fail as a result of stress-induced bond scission as Zhurkov's idea would have it.

$U_c^{\neq}$ is instead the activation energy of visco-elastic creep or flow. We suggest that a highly crystalline, *imperfect* fiber is essentially immobile unless molecules can be activated or released into motion, however minute. This could happen if

melting occurs on a microscopic scale within a real, inhomogeneous fiber, which must have a corresponding inhomogeneous stress distribution. In this fashion microscopic melting and recrystallization follow the ever shifting overstressed zones and provide ephemeral molecular motions that eventually lead to failure. The activation energy should, therefore, be that of melting (fusion), and that is just the energy of melting, or the heat of fusion since the volume change is negligible. We know from Krausz and Eyring [12] that the kinetic unit of molten polymer flow is a sub-molecular segment of approximately 25 methylene units. At 25°C, this number should be larger. The heat of fusion of polyethylene at 25°C is 3.43 kJ/mol of CH_2 units [13]. Thus, the activation energy of 107 kJ/mol corresponds to melting 31 methylene units—a reasonable value for flow at 25°C.

If $U_c^{\neq}$ relates to slip (melting), so too must $V_c^{\neq}$. The activation volume is the volume through which a unit must pass in moving from an equilibrium position of minimum potential energy to a position of maximum potential energy that the unit must surmount and pass over in order to slip or flow. Referring to Fig. 1, the position of least potential energy is at the left, where all methylene groups are farthest apart; repulsive forces here are minimum. The configuration at the right, where the center chain is shifted horizontally by one methylene unit, bringing all units into greater conflict with neighboring chains, is of maximum potential energy because of the close proximity of non-bonded methylene units. Here, the repulsive forces are maximum. Then clearly the activation length $L_c^{\neq}$ is that of a lateral shift by the amount of a spacing of one methylene unit. Multiplying this length by the cross-sectional area A of a crystalline chain gives the activation volume $V_c^{\neq} = L_c^{\neq} A$, which is on a molar basis the molar volume of crystalline methylene units. That is, $V_c^{\neq} = 1.4 \times 10^{-5}$ m³/mol for polyethylene at 25°C. This is within 15% of the average experimental value already mentioned.

Of course, the stress causing slip or melting is that on the crystal *c*-axis, which is not necessarily the fiber stress that is actually measured. Without a homogeneous stress

U_L low energy →slip→ U_H high energy

C-C-C bond angle = 109.5°,
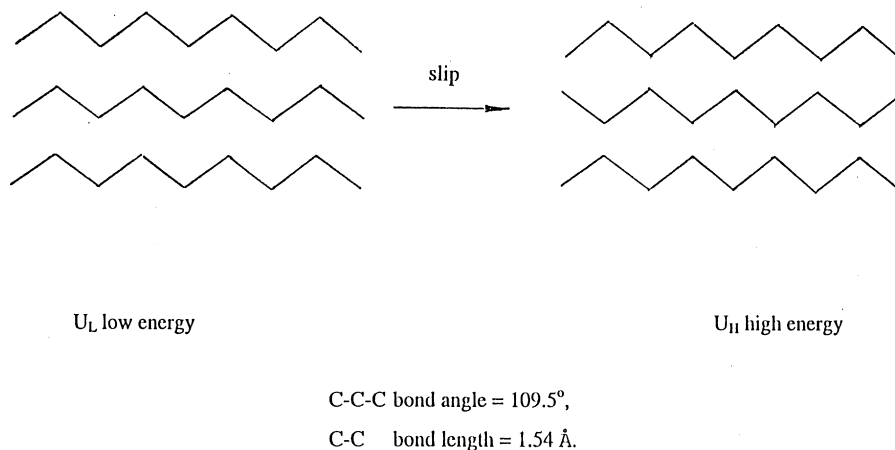
C-C   bond length = 1.54 Å.

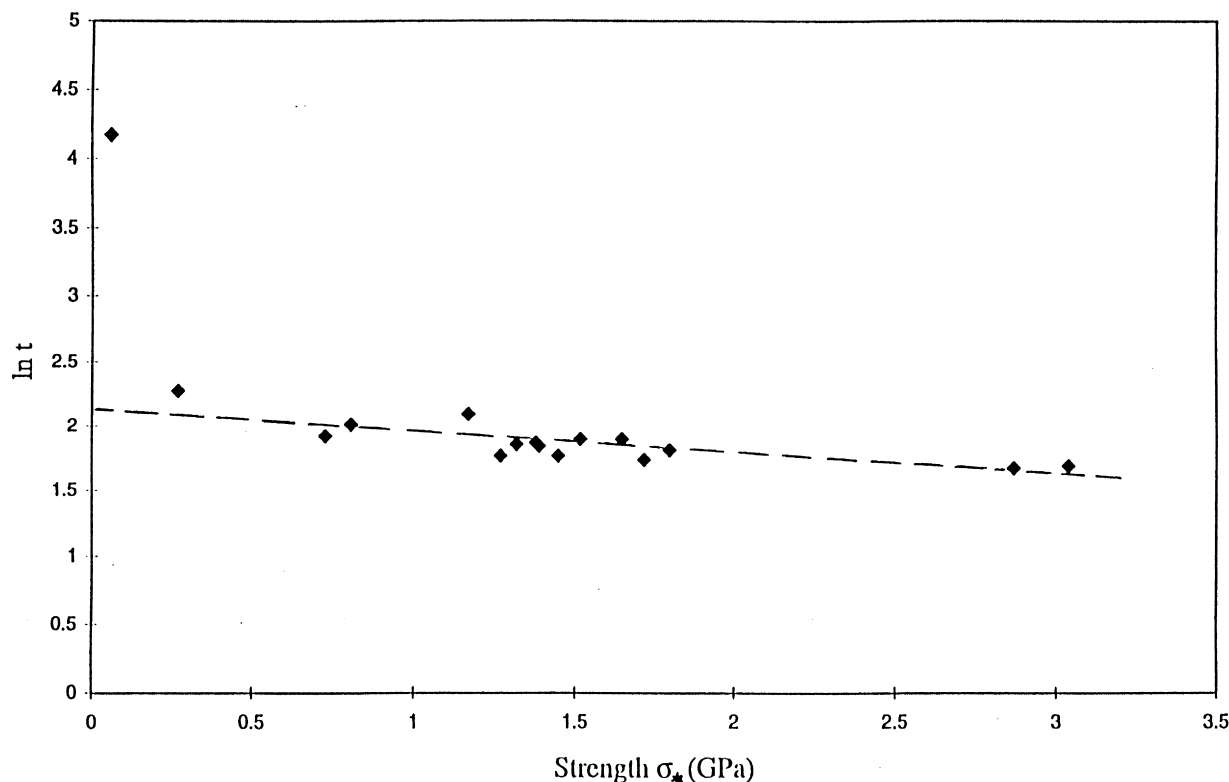Fig. 1. Schematic (not actual) diagram of polyethylene molecular slippage.

Fig. 2. Breaking time $t = t_B$ versus strength for the constant strain rate experiments of Ref. [14].

distribution the two will differ and generate an erroneous apparent activation volume $V_{app}^{\neq} = \gamma V_c^{\neq}$, where γ is a coefficient incorporating the necessary stress inhomogeneity. The apparent activation volume is also sensitive to errors in the fiber stress in an inverse fashion. If the value of the fiber stress is twice its true value because of error, the determined value of the activation volume will be one-half its true value, and vice versa. Stress error may result from calibration error, inconstant fiber cross-section along its length, surface wedges, incorrect cross-section determination, and large scale inhomogeneity within the fiber (affecting the local modulus). These errors are also included in the coefficient γ. It is, therefore, quite clear that wide, incoherent variations in activation volume should be commonly observed.

If indeed Eq. (7) applies to the constant rate of strain procedures, ln (t_B) must vary linearly with σ_*. Data in the literature for polyethylene fibers [14] are plotted in Fig. 2. Breaking time was calculated from breaking strain using Eq. (10) and $\dot{\varepsilon} = 0.011\ s^{-1}$ as reported. The result is linear, except for one point at very low stress where deviations from linearity are well known, and expected [6]. From the intercept and slope $U^{\neq} = 18.9$ kcal/mol and $V^{\neq} = 4.13 \times 10^{-7}$ m^3/mol, respectively. These values differ from those of creep experiments, but such changes are due to constraints imposed on time by a controlled rate of strain, a variable programmed into the instrument. Here we do not affix the

subscript c to $U^{\neq}$, $V^{\neq}$ in order to distinguish them from the corresponding creep values $U_c^{\neq}$, $V_c^{\neq}$.

In creep, the rate of strain $\dot{\varepsilon}_c*$ is obtained from the time derivative of Eq. (8):

$$\dot{\varepsilon}_c* = \frac{\sigma_*}{\tau_c K}\left(1 + \frac{1}{e}\right)$$

which upon combination with Eq. (11), for constant strain rate $\dot{\varepsilon} = \dot{\varepsilon}*$ gives for the ratio of breaking times (or retardation times) at the same stress and modulus:

$$\frac{\tau_c}{\tau} = \left(1 - \frac{1}{e^2}\right)\frac{\dot{\varepsilon}}{\dot{\varepsilon}_c*}.$$

The equation shows clearly that the time ratio is determined solely by strain-rate ratio.

Now, applying Eq. (7) to both experimental conditions, creep and constant strain rate, we have in the limit $\sigma_* \to 0$

$$\frac{\tau_c^0}{\tau^0} = \exp\left[\frac{(U_c^{\neq} - U^{\neq})}{RT}\right]$$

or

$$U_c^{\neq} = U^{\neq} + RT\ln(\tau_c^0/\tau^0), \tag{15}$$

where the superscript 0 indicates zero breaking stress. As τ^0 (or τ) is determined by the strain rate $\dot{\varepsilon}*$, Eq. (15) reveals how $U^{\neq}$ is related to $\dot{\varepsilon}*$. If $\dot{\varepsilon}*$ is increased, τ (and τ^0) must
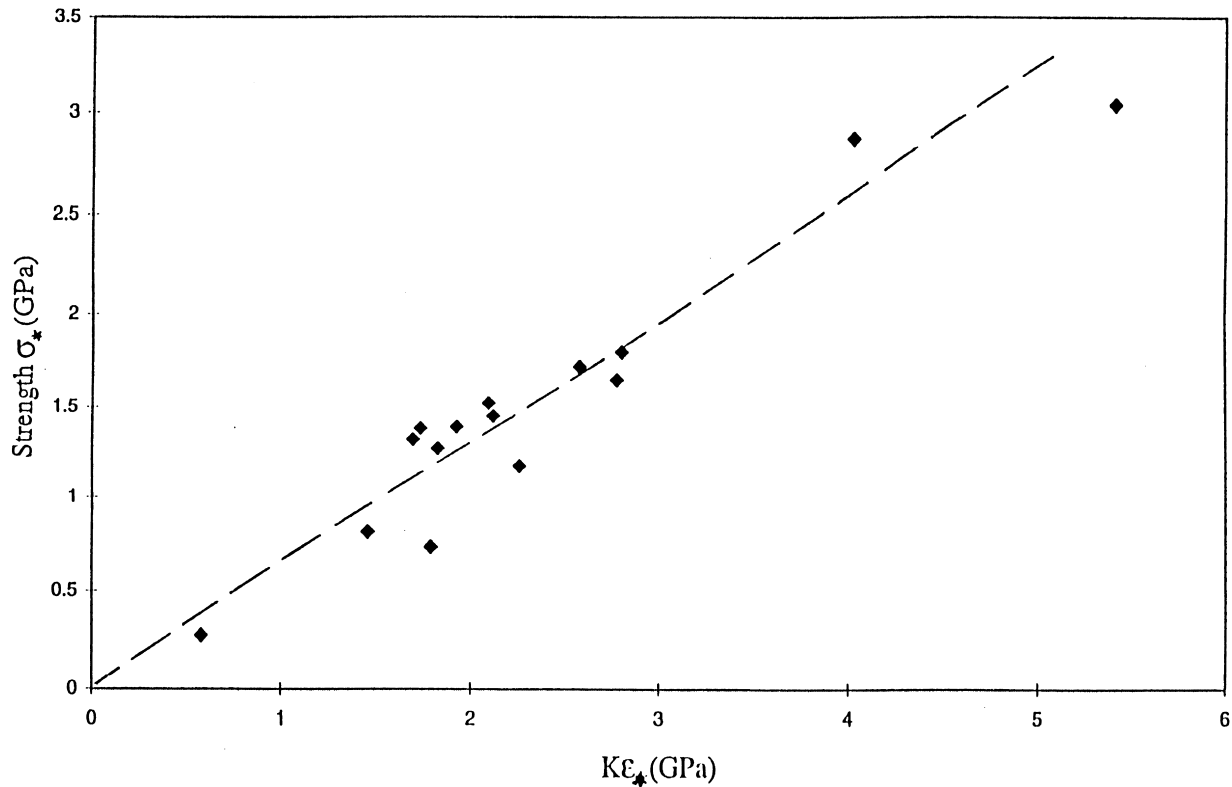
Fig. 3. Strength σ_* versus $K\varepsilon_*$ for the data in Ref. [14].

decrease. That is, a greater rate of strain must decrease the time to break, and therefore, $U^{\neq}$ must decrease also. Note that τ^0 for a set of *identical* strain rate experiments represents the following condition:

$$\sigma_* \propto (\omega K_i)^{1/2} \to 0$$

which requires a set of *non-identical* fibers. In this situation the breaking stress σ_* cannot be arbitrarily chosen for *identical* fibers, in contrast to creep. Identical fibers stretched at the same constant rate (machine driven) break at the same stress.

To find a corresponding relationship between $V^{\neq}$ and $V_c^{\neq}$, we focus on the point where breaking times and breaking stresses are equal in the two experiments; i.e. $\tau_c \equiv \tau, \sigma_*^c \equiv \sigma_*$. Using these conditions and Eq. (7) for both experiments, we have

$$\frac{\tau^0}{\tau_c^0} e^{-\frac{\sigma_*}{RT}(V^{\neq}-V_c^{\neq})} \equiv 1$$

or

$$V_c^{\neq} = V^{\neq} + \frac{RT}{\sigma_*} \ln(\tau_c^0/\tau^0). \tag{16}$$

Substitution of Eq. (15) into Eq. (16) gives

$$U^{\neq} - \sigma_* V^{\neq} = U_c^{\neq} - \sigma_* V_c^{\neq}. \tag{17}$$

In Eq. (16) and (17), the stress σ_* is not general but the specific stress at which $\tau_c = \tau$.

4. Experimental proof II

It remains to prove Eq. (13). For this we use the same data from the literature [14], plotted in Fig. 3 as σ_* versus $K\varepsilon_*$. The experimental slope is 0.64, compared to the theoretical value of 0.632—about 2% difference. The clear linearity of the plot validates our identification of breaking time with a visco-elastic relaxation time, and the close agreement of the experimental slope with our theoretical value (0.632) appears to justify our consideration of a single relaxation time rather than a relaxation spectrum. A spectrum is probably not required for crystals, for which we expect a nearly monodisperse distribution. At any rate this question is to be answered by experimentation and causes no problem of serious consequence. The figure supports a single relaxation time. This completes our proof that the mechanism of fracture is identical to the mechanism of visco-elastic flow. Additional experimental proof appears in the following paper [11].

5. The Imperfect fiber

Returning to the imperfect fiber, as represented by the approximations, Eqs. (4)–(6), we now consider a means to convert the approximations into equivalencies nearly on par with the perfect fiber represented by Eqs. (1)–(3). This requires that Eqs. (4)–(6) be constrained to the reversibility requirement of equilibrium thermodynamics upon which the
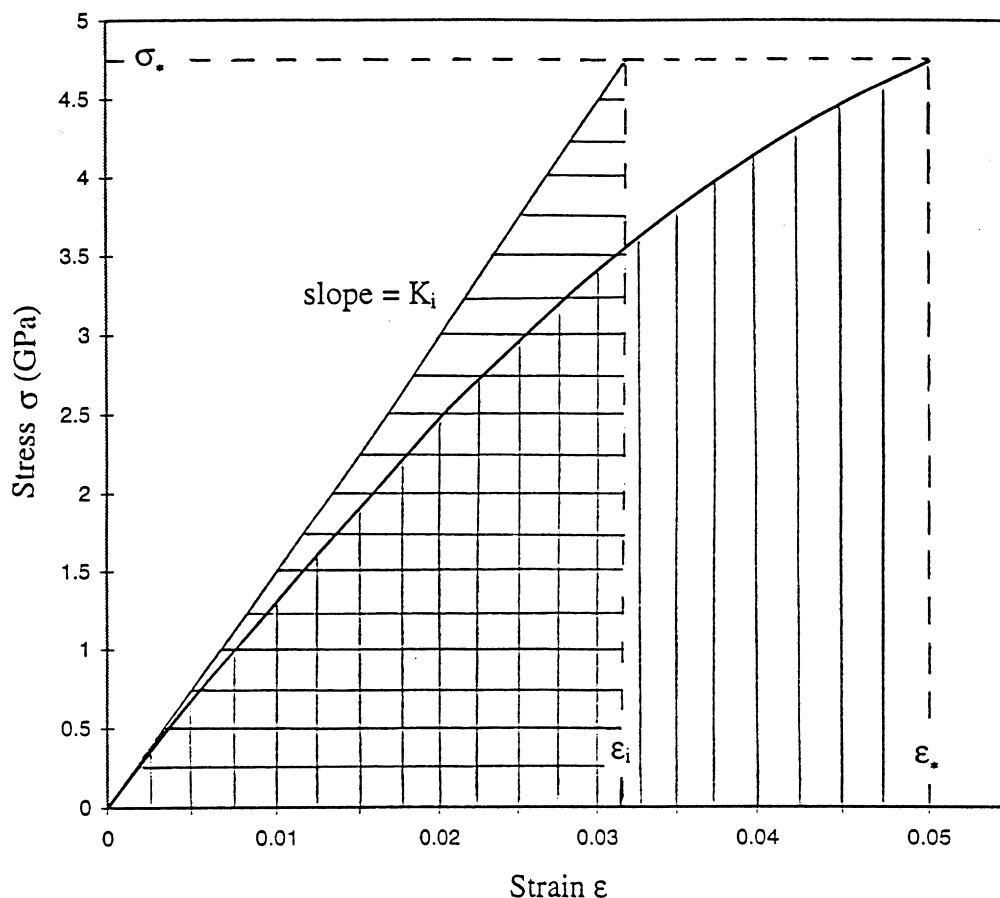
Fig. 4. Theoretical behavior of stress versus strain for a constant strain rate process, Eq. (1). $t_B = \tau = 5$ s, $K_i = 150$ GPa, $\varepsilon = 0.01$ s^{-1}, $\sigma_* = 4.74$ GPa. Shaded areas are defined in text, Eqs. (20) and (21).

fusion theory of fracture is founded. Note that Eqs. (4)–(6) actually represent, and correctly so, a *perfect* fiber of modulus K'', heat of fusion $\Delta H_v'' \approx \omega \Delta H_v$, and melting temperature T_o, just as rigorously as Eqs. (1)–(3) represent a *perfect* fiber of modulus K_c, heat of fusion ΔH_v, and melting temperature T_o. Recognizing this, we simply define an *equivalent perfect* fiber—i.e. an *equivalent perfect* crystal—that has the same modulus, heat of fusion, and melting point as the real, imperfect fiber. The modulus is the *initial* modulus of the imperfect fiber. Further, we require the load on the equivalent fiber to be the same at all times as that on the real fiber. Consistent with the Hookean elastic behavior incorporated into the fusion theory, the equivalent perfect fiber must be reversibly Hookean also. The various properties of the equivalent fiber are denoted by the subscript i. Thus, Eqs. (4)–(6) are relevant to the properties K_i, ΔH_i, ε_i (Hookean strain), and T_i, all of which represent equivalent equilibrium, reversible components of the real visco-elastic fiber. The equivalent fiber is simply the elastic component of the real fiber absent the viscous, kinetic component.

Properties of the real fiber and its equivalent fiber are shown in Fig. 4. Young's modulus, K_i, is the initial slope of the stress–strain curve. Work of rupture of the equivalent fiber, W_i, is less than that of the imperfect fiber, W_*. So too is

the strain at break, $\varepsilon_i < \varepsilon_*$. For the relationships between the real and equivalent fibers, we have:

$$\sigma_* = K_i \varepsilon_i = \left(1 - \frac{1}{e}\right) K_i \varepsilon_*, \tag{18}$$

$$\varepsilon_i = \left(1 - \frac{1}{e}\right)\varepsilon_*, \tag{19}$$

$$W_* = \frac{K_i \varepsilon_*^2}{e} = \left[\frac{2e}{(e-1)^2}\right] W_i = \text{Area (||||) in Fig. 4}, \tag{20}$$

$$W_i = \frac{\sigma_*^2}{2K_i} = \frac{K_i \varepsilon_i^2}{2} = \frac{\sigma_* \varepsilon_i}{2} = \text{Area (≡) in Fig.4}. \tag{21}$$

The corresponding thermodynamic equations pertaining to the equivalent fiber are

$$\sigma_i = \sigma_* = [2K_i W_i]^{1/2}, \tag{22}$$

$$\varepsilon_i = [2W_i/K_i]^{1/2}, \tag{23}$$

$$\varepsilon_* = \left(\frac{e}{e-1}\right)[2W_i/K_i]^{1/2}, \tag{24}$$

$$W_i = \Delta H_i(1 - T/T_i). \tag{25}$$

These two sets, Eqs. (18)–(21) and Eqs. (22)–(25), appropriately combine the kinetic and thermodynamic features of fracture of polymer crystalline fibers (of finite molecular weight polymers).

For highly crystalline fibers (nearly perfect), a good approximation is to let $\Delta H_i \approx \omega\Delta H_v$ and $T_i \approx T_o$, so that

$$W_i \approx \omega\Delta H_v(1 - T/T_o). \tag{26}$$

The preceding equations then become identical to Eqs. (4)–(6), with the exception of Eq. (6) which must be replaced by Eq. (24). The breaking strain given by Eq. (6), now seen to be incorrectly labeled ε_*, is in fact the breaking strain ε_i of the equivalent fiber, Eq. (23), and the breaking strain ε_* of the real fiber is now seen to be that of Eq. (24).

As crystallinity progressively decreases, we expect the divergence $T_i < T_o$ in conformity with experimental observations. Another source of error is associated with the work W_i. Eqs. (25) and (26) contain the approximation that the heat of fusion is independent of temperature [5]. The effect of this approximation is to overstate the value of W_i by perhaps several percent, whereas its true value must be $W_i < \omega\Delta H_v(1 - T/T_o)$.

The foregoing equations for the imperfect fiber are experimentally analyzed and verified in the following paper [11].

6. Discussion

Differences between the imperfect and perfect fibers are several: crystallization, order, orientation, extensibility, modulus, strength, reversibility, etc. The perfect fiber, which is completely crystalline, therefore perfectly oriented, is thermodynamically uncomplicated because its perfect fibrilliform crystal structure is both uniform and elastically reversible. Molecular weight of its constituent polymer is large but finite. Because the perfect fiber is devoid of all defects, surface and interior, its work of failure must be determined by the tensile work required to induce melting provided a failure mechanism of lower work is not available. Ultra-stable infusible substances such as graphite, which is a rigid two-dimensional platelet crystal, may be infusible under any load at room temperature. But most linear crystalline polymers should qualify for the fusion mechanism. For these materials the reversible work of fusion (failure) is an invariant characterization constant at a specified T, P. So too is the modulus, ultimate strength and strain.

The definition of the perfect fiber is not arbitrary and cannot be changed whimsically to suit an individual fancy. The concept refers to an actual real linear crystalline polymer in hand and takes into account any and all of its thermodynamical characteristics. Tacticity is an example. Molecular weight is another, at least in principle. But in practice molecular weight is of no consequence for the perfect fiber, especially high molecular weight. In the realm of high, but finite, molecular weight, fiber (crystal) thermodynamics are essentially independent of variations in the small number of molecular end units; melting temperature, heat and entropy of fusion, and fiber modulus are not affected. Neither does molecular weight distribution matter for the perfect fiber. Nowhere in the fusion theory do these factors appear [1,5].

The perfect fiber is an *ideal* fiber; its thermodynamic state is a reference state, or a standard state of unit activity at standard temperature and pressure. *Ideal* refers to the ultimate standard of fiber perfection for the material in question. *Perfect* and *ideal* are interchangeable terms.

The perfect fiber cannot be prepared via existing spinning technology. Real fibers of real polymers—always of large but finite molecular weight—are imperfect, never ideal. The extent of imperfection depends upon polymer molecular weight and distribution, and various details of the specific preparation process, which significantly modify properties such as strength, modulus, work, and reversibility. Since the only unique definitive state of a polymer fiber is its ideal (perfect) state, completely described by state variables temperature and pressure, a real (imperfect) fiber might be considered (and analyzed) as a variation or deviation from its ideal state. In this view, fibers of few imperfections (i.e. nearly perfect fibers) are more accurately represented than those with major imperfections; fibers of high crystallinity and ultra-high draw ratios are best. At the other extreme major difficulties should be anticipated.

Real (imperfect) fibers are partially crystalline and visco-elastic (mechanically irreversible). An *equivalent* fiber is introduced to account partially for these difficulties. The *equivalent* fiber is defined as a reversible, Hookean fiber that behaves as a perfect fiber possessing the same bulk thermodynamic properties as the actual fiber. Its modulus is that of the initial Young's modulus of the real fiber, K_i, and its strength is the same as the real fiber's, which by Eqs. (22) and (26) is

$$\sigma_* \approx [2\omega K_i W_c]^{1/2}. \tag{27}$$

The work of failure of the *perfect* fiber is W_c and that of the *equivalent* fiber is $W_i \approx \omega W_c$. Because strength is proportional to $(\omega K_i)^{1/2}$, Eq. (27), some facets of imperfection—crystallinity, morphology, draw ratio, orientation, molecular weight and molecular weight distribution, etc.—are incorporated into the values of ω and K_i to a first approximation. Ideally, the variation of σ_* with the product $(\omega K_i)^{1/2}$ represents a master line of slope $(2W_c)^{1/2}$ and intercept of $\sigma_* = \sigma_c = (2K_cW_c)^{1/2}$ at the position $\omega = 1$ (i.e. $\omega K_i \to K_c$). All fibers of a kind should scatter along and about this master line, with nearly perfect fibers collecting into the high strength region. But the equivalent fiber is

merely an approximation of a nearly perfect fiber. Its validity and usefulness might be questioned as crystallinity and orientation progressively decrease—i.e. as ωK_i decreases. In such cases we should expect $\sigma_* < [2\omega K_i W_c]^{1/2}$. Thus, at high ωK_i the strength σ_* is better represented by Eq. (27) than at smaller ωK_i. The line drawn from the origin through the high points, $(\omega K_i)^{1/2}$; of nearly perfect fibers should supply a good approximation of W_c via the slope. This line, therefore, is not strictly a master line for all fibers of a kind, but only so for high strength nearly perfect fibers, whose points fall along and about the line at the high end and below the line at the low end where the equivalent fiber concept fails.

A series of fibers of various strengths, moduli, and crystallinities may be plotted in accordance with Eq. (27) to determine from the slope an experimental value of W_c for the perfect fiber. As W_c may be independently calculated, essentially a priori, with the fusion theory [5], a direct means of validation or refutation of the theory is readily available. If the value of W_c is known, we require only σ_c or K_c or ε_c to characterize the perfect fiber completely. For example, the value of σ_c might be found by extrapolation of strength σ_* versus ω to $\omega = 1$. This procedure is perfectly valid since a *fiber* of 100% crystallization can be nothing but a perfect fiber. How else can complete crystallization of a fiber exist?

It is necessary to emphasize that the equivalent fiber is not real, but only hypothetical and imaginary, an artifice constructed to circumvent detailed morphological depictions of actual real fibers that generally are impossible to detail with satisfactory accuracy. In the limit of nearly perfect fibers, deviating but slightly from the perfect, the artifice should be satisfactory. However, for usual fibers (roughly 50% crystallization and draw ratios of about 1 to 5 or 6) of say nylon, polyester, etc., only qualitative accuracy, or a little better, should be expected. This is because deformational work of non-crystalline regions within the fiber is omitted from our theory. If crystallinity and orientation are high, this omission should not be serious. If orientation (i.e. draw ratio) is low, fiber morphology changes during failure tests (cold drawing), which is not included in the theory. An undrawn polyethylene fiber spun from dilute solution, after drying can be drawn by a factor of 100 or more.

Drawing, cold and hot, enhances the mechanical properties of polymer fibers. Both modulus and strength are increased by drawing. The modulus is influenced by the degree of crystallization, which converts a portion of the soft, pliable amorphous polymer into strong, rigid, inextensible high modulus crystalline regions. The greater the crystallization, the greater the fiber modulus. Fiber morphology also affects the modulus; a higher proportion of, effectively, parallel crystalline-amorphous coupling translates into a higher fiber modulus. Thus, K_i (or K^I) reflects both the degree of crystallization and fiber morphology. As a rough, but useful generalization, we can say that for a given fiber morphology, greater crystallization produces a greater modulus, for the simple reason that soft pliable regions in the fiber are replaced by hard, inextensible crystalline zones; and that at constant crystallization, higher draw ratios rearrange the fiber morphology to produce higher moduli—both crystalline and amorphous regions are affected by drawing. Hence, the fusion theory of strength correlates strength with ω (crystallization) and K_i (morphology and crystallization).

The degree of crystallization ω determines the heat requirement for melting, or the mechanical work of failure. By the fusion theory of strength, melting corresponds to fiber failure. Solid, hard crystalline zones are converted into a soft, liquid-like melt devoid of dimensional stability. It is tempting to consider molecular slippage in amorphous areas to be a cause of failure, since amorphous slippage must involve less energy than fusion. But this cannot be correct. Which molecules slip? And where do they slip to? In a real fiber, crystallites are connected to one another by amorphous tie chains that also participate in the crystalline regions. They are all the same molecules, except for a few dangling, unconnected, molecular end chains. Without this molecular continuation through crystal–amorphous–crystal regions there can be no fiber at all. This connectivity provides necessary dimensional stability. A tensile force on the fiber cannot produce amorphous slippage and cause rupture: there is no place to slip to if both ends of the tie molecules are firmly embedded in crystallites. But the tie molecules transmit forces to the crystallites that, if sufficient, cause melting, consequent overall molecular slippage, and recrystallization with or without fiber rupture.

An important principle established by this work is the condition of fracture $t_B \rightarrow \tau$, where τ is a visco-elastic retardation/relaxation time. This principle requires that failure stress σ_* be proportional to the product of initial modulus K_i and failure strain ε_*. For the simple visco-elastic models used herein the proportionality constant is 0.613 for creep and 0.632 for constant strain-rate deformations. More complex models as well as a possible retardation/relaxation spectrum may refine these numbers. The principle aids in the analysis of fibers and in the construction of the equivalent fiber required for a thermodynamic analysis of failure. But the equivalent fiber can be constructed with or without the fracture principle. It stands firm in its own right regardless of activation energies and volumes. So too is the fusion theory of imperfect fibers independent of such factors.

Acknowledgements

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