

Statistics and Microphysics of the Fracture of Glass

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Abstract

The tensile strength of fused silica fibers is believed to approach its intrinsic value at low temperature, and modern experiments indicate very small, perhaps unmeasured, intrinsic dispersion in this strength. I consider the application of classical “weakest link” models to this problem in an attempt to determine the number and therefore the nature of the failure sites. If the skewness as well as the dispersion (Weibull modulus) of failure strengths are measured it may be possible to determine both the number of sites and the distribution of their strengths. Extant data are not sufficient, but I present calculated skewnesses for comparison with future data.

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I INTRODUCTION

Fused silica optical fiber is one of very few materials whose tensile strength, measured at low temperature (77°K), is believed to equal its theoretical limiting strength^{1,2}. Failure occurs at strains of about 0.2, extraordinarily large for a brittle material, but consistent with the idea that its strength is limited only by the strength of its constituent molecular bonds. In addition, it fails under accurately reproducible loads, which is very unusual for a brittle material. These properties may be explained by the absence, in properly prepared samples, of surface cracks which would concentrate stress.

The remarkable properties of glass fiber, if carefully manufactured and protected from abrasion by a soft coating, have been recognized for several decades^{3,4}. Most research has been concerned with the fracture of glass under tension at temperatures comparable to room temperature, at which it is subject to chemical attack by water vapor or liquid and shows static fatigue⁵. However, at temperatures around 77°K activation barriers are believed to reduce the rate of chemical attack to a negligible level, and the ultimate material strength may be observed.

The results of early experiments⁴ at 78°K found scattered tensile strengths of up to 130 Kbar. Later experiments⁶ on fused silica measured tensile strengths as high as 150 Kbar, but also showed substantial scatter; these authors found no evidence for a significant difference between the strength measured at 77°K and that at 4°K. More recent experiments^{7,8} on fused silica at 77°K reported very little scatter and inferred a limiting tensile strain in the range 0.18–0.21; using the zero-stress value of Young’s modulus this implies a limiting stress of ≈ 140 Kbar.

Despite the internal consistency of the data^{7,8} the absolute strain at failure is not known quantitatively, because this experiment used a two-point bending apparatus, whose analysis depends on a theory which assumes a slender fiber, small strain, and linear stress-strain relation, none of which are quantitatively valid at these values of strain.

Silica-based glasses with compositions other than pure SiO₂ qualitatively resemble

fused silica, but are typically somewhat weaker⁹. At higher temperatures chemical attack makes the strength of glass depend on the temperature, chemical environment (humidity and pH), and the duration of loading (static fatigue is evident), and measured tensile strengths are typically a factor of three less than at 77°K^{4–13}.

The reproducibility of measurements of strength is usually described by the Weibull modulus^{14,15} m ; the fractional dispersion in measurements of failure load is $\approx [m(m - 1)]^{-1/2}$. Most engineering ceramics¹⁵ have $m \approx 10$, and glass with surfaces abraded deliberately or by ordinary handling¹⁶ has m in the range 3–7. Measured^{7–11,13} Weibull moduli for modern fused silica optical communications fiber are in the range 30–100, both at low temperatures and around room temperature. It has been argued¹⁷ that even this small apparent dispersion is the consequence of dispersion in fiber diameter (and hence in stress at a given applied force) rather than intrinsic variation in the properties of the glass.

The distribution of failure stresses may contain useful information about the mechanism of failure. For example, brittle materials, including glass, with abraded or damaged surfaces have empirical tensile strengths far below their ideal strengths. They also have small Weibull moduli. These facts are the consequence of stress concentration at flaws³, usually surface scratches; the inevitable variation from sample to sample in the size and shape of these flaws produces variation in measured sample strength and gives a small Weibull modulus.

Even the best glass fibers should show some level of sample-to-sample variation. Because glass is amorphous its chemical bonds are each in a subtly different environment, and some should be weaker, or strained more by a macroscopic strain field, than others. In addition, real silica glass is not perfectly pure SiO₂ (or Si_{*x*}Ge_{1–*x*}O₂ in an optical fiber), but contains chemical impurities which may locally weaken it.

The purpose of this paper is to develop simple statistical models of the dependence of the distribution of failure strengths on the number of independent elements N whose weakest member initiates failure. If the distribution of material strength is measured, and

the basic parameters of the model are known, it will then be possible to estimate N . The value of N constrains the nature of the sites at which failure is initiated: if N is comparable to the number of atoms in the sample these must be ordinary Si—O bonds; if N is of order the number of transition metal impurity atoms then these are implicated, while a small N (in the range 10 – 10^4 , for example) would implicate macroscopic flaws or heterogeneities, such as the surface scratches of inclusions which are responsible for the low strength and low Weibull modulus of ordinary glass. In the case of room-temperature failure, surface sites for chemical attack also need be considered.

Statistical “weakest link” theories of fracture are not new^{18,19}. What is new, since the foundations of this subject were laid, is the development of optical communications fiber as a mass produced material whose strength, at least at low temperature, approaches its ideal value because macroscopic samples may be *completely* free of stress-concentrating flaws of greater than atomic size. Hence its fracture statistics contain information about the microphysics of its ideal strength.

II DISPERSION OF FAILURE STRESS

In “weakest link” failure models a sample is assumed to consist of N sites, or links, each of which is described by a fracture readiness parameter α , which may be considered a stress concentration factor, or the reciprocal of a link’s ideal strength. The values of α are distributed according to a distribution $f(\alpha)$, which is defined for $\alpha > 0$ and normalized

$$\int_0^\infty f(\alpha') d\alpha' = 1. \tag{1}$$

The sample fails if the largest fracture readiness parameter found among the N sites, α_{max} , exceeds a value α_0 . The probability that it does not fail is, to good approximation if $N \gg 1$,

$$\mathcal{P}(\alpha_0) \approx \exp\left(-\int_{\alpha_0}^\infty N f(\alpha') d\alpha'\right). \tag{2}$$

The probability that failure occurs for a value of α_0 between α and $\alpha + d\alpha$ is $P(\alpha) d\alpha$, where

$$P(\alpha) = Nf(\alpha) \exp\left(-\int_{\alpha}^{\infty} Nf(\alpha') d\alpha'\right). \quad (3)$$

Unfortunately, we have no *a priori* knowledge of the functional form of $f(\alpha)$. I therefore consider several possible forms. The most useful way to parametrize the results is as the ratio of the width w of $P(\alpha)$ to the value α_{max} at which $P(\alpha)$ is a maximum; in terms of the Weibull modulus

$$\frac{w}{\alpha_{max}} \approx \frac{1}{[m(m-1)]^{1/2}}, \quad (4)$$

and the approximation is almost exact if w is defined as the dispersion of $P(\alpha)$

$$w \equiv \left(\left| \frac{d^2 \ln P(\alpha)}{d\alpha^2} \right|_{\alpha=\alpha_{max}} \right)^{-1/2} \quad (5)$$

and $m \gg 1$.

A “boxcar distribution” is defined

$$f(\alpha) = \begin{cases} 1/\alpha_b, & \text{if } 0 \leq \alpha \leq \alpha_b; \\ 0, & \text{if } \alpha > \alpha_b. \end{cases} \quad (6)$$

Here $\alpha_{max} = \alpha_b$. The full width at half maximum of $P(\alpha)$ $w' = \alpha_{max} \ln 2/N$ and the fractional width is

$$\frac{w'}{\alpha_{max}} = \frac{\ln 2}{N}. \quad (7)$$

This distribution implies unmeasurably small m , but is unrealistic *a priori* (why should the distribution of fracture readiness drop discontinuously from a constant value to zero?). It also disagrees with available data⁷⁻⁹ on glass at low temperatures where its intrinsic strength appears to be achieved (as well as with all other data on brittle materials).

An exponential distribution is defined

$$f(\alpha) = \frac{1}{\alpha_0} \exp(-\alpha/\alpha_0). \quad (8)$$

Then

$$\frac{w}{\alpha_{max}} = \frac{1}{\ln N}. \quad (9)$$

If $f(\alpha)$ is exponential then a useful estimate of N may be possible because w/α_{max} should be measurable and is sensitive enough to N to constrain it significantly.

A power law distribution with $p > 1$ is defined

$$f(\alpha) = \begin{cases} (p-1)\alpha_0^{p-1}\alpha^{-p}, & \text{if } 0 < \alpha_0 \leq \alpha; \\ 0. & \text{if } \alpha < \alpha_0, \end{cases} \quad (10)$$

Then

$$\frac{w}{\alpha_{max}} = \frac{1}{[p(p-1)]^{1/2}}. \quad (11)$$

The power law exponent p equals the Weibull modulus m and is independent of N . If $f(\alpha)$ is a power law then measurements of m provide no information about N . This is implausible (as well as disappointing) because the very large reported values of m would imply implausibly steep distributions of α .

A Gaussian distribution is defined

$$f(\alpha) = \frac{2}{\alpha_0\pi^{1/2}} \exp \left[- \left(\frac{\alpha}{\alpha_0} \right)^2 \right]. \quad (12)$$

For this distribution α_{max} and w are found by successive approximation. The result is

$$\begin{aligned} \frac{w}{\alpha_{max}} &\approx \left\{ 2 \left[1 + 2 \ln N' \left(1 - \frac{\ln \ln N'}{2 \ln N'} \right)^{1/2} \right] \left(\ln N' - \frac{1}{2} \ln \ln N' \right) \right\}^{-1/2} \\ &\approx \frac{1}{2 \ln N'}, \end{aligned} \quad (13)$$

where $N' \equiv N/\pi^{1/2}$ and the simple approximation in the second line of Eq. 13 is usually accurate to better than 10%. $P(\alpha)$ is shown in Fig. 1 for several values of N of interest.

The stretched exponential function is defined

$$f(\alpha) = \frac{C(\nu)}{\alpha_0} \exp \left[- \left(\frac{\alpha}{\alpha_0} \right)^\nu \right]. \quad (14)$$

This is a general form widely used when the actual functional form is unknown, and includes the simple exponential and Gaussian as special cases. The normalizing constant $C(\nu) \equiv \nu/\Gamma(1/\nu)$ and $N' \equiv NC(\nu)/\nu$. By successive approximations

$$\begin{aligned} \frac{w}{\alpha_{max}} &\approx \frac{\left\{1 - \frac{1}{2 \ln N'} \left[\frac{\nu-1}{\nu} - \left(\frac{\nu-1}{\nu} \right)^2 \ln \ln N' \right] \right\}}{\nu \ln N' \left(1 - \frac{\nu-1}{\nu} \frac{\ln \ln N'}{\ln N'}\right)^{1/\nu}} \\ &\approx \frac{1}{\nu \ln N'}. \end{aligned} \quad (15)$$

It is evident that if $f(\alpha)$ is, or can be fitted to, a stretched exponential or to one of its special cases useful and plausible estimates of $N \approx \exp(\alpha_{max}/(w\nu))$ may be obtained. However, the inferred value of N depends very sensitively on ν , and measurement of m alone for a sample of test objects of a single size does not determine ν . Measurement of two or more populations of very different-sized test objects of the same material (for which N is proportional to the size) may determine both N and ν , and may be feasible; for example, in two-point bending experiments⁷⁻⁹ on optical fiber of 125μ diameter the number of atoms N_a at significant risk of initiating fracture (the fraction with stresses within about $1/m$ of the maximum, which are found only close to the outside of the sharpest part of the bend) is $N_a \approx 5 \times 10^{14}$, while in tensile loading of a 50 m gauge length¹⁰ of fiber $N_a \approx 4 \times 10^{22}$ atoms are uniformly stressed. Two or more measurements of m in which very different numbers of atoms are stressed permit simultaneous determination of both the ratio N/N_a and ν , although no extant data serve the purpose.

III SKEWNESS

A possible method of determining ν , and hence N , is to measure the skewness of $P(\alpha)$:

$$s \equiv \frac{\int_0^\infty (\alpha - \alpha_{max})^3 P(\alpha) d\alpha}{w^3 \int_0^\infty P(\alpha) d\alpha}. \quad (16)$$

The skewness is not small; see Fig. 1. It is also not readily estimated analytically because the Taylor expansion of $P(\alpha)$ about α_{max} does not converge sufficiently rapidly, but it may

be calculated numerically. Values of the skewness, as a function of ν and N , are shown in Fig. 2.

The values plotted were computed using cutoffs on the integrals of $\pm 5w$ from α_{max} , with w defined self-consistently using the same cutoff. The reason for this is that $P(\alpha)$ has a long tail toward increasing α which contributes significantly to the skewness, but which is unlikely to be observed in a real experiment with a reasonable number of samples because there will probably be no samples that far out in the tail. The skewness computed without this cutoff is significantly larger, typically by $O(10\%)$.

When comparing experimental data to Fig. 2 a similar cutoff must be applied to the data. This will, in addition, exclude samples which are anomalously weak because of mechanical damage or other gross flaws, which otherwise must be excluded *ad hoc*. If the number of measurements is not large it may be necessary to choose a narrower cutoff, and to recompute Fig. 2 accordingly.

IV DISCUSSION

It is generally assumed that the observed strength of pristine glass fibers at low temperatures (and possibly also at higher temperatures in an inert environment) is the intrinsic strength of the material. However, this has not been proved, and may not be so. For example, the strength could be limited by the presence of trace impurities, in which case their reduction or elimination would increase the strength.

The actual intrinsic strength (or, equivalently, the limiting strain at failure) of fused silica is not accurately known. As discussed above, obtaining the intrinsic strength from two-point bending experiments⁷⁻⁹ requires use of the nonlinear stress-strain relation, which is not known to the required strain level, in a three-dimensional elastostatic calculation. Nonlinear stress-strain data^{4,20} extend up to strains of about 0.16, but show the Young's modulus still increasing with strain. This sense of nonlinearity is the same as that found for rubbery elastomers, in which polymer chains are easily straightened at small stress,

but which become much stiffer when stretched to their full length; the analogous effect in silica glass involves the comparatively soft bending of the O—Si—O bond angles towards 180° , followed by the greater resistance of the bonds to extension. However, in elementary models²¹ of zero temperature ideal strength the effective Young's modulus must decrease to zero at the point of failure, which corresponds to the inflection point of the interatomic potential; there is as yet no sign of this decrease in the data. This is qualitatively consistent with the reported^{7,8} limiting strains of 0.18–0.21, but the uncertainty of this value and the lack of modern data on the stress-strain relation at high strain call for further experiments.

It should be considered whether the observed reduction in strength of optical fiber at room temperature may in part be the consequence of thermal excitation, reducing the mechanical work required to disrupt a bond. In order of magnitude this is plausible: the greatest reduction in required mechanical work per bond is $\approx k_B T \ln N_t \approx 80k_B T$, where the number of trials of bonds $N_t \approx N_b t / \omega$, where N_b is the number of bonds in the sample, t the duration of the experiment and ω a typical vibration (or vibrational relaxation) frequency. Evaluating at room temperature and dividing by the volume per bond yields a reduction in limiting stress ≈ 100 Kbar, approximately equal to the measured reduction in failure stress between 77°K and room temperature. However, a proper evaluation of thermally assisted fracture takes the form of nucleation theory²², which predicts a temperature dependence of the strength quite different from the available data⁶ (only vacuum data are relevant). In addition, spontaneous thermal nucleation of fracture is not characterized by a waiting time. Such a waiting time is observed^{9,11,12} in experiments in hostile chemical environments, but it is not known if there is a waiting time in an inert environment.

Most of the extant data on the failure of glass fibers were obtained in warm humid or wet environments in which glass is subject to corrosion by water. Neither the methods of this paper nor nucleation theory are directly applicable to failure by stress corrosion, but these data do show large (typically in the range 30–100) Weibull moduli. It may be that a modified version of weakest link theories, in which the parameter α represents reactivity

rather than stress concentration or mechanical bond strength, may be applicable. In that case the inferred value of N would provide information about the number and kind of surface sites vulnerable to chemical attack.

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Figure Captions

Figure 1: Distribution $P(\alpha)$, normalized to $P(\alpha_{max})$, as a function of $(\alpha - \alpha_{max})/w$ for a Gaussian $f(\alpha)$. The solid curve is for $N = 10^2$, short dashed curve for $N = 10^5$ and long dashed curve for $N = 10^{20}$ ($N = 10^{15}$ is indistinguishable from $N = 10^{20}$ at the resolution of the figure, but these values may be distinguished by their different values of w/α_{max} and predicted m). The substantial skewness is evident.

Figure 2: Contour graph of calculates skewness of $P(\alpha)$ as a function of ν and N . Integrations (to calculate both skewness and dispersion) were self-consistently truncated at $|\alpha - \alpha_{max}| = 5w$.