Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Non-Crystalline Solids 316 (2003) 114–124

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Section 5. Fibers

The intrinsic strength and fatigue of oxide glasses

C.R. Kurkjian [a], P.K. Gupta [b,*], R.K. Brow [c], N. Lower [c]

[a] Rutgers University, Piscataway, NJ 08854, USA
[b] Department of Material Science and Engineering, The Ohio State University, 177 Watts Hall 2041, College road, Columbus, OH 43210-1178, USA
[c] University of Missouri – Rolla, Rolla, MO 64509, USA

Abstract

Recent studies on the strength of glass fibers suggest that the time is ripe for new, fundamental studies in this area which may significantly advance our understanding of the intrinsic strength of glasses. In order to set the stage, in this paper we define various terms (intrinsic and extrinsic strength and inert and environmental fatigue) and analyze techniques for their measurement. We illustrate and evaluate these parameters by means of literature data on silica and E-glass. In addition we present some preliminary new data on E-glass fibers using 2-point bending. These new data report higher strength than previously reported and some possible reasons for this are given. While these comments deal primarily with the science of strength, a better understanding of these issues may lead to improvements in glass technology and glass products.

PACS: 62.20.–x; 62.20.M; 62.40; 46.50

---

1. Introduction

In spite of a large number of papers written on the subject of the strength of glass since the seminal one of Griffith in 1920 [1], few have reported values of intrinsic strength (i.e., the strength of 'flaw-free' glasses). Recently the authors have published papers which discuss the intrinsic strength of glasses and present new experimental data. The reader is referred to these papers for a more complete discussion [2–5]. In this paper we will:

1. Define the terms intrinsic strength and fatigue.
2. Discuss methods of measurement.
3. Suggest guidelines for determining whether intrinsic values have actually been obtained.
4. Illustrate these parameters using literature data for silica and E-glass.

2. Definitions

2.1. Intrinsic strength (σ^*)

The intrinsic properties of glasses vary with composition and thermo-mechanical history because of changes in the underlying atomistic structure and bonding. Examples of such intrinsic

---

[*] Corresponding author. Tel.: +1-614 292 6769; fax: +1-614 292 1537.
E-mail address: gupta.3@osu.edu (P.K. Gupta).

0022-3093/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S0022-3093(02)01943-9

properties include thermodynamic properties such as density, heat capacity, and thermal expansion coefficient as well as transport properties such as electrical conductivity and viscosity. Generally, strength (i.e., tensile strength) is not considered intrinsic because of its extreme sensitivity to extrinsic microdefects that are invariably present either on the surface or in the bulk of glass samples. Strength measured in the absence of extrinsic defects is called intrinsic strength, σ^*. It is important to emphasize that the intrinsic strength includes the effects of all intrinsic defects that are expected to be present as a result of thermal fluctuations. The intrinsic strength of a homogeneous glass of a composition, C, depends, in general, on the test temperature, T, and as discussed in the next section, the testing environment (X) and the time of testing (τ, or the strain rate). Thus, one may write

$$\sigma^* = \sigma^*(C, T, X, \tau). \quad (1)$$

2.2. Fatigue: environmental vs. inert

Fatigue, or delayed failure, is the slow breaking of the bonds in a glass structure under the application of stress. For extrinsic strength, fatigue is due to the 'slow growth' of a pre-existing crack. Fatigue is also observed in pristine (flaw-free) fibers and is believed to be caused by 'slow' crack nucleation. As a consequence of slow bond breaking, the measured strength (σ) of a glass depends on the time (τ) of loading or on the rate of loading. Fatigue is most pronounced when moisture is present in the testing environment. We refer to the environmentally enhanced fatigue as *environmental fatigue*. Fatigue under inert conditions (such as vacuum) is referred to as *inert* (or intrinsic or thermal-fluctuation) fatigue. To avoid confusion between intrinsic strength and intrinsic fatigue, we prefer to use the term 'inert fatigue'. The notion of inert fatigue is controversial [6–9]. There have, however, been observations [10–12] of slow crack growth in vacuum. This suggests that while the magnitude of the effect may be small, inert fatigue is, and, in principle, should be present.

Being a time-dependent phenomenon, fatigue can be prevented by rapid testing: by testing in times on the order of the typical vibration time, τ_{vib} ($\sim 10^{-13}$ s). Empirically, fatigue is described approximately by an equation of the type

$$\tau = \tau_{\mathrm{vib}} \exp\left[\frac{E(X,C)}{kT}\left(1 - \left\{\frac{\sigma}{\sigma_0(T,C)}\right\}\right)\right]. \quad (2)$$

Here $E(X, C)$ is the zero-stress environment-dependent activation energy for a glass of composition C, k the Boltzmann's constant, T the test temperature, σ the measured strength at the test time (τ), and σ_0 the strength measured in time τ_{vib} such that fatigue does not occur. We refer to σ_0 as the fatigue-free strength.

2.3. The measured strengths

Depending on whether the strength is intrinsic or extrinsic and whether fatigue is absent, inert, or environmental, one can measure six types of strengths. These are listed in the chart below:

	Types of measured strengths		
	Fatigue-free	Inert	Environmental Fatigue
Intrinsic	σ_0^*	σ_{i}^*	σ^*
Extrinsic	σ_0	σ_{i}	σ

2.4. Inert strength

The inert strength, σ_{i}, is the strength measured under conditions when there is no environmental fatigue. An expression for inert strength can be obtained after substituting the inert activation energy, $E_{\mathrm{i}}(C)$, in Eq. (2):

$$\sigma_{\mathrm{i}}(T, C, \tau) = \sigma_0(T, C)[1 - \{kT/E_{\mathrm{i}}(C)\}\ln(\tau/\tau_{\mathrm{vib}})]. \quad (3)$$

This equation shows that the inert strength for a given composition and temperature depends on the duration, τ. However, because $E_{\mathrm{i}}(C) \gg kT$ and the range of strain rates in typical strength experiments is small, the observed time dependence of the inert strength is small.

2.5. Fatigue-free intrinsic strength

This refers to the intrinsic strength in the absence of any fatigue (environmental or inert). The fatigue-free intrinsic strength, $\sigma_0^*(T, C)$, of a glass is free from all extrinsic influences (flaws and environment) as well as from inert fatigue and therefore represents the best experimental measure of the theoretical strength of a glass. The variation of both the fatigue-free intrinsic strength and inert intrinsic strength with composition and temperature reflect the intrinsic influence of changing atomic level structure and bonding in glasses.

3. Measurement of intrinsic and inert strengths

3.1. Intrinsic strength

The first question that arises is ‘how does one measure the intrinsic strength of a glass?’ This is equivalent to asking whether a test sample is flaw-free. This is difficult to answer because there is no simple test to make sure that a sample is free of all extrinsic flaws. However, the probability of the presence of extrinsic flaws decreases with decrease in the test sample volume and surface. We have suggested conditions that we believe provide the best hope of measuring the intrinsic strengths of glasses [3]:

(a) Use of thin (diameter $\leqslant 125$ μm) melt-(or perform-) drawn fibers whose bulk (by sufficiently long melting) and surface (by careful handling or by on-line coating) have been protected from extrinsic flaws.
(b) Use of 2-point bending technique to measure the fracture strain. This technique does not require gripping of the fiber ends and allows testing of a very small gauge length (estimated gauge length less than 1 mm) of a fiber sample.
(c) Testing the fibers soon after forming with minimum additional handling. The greater the time between forming and testing, the greater is the probability of extrinsic flaws forming on a bare fiber surface. Gupta [4] has recently suggested the following three criteria as a test for a set of strength data to be considered intrinsic:

(a) No dependence of measured strength on fiber diameter or length.
(b) The coefficient of variation in strength values is about two times the coefficient of variation in the fiber diameter values.
(c) High measured fracture strengths (or fracture strains).

3.2. Inert strength

The second question is ‘how does one measure the inert strength of glass?’ By definition, the inert strength must be measured under conditions where the effects of environment-induced reactions are avoided. This can be achieved in four ways:

(a) testing in vacuum [13–15] or in a dry environment [16],
(b) testing hermetically coated fibers in normal environment [17],
(c) testing at a sufficiently low temperature where the kinetics of the environmentally induced reaction are arrested [14,18], or
(d) testing in normal environment using very rapid strain rates.

All approaches have been tried experimentally. The use of vacuum or controlled dry environments require excessive handling of samples and as a result increases the probability of extrinsic flaws. Use of hermetic coatings is not convenient on a routine basis in most labs as it requires special coating equipment and fiber forming set up. The maximum experimental strain rates are generally limited to about 1% s^{-1}. Thus inert strengths are tedious to measure except at low temperatures where environmental fatigue is suppressed.

3.3. Liquid nitrogen temperature strength

Of special interest are strength measurements at the boiling point of liquid nitrogen (77 K) because they can be carried out with relative ease. We denote the strength measured at 77 K as σ_{77} (and σ_{77}^* when intrinsic). It is well established that σ_{77} is free of environmental fatigue as the reaction kinetics of water and silica are extremely slow at 77 K. However, there is a small effect of inert fatigue and as a consequence σ_{77} is somewhat less than the fatigue-free strength, σ_0 [18].

3.4. Fatigue-free strength, σ_0

Values of the fatigue-free strength (free of both inert and environmental fatigue) can be obtained by testing at extremely low temperatures (such as the boiling point of the liquid helium i.e., at 4 K). By testing at such a low temperature, it is possible to suppress not only the environmental fatigue but also the inert fatigue. Only one measurement has been made, to our knowledge, of intrinsic strength at 4 K [18]. In the case of carefully prepared silica fibers, failure stress ~14.4 GPa with a very narrow strength distribution, (variance ~ 0.74) have been measured by Proctor et al. [18] at liquid helium temperature. We believe that this value represents the fatigue-free intrinsic strength of silica. Because there is no fatigue whatsoever, σ_0 is expected to be relatively constant with respect to temperature.

We have recently reviewed most of the literature that seemed to have a bearing on inert intrinsic strength [3]. In the present paper, we discuss only the previous experimental work on two oxide glasses for which there is extensive work. This will allow us to illustrate several important points.

4. Illustrations from the literature

4.1. Silica

The work of Proctor et al. [18] was critical to the development of long length silica optical fibers having high strengths. They studied the strength of hand-drawn uncoated silica fibers in tension. Each fiber was individually drawn and its diameter measured. Strengths were measured from 4 to ~700 K, in air, vacuum and as a function of time (Figs. 1 and 2). From these figures we can illustrate all of the pertinent points for this discussion.

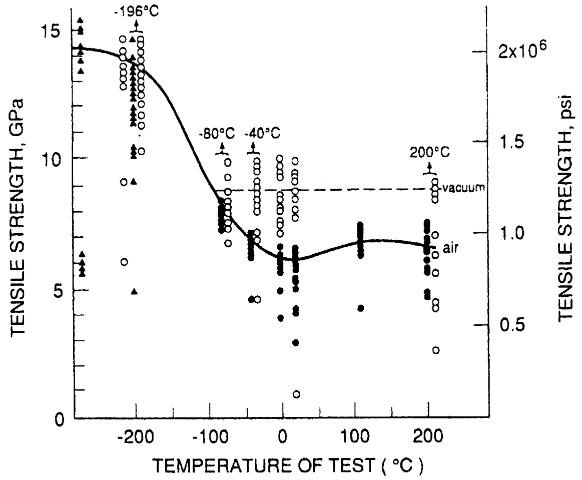

Fig. 1. Strengths of silica fibers as a function of temperature. Fibers tested in liquid helium or liquid nitrogen (filled triangles), fibers tested in vacuum (open circles), and fibers tested in air (filled circles) (from [18]).

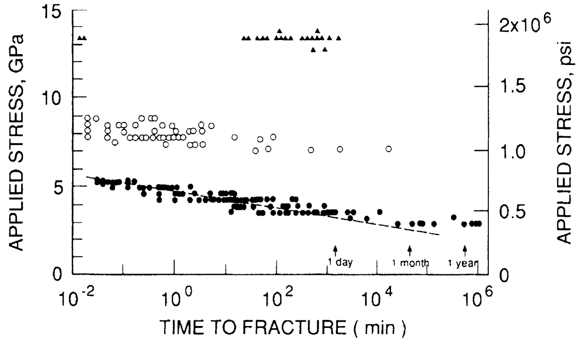

Fig. 2. Time dependence of tensile strength of silica fibers (from [18]) in vacuum at 77 K (filled triangles), in vacuum at room temperature (open circles), and in air at room temperature (filled circles).

(a) Intrinsic strength at room temperature under ambient conditions.
(b) Inert intrinsic strength at room temperature.
(c) Temperature dependence of inert intrinsic strength.
(d) Inert fatigue.
(e) Environmental fatigue.

4.1.1. Room temperature intrinsic strength

It has been possible by carefully controlling the material preparation and fiber drawing, including good diameter control and in-line-coating, to measure high strengths with extremely low dispersion for silica fibers. These studies in tension [18,19] and in 2-point bending [20] by several different investigators yield a consistent strength value for silica of about 5.5–6 GPa at room temperature (depending on measurement time) with a very small dispersion, $v \leqslant 1\%$. Additionally, however, it was discovered by careful measurements on such silica fibers with known diameter variations, that the strength was essentially single-valued. It was found that the only apparent variation in measured strength was the result of diameter fluctuations. It was thus suggested that these fibers were 'flaw-free' [19].

4.1.2. Inert intrinsic strength at room temperature

Smith and Michalske [15] measured ~11–14 GPa at room temperature and 10^{-8} Torr, in tension. This is in agreement with the measurement of ~18% strain measured by Griffioen [13] at room temperature and ~10^{-8} Torr ($\sigma \sim 12.5$ GPa if the high strain modulus is essentially the zero-strain modulus: i.e., 70 GPa). These values are shown in Table 1 together with another interesting measurement. Bogatyrjov et al. [17] measured a tin-coated silica fiber at room temperature and found a value of ~14.5% strain. As indicated in the Table, this corresponds to ~10.2 GPa using $E = 70$ GPa, or ~11.3 GPa using his E-values from $E = E_0(1 + 3\varepsilon)$. On the basis of these results, we may conclude that the inert intrinsic strength of silica, for a testing time of 1–10 s, at room temperature is ~10–12 GPa.

4.1.3. Temperature dependence of inert intrinsic strength

Proctor et al. [18] measured ~12–13 GPa at 77 K, but ~14 GPa at 4 K in tension. France et al. measured a 2-point bend strain of ~18% at 77 K [18]. The inert intrinsic strength appears to be about 12.5 GPa at 77 K and ~14 GPa at 4 K.

4.1.4. Environmental fatigue

Fig. 2 shows the time dependence of the strength of fused silica with and without water in the ambient. The time dependence that is seen in the presence of water causes the well-known environmental fatigue. The combination of the applied stress and the reaction of water with the Si–O bond results in a reduction in the measured strength as a function of time. As indicated above, the activation energy for this process is ~100 kJ/mol. While it is generally accepted that the time dependence should actually be exponential in time, the normal description of environmental fatigue is given in terms of a parameter n defined as

$$n = -\mathrm{d}\ \ln t/\mathrm{d} \ln \sigma. \tag{4}$$

For silica and silicate glasses, the n-values ranges from 15 to 50.

4.1.5. Inert fatigue

As indicated above, it has been shown [8] that even in vacuum, a time dependence of strength is expected and is observed in some materials. This is the result of the increasing thermal energy (kT) available as the temperature is increased above absolute zero. This is illustrated by Eq. (3).

A compilation of the activation energies, $E_\mathrm{i}(C)$, from crack propagation studies [10] as well as strength studies on low and high strength glasses in vacuum [21] is shown in Table 2. Kartashov and Bartenev [21] illustrated inert fatigue in both high and low strength silicate glasses and silica. A problem is that the source for the data in Kartashov and Bartenev's paper is unclear. Wiederhorn et al. [10] observed comparable slow crack growth in vacuum in soda lime and alumino-silicate glasses, but not in silica. Subsequent work by Gonzalez [11] and by Michalske et al. [12] however, did

Table 1
Strengths of silica fibers

300 K [13] (UHV) (2-point bend)	300 K [15] (UHV) (tension)	300 K [17] (hermetic) (2-point bend)	77 K [18] (tension)	77 K [20] (2-point bend)	4 K [18] (tension)
$\varepsilon = 0.18$ $\sigma = 12.6$ GPa[a]	$\sigma_{\mathrm{UHV}} = 11$–$14$ GPa	$\varepsilon = 0.145$ $\sigma \sim 10.2$ GPa[a] $\sigma \sim 11.3$ GPa[b]	$\sigma \sim 12.5$ GPa	$\varepsilon = 0.18$ $\sigma = 12.6$ GPa[a]	$\sigma \sim 14$ GPa

[a] $E = 70$ GPa.
[b] $E = E_0(1 + 3\varepsilon)$.

Table 2
Vacuum crack growth and 'inert fatigue' activation energies

Glass	$E_i(C)$ /kJ/mol (kcal/mol)	Ref.
61% lead	348 (83.1)	Wiederhorn et al., crack growth [10]
Aluminosilicate	705 (176)	
Borosilicate crown	275 (65.5)	
Soda-lime-silicate	605 (144)	
Soda-lime-silicate[a]	540 (135)	Kartashov and Bartenev, fatigue [21]
Alumino-silicate[b]	880 (220)	
Silica[b]	300 (75)	

[a] Low strength.
[b] High strength.

show such stable slow crack growth in silica at UHV. In fact Michalske et al. found such behavior at both 300 and 100 K although their interpretation is concerned mainly with the effect of the high frequency relaxation known to be present in silica glass. While Kartashov and Bartenev [21] had apparently shown a time dependence of strength for these three glasses in vacuum better data are needed to solidify this argument.

According to the literature then, there is slow crack growth in vacuum in all glasses that have been measured. In addition, Kartashov and Bartenev [21] interpreted vacuum strength tests on high strength fibers in terms of inert fatigue. In what follows we discuss other measurements that also indicate the presence of this effect in high strength silica.

Table 1 is a tabulation of strength data for silica discussed above, under conditions where water is presumably not a factor. The tin-coated fiber produced by Bogatyrjov et al. [17] apparently showed essentially inert strength at room temperature. Thus the tin coating appears to be hermetic and the behavior would be expected to mimic that of a glass in vacuum. They studied the time dependence of the strength of these fibers at room temperature in air. These data are shown in Fig. 3. A time-dependence is clearly shown, although the data are not well enough defined. They calculate a value of $n \sim 135$ which is much higher than the values normally found (15–50) for silica fibers under any conditions, and may be assumed, for the moment at least, to be essentially a water-free value (n_i).

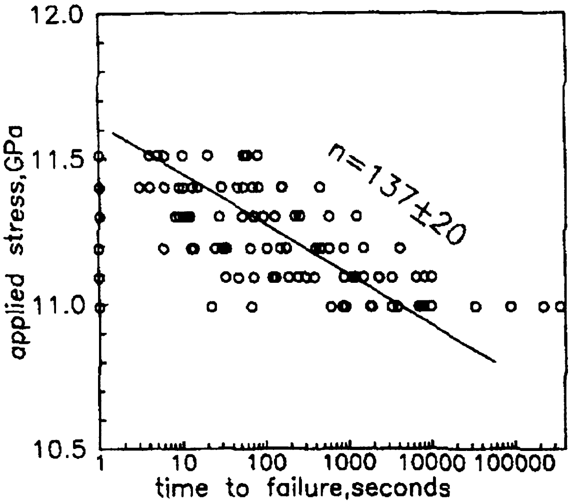

Fig. 3. Two point bend measurements of the time dependence of the tensile strength of tin-coated silica fibers at 300 K (from [17]).

Additional support for inert fatigue comes from a consideration of the data of Proctor et al. [18] in Fig. 1. Assume that the apparent decrease in the strength from 4 K ($\sigma_4 = 14$ GPa) to 77 K ($\sigma_{77} = 12.5$ GPa) seen by Proctor et al. is due to inert fatigue, and that the activation energy of this process in the absence of water is the Si–O bond strength (E_i (silica) ~400 kJ/mol). Using Eq. (3), the strengths at 77 and 300 K are estimated to be ~13 and ~11 GPa, respectively. This is in rough agreement with the other numbers shown in Table 2. This supports the possibility of the presence of inert fatigue.

4.2. E-glass

In Refs. [3,4] we have given details of the history of measurements that have been made on soda-lime and E-glasses. Such discussions will not be repeated here. Suffice it to say that following the early initial work of Otto [22] and Thomas [23], the exhaustive and conclusive work of Cameron [24] has resulted in a very good understanding of the inert intrinsic strength of E-glass and the factors that affect it. These results may be summarized as follows:

Table 3
Strengths of E-glass fibers

300 K [4] (air) (tension)	300 K [5] (2-point bend)	77 K [4] (tension)	77 K [5] (2-point bend)
$\sigma = 3.5$ GPa	$\varepsilon = 0.045$ $\sigma = 3.5$ GPa[a]	$\sigma = 5.8$ GPa	$\varepsilon = 0.105$ $\sigma = 8.25$ GPa[a]

[a] $E = 78$ GPa.

(a) There is no diameter dependence of strength, at least in the range from ~5 to 20 μm.

(b) If a minimum 'soaking treatment' of at least 1450 °C and 1 h is employed, fibers drawn at 1250 °C will show an essentially single high strength mode. This strength is ~3.6 GPa at 300 K and 5.8 GPa at 77 K (inert strength).

(c) While Cameron measured the tensile strength from 300 to 77 K, measurements at $T < 77$ K were not made and therefore an estimate of the inert fatigue as was made for silica is not possible.

Gupta [4] has recently found good agreement with these earlier results. These results are shown in Table 3.

5. Experimental

Below, we present some new data on commercial E-glass, obtained using an experimental procedure that we suggest can most easily lead to the measurement of inert/intrinsic strengths of a variety of glass compositions. While these data have been recently published [5], this publication may not be readily available. In addition, we use it here to illustrate our procedure.

In the new work presented here, a two-point bending technique was employed [25]. In this case, the fiber is bent between two metal plates. One of the plates is stationary, while a computer-controlled stepper motor drives the other. These plates are highly polished to reduce the risk of contact damage to the fiber. More importantly, the curvature of the fiber is zero where it contacts the plates and thus the stress here is also zero. This is not the case when 3 or 4 point bending is employed and sample damage may affect the apparent strength. The principal drawback to the use of the 2-point technique as employed in this work is that the bend diameter at failure is measured. This means that the failure strain and not the failure stress is obtained. A knowledge of Young's modulus and its strain dependence are required to convert strain into stress.While this may not often be a major problem, in the case of silica it is. It is known that the modulus of silica increases with strain (stress) roughly according to: $E = E_0(1 + 3\varepsilon)$, where ε is the strain. This has been verified only to about 6% strain [26]. Clearly this equation must break down at some higher value of strain. An estimate of the Young's modulus at 18% strain can be obtained by dividing the tensile strength at 77 K measured by Proctor et al. (~12.5 GPa, by the bending strain obtained by France at 77 K (18%). This results in a value of ~69.5 GPa, very near the zero stress modulus (70 GPa). While no data are available for glasses other than silica at high tensile strains, it is known that their behavior is 'normal', i.e., the modulus decreases with tensile strain.

Pukh and co-workers have used a three-point bending technique on thin fibers, which measures the stress directly [27]. A drawback of this technique is the somewhat unknown behavior at the supports. Both the possibility of damage and the lack of detailed knowledge of the friction at these points may be a problem.

In any case, however, it must be borne in mind that values of E for glasses as found in the literature show quite a spread. Factors affecting these values are the actual glass composition as well as the temperature and fictive temperature. Fictive temperature effects may be as high as 10%, while the effect of differences in measurement temperature may be ~5%. It is thus desirable to measure the modulus on the fibers at the temperature of the strength measurement. In the present work zero strain values of $E = 78$ GPa obtained on fibers by an acoustic technique [26] at room temperature was used.

The fibers studied in the present work were updrawn continuously from the free surface of a melt in a Pt crucible at 1300 °C. The fibers were drawn through a water-cooled copper coil for viscosity control. Prior to pulling fibers, the glass melt was held at 1550 °C in air for 4 h. This high temperature soak eliminates the thermal history effects noted by Cameron [24] and yields fibers with very narrow distributions of failure strain. This procedure was found to be important for several reasons. The size, circularity and uniformity of the fiber diameter are more easily controlled than in hand drawing. The variation in the glass composition from fiber to fiber is also expected to be reduced. This continuous drawing was accomplished by replacing the normal drawing drum with a drawing cage [28]. Here, contact of the fiber with the surface of the drum is avoided by using 12 machined rods evenly spaced around the 450 mm diameter, 450 mm long cage rather than a drum surface. Lengths of untouched fiber ~113 mm between these rods are obtained. Such lengths are convenient for testing in the 2-point bender.

6. New results for E-glass

6.1. Strength

Fig. 4 shows Weibull plots of failure strain at 77 and 298 K (50% RH) for E-glass fibers of about 100 μm in diameter. The median fracture strain is $\varepsilon_{77} \sim 12.8\%$ and v about 1%. Using the measured value of $E = 78$ GPa, a value of $\sigma_{77} \sim 10$ GPa is obtained. This is significantly greater than the value of ~6 GPa obtained by Cameron [24] and Gupta [4] at 77 K for 10 μm diameter fibers. The strength value at room temperature is about 4 GPa comparable to 3.5 GPa reported by previous workers in pure tension [4,24]. A possible reason for the difference in the 77 K values may be a major decrease in E of fibers at 77 K or a drop in E with increase in applied strain. If the tensile strength is 6.0 GPa at 77 K and the fracture strain is ~12%, the modulus required to bring about agreement is ~50 GPa. Reasons for the difference in reported strengths at 77 K for E-glass between 2-point bend and pure tension need to be resolved.

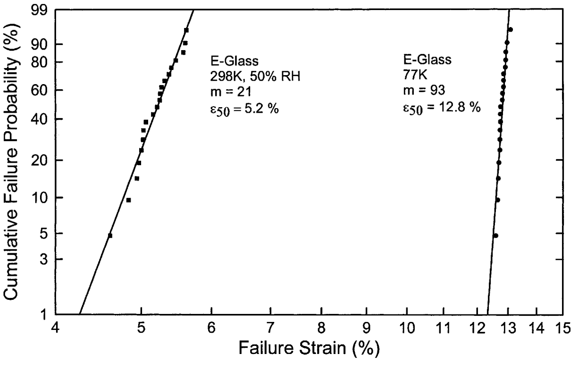

Fig. 4. Weibull plot of the fracture strains for 2-point bend E-glass fibers (about 100 μm diameter) at 77 and 300 K (50% RH).

Although the uncertainty about the strain, the temperature, and the fictive temperature dependence of E is important, overall, the simplicity of the 2-point bend measurement is attractive, especially at conditions other than ambient. On the other hand, 2-point bend tests are practically restricted to diameters greater than 100 μm.

6.2. Fatigue

As expected, the n-values for environmental fatigue for E-glass are of the order of 20–30 and show little variation with humidity in the normal humidity range [5]. No attempt has been made to make any evaluation of the inert fatigue.

7. Correlations between strength and other intrinsic properties

Marsh [29] reviewed previous estimates of theoretical strength of silica glass. There have been several estimates using an equation of the type: $\sigma_0^* \sim [E\gamma/a]^{1/2}$. These values range from ~7 to ~20 GPa. Naray-Szabo and Ladik [30] estimated a value of ~25 GPa by considering more specifically the Si–O bond strength and the number of bonds per unit glass volume. Hillig [31] also estimated a value of ~25 GPa by modifying the usual estimate of $E/5$ to account for the change of E with strain. Marsh [29] made an estimate of similar magnitude by making use of a value of flow stress (from indentation measurements) at the critical fracture velocity. In our opinion, reliable estimates of the theoretical strength are not available for glasses.

It has been frequently postulated that intrinsic strength should be directly related to the Young's modulus (E). That this cannot be entirely true is seen from the fact that the Young's modulus is determined by the harmonic part of the atomic interactions while the strength is determined by the highly anharmonic part (i.e., the inflection point) of the interactions. Indeed, the macroscopic Young's modulus (or some other suitable elastic modulus) must approach zero for all compositions at their respective fracture strains. The data shows no correlation of intrinsic strength with either $E^{1/2}$ or K_{IC} [2,3].

Bartenev and Sanditov [32] have suggested a correlation between strength and a number of other physical parameters. The correlation of a calculated strength with indentation hardness is shown in Fig. 5. This may seem surprising since there is flow under a pointed indenter while the fracture is expected to be brittle. In addition, the flow has been shown to be different in the case of silica (compaction or volume flow) than in the case of 'multicomponent' glasses (shear flow). However, it is not unreasonable when one considers that both failure in tension and flow during indentation are accomplished by the breakage of Si–O–Si bonds or Si–O–Na bonds in the two types of glasses. The problem with Bartenev's correlation is that the strength is not experimentally measured. On the other hand, Marsh [29] and Kurkjian et al. [33] showed a strong quantitative correlation between the hardness and strength of silica and soda-lime glasses as a function of both rate and temperature of testing. The data presented for phosphate glasses, however, did not show any such correlation between strength and hardness [3].

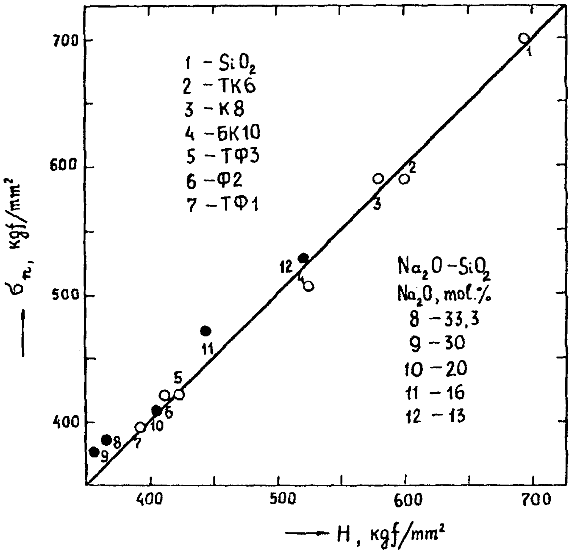

Fig. 5. The correlation between calculated ultimate strength and experimentally measured Vickers hardness for various silicate glasses (from [32]).

It seems more reasonable to correlate intrinsic strength with the glass transition temperature which represents the breakage of bonds by thermal energy and is dominated by the anharmonic part of the interaction potential as is intrinsic strength. Indeed such a correlation has been demonstrated by Bartenev and Sanditov [32] for the alkali-silicate glasses.

8. Modeling

Theoretical understanding of intrinsic strength has been almost non-existent. However, some attempts have been made to examine strength using MD simulations.

Woodcock et al. [34] carried out the first MD simulation of simple ionic systems in 1976 using the pairwise Born–Mayer–Huggins (BMH) potentials. Since then, much work has been reported on MD simulations of structure and various properties (such as vibrational frequencies, expansion coefficients, and diffusion coefficients) of silicate glasses.

Soules and Busbey [35] first reported studies of the intrinsic strength of silica glass in 1983. They also used the BMH pair potentials for Si–O, O–O, and for Si–Si pair interactions [36]. For silica glass, they observed a maximum in the stress–volumetric strain curve corresponding to a stress of about 24 GPa (a strain of about 23%). A similar calculation for cristobalite gave a strength of 70 GPa (at about the same percentage strain as in the case of glass). Further, they observed that the strain energy was released by the nucleation and growth of cavities in the structure.

Simmons [37] has studied the strength of pure silica in uniaxial tension at several strain rates using the BMH potential (similar to those used by Soules [36]). Strength of 30 GPa (at a strain of 20%) was calculated and the fracture was observed to consist of growth and coalescence of the 'pre-existing voids in the structure'.

Liao [38] has studied stress–strain behavior of silica using the BKS potential [36]. He reports that the strength becomes strain rate independent and is about 13 GPa and a strain of about 22%. Once again, the fracture process is controlled by the nucleation, growth, and coalescence of cavities.

In summary, the MD results for silica glass show that

(a) while the strength values vary from 13 to 30 GPa depending on the details of the interaction potential, the fracture strain values are pretty much the same in all studies; about 20– 23%,
(b) all MD studies find that the fracture process in glass is by the nucleation, growth, and coalescence of cavities,
(c) MD simulations have not been very successful largely because the anharmonic parts of the atomic interactions are not well known.

Since a crack must ultimately form prior to the fracture of a glass, it is reasonable to assert that the intrinsic strength must be controlled by 'crack nucleation'. Crack nucleation in a crystalline solid is relatively easy to model provided, of course, the crystal structure and the interatomic potentials are known. A crack nucleates at some intrinsic point defect in the crystal and grows in a plane normal to the applied tensile stress. Crack nucleation in a glass, on the other hand, is much more difficult to conceptualize since the microscopic stresses are not distributed homogeneously in the random network of glass. Because of its topological disorder, it is likely that the second and later bonds do not break in the immediate vicinity of the very first broken bond. This leads to a zone of broken bonds which ultimately percolate leading to nucleation of a microcrack.

This simple picture assumes that the glass network is static. A glass network is most likely not static under large stresses. The structure may rearrange (or relax) under the application of stresses as the bonds are gradually breaking. In fact, stress relaxation is not new and has been much studied but mostly at higher temperatures (near T_g) [39]. Stress relaxation may also occur at room temperature under high stresses. Indeed flow has been observed at room temperature in indentation studies. Thus the influence of structural/stress relaxation under high stresses on crack nucleation makes the intrinsic strength time/rate dependent.

It appears from this discussion that a true understanding of the intrinsic strength of glass does not exist at present and will require simultaneous investigations in simple glasses of structure and point defects under high stresses as well as intrinsic strength.

9. Summary

In this paper, we have defined the intrinsic strength of a glass. We suggest that a 'high strength', a narrow strength distribution ($v \leqslant 5\%$ or Weibull $m > 20$) and insensitivity to sample size should be the criteria for considering strengths to be intrinsic. An additional feature which is often overlooked has been stressed here – that is the issue of 'inert' or 'intrinsic' fatigue. We have shown that there are three types of intrinsic strengths: fatigue-free σ_0^*, inert σ_i^*, and environmental-fatigue, σ^*. By definition, the inert intrinsic strength must be measured on a perfect flaw free sample in the absence of water. For a given composition and at a fixed temperature: $\sigma_0^* > \sigma_i^* > \sigma^*$. We have discussed methods of measurements for all three types of intrinsic strengths. It has been shown that a careful consideration of the conditions of glass preparation and testing are extremely important. The use of fibers rather than bulk glass simplifies both of these issues.

Further, we have discussed the intrinsic strengths of silica and E-glass since these are the only glasses for which relatively complete and adequate results are available. While additional work on silica is required, quite a good picture of its behavior has been gained. As seen, no work on the inert fatigue of E-glass (or in fact on any inorganic glass except silica) is available. New measurements of the types mentioned in this paper will be invaluable to complete our understanding of the mechanical behavior or inorganic glasses. An understanding of the fatigue-free and inert intrinsic strengths of simple glasses is important if the overall mechanical behavior of these materials is to be improved.

References

[1] A.A. Griffith, Philos. Trans. Roy. Soc. A 221 (1920) 163.

[2] C.R. Kurkjian, J. Non-Cryst. Solids 263&264 (2000) 207.

[3] C.R. Kurkjian, P.K. Gupta, Proceedings of the XI International Congress on Glass, Edinburgh, 2001.

[4] P.K. Gupta, Proceedings of the Euroconference on High Performance Fibers, 19–24 October 2000, Majorca, Spain.

[5] R.K. Brow, N.P. Lower, A.J. Lang, C.R. Kurkjian, Structure and the Intrinsic Strength of Glass, Otto Schott Colloquium, Jena, 2002.

[6] S.M. Cox, J. Soc. Glass Tech. 32 (146) (1948) 127.

[7] C. Gurney, S. Pearson, Proc. Phys. Soc. (London) 62 (8) (1949) 469.

[8] S.N. Zhurkov, B.N. Narzullaev, J. Tech. Phys. 23 (1953) 1677.

[9] V.P. Pukh, S.A. Laterner, V.N. Ingal, Sov. Phys., Solid State 12 (1970) 881.

[10] S.M. Weiderhorn, H. Johnson, A.M. Diness, A.H. Heuer, J. Am. Ceram. Soc. 57 (8) (1974) 336.

[11] A.C. Gonzalez, PhD thesis, Penn State University, 1991.

[12] T.M. Michalske, W.L. Smith, J.H. Houston, J. Appl. Phys., 76 (1994) 2109.

[13] W. Griffioen, PhD thesis, University of Eindhoven, The Netherlands, 1994, p. 199.

[14] W.J. Duncan, P.W. France, S.P. Craig, in: C.R. Kurkjian (Ed.), Strength of Inorganic Glass, Plenum, 1985, p. 309.

[15] W.A. Smith, T.M. Michalske, DOE contract # DE-AC04-0DPOO789 1990.

[16] J.L. Mrotek, M.J. Matthewson, C.R. Kurkjian, J. Non-Cryst. Solids 297 (2001) 91.

[17] V.A. Bogatyrjov, M.M. Bubnov, E.M. Dianov, A.M. Prokhorov, S.D. Rumyantsev, S.L. Semjonov, JETP Lett. 14 (1988) 343.

[18] B.A. Proctor, I. Whitney, J.W. Johnson, Proc. Roy. Soc. A 297 (1967) 534.

[19] C.R. Kurkjian, U.C. Paek, Appl. Phys. Lett. 42 (1983) 251.

[20] P.W. France, W.J. Duncan, D.G. Smith, K.J. Beales, J. Mater. Sci. 18 (1983) 785.

[21] E.M. Kartashov, G.M. Bartenev, Phys. Chem. Glasses (Russia) 7 (1980) 126.

[22] W.H. Otto, J. Am. Ceram. Soc. 38 (1955) 122.

[23] W.F. Thomas, Phys. Chem. Glasses 1 (1960) 4.

[24] N.M. Cameron, Glass Tech. 9 (1968) 14.

[25] M.J. Matthewson, C.R. Kurkjian, S.T. Gulati, J. Am. Ceram. Soc. 69 (1986) 815.

[26] J.T. Krause, L.R. Testardi, R.N. Thurston, Phys. Chem. Glasses 20 (6) (1979) 135;
see also B.A. Proctor, Phys. Chem. Glasses 31 (2) (1990) 78.

[27] See for instance L.G. Baikova, Y.K. Federov, V.P. Pukh, T.P. Kazannikova, L.G. Tikhonova, M.F. Kireenko, Phys. Chem. Glasses (Russia) 19 (1993) 380.

[28] N. Lower, 2001, unpublished work.

[29] D.M. Marsh, Proc. Roy. Soc. 279 (1964) 420.

[30] I. Naray-Szabo, J. Ladik, Nature 188 (1960) 226.

[31] W.B. Hillig, Symposium sur la resistance mecanique du verre er les moyens de l'ameliorer, Union Scientific du Verre, Charleroi, Belgium, 1961.

[32] G.M. Bartenev, D.S. Sanditov, J. Non-Cryst. Solids 48 (1982) 405.

[33] C.R. Kurkjian, G.K. Kammlott, M.M. Chaudhri, J. Am. Ceram. Soc. 78 (1993) 737.

[34] L.V. Woodcock, C.A. Angell, P. Cheeseman, J. Chem. Phys. 65 (4) (1976) 1565.

[35] T.F. Soules, R.F. Busbey, J. Chem. Phys. 78 (10) (1983) 6307.

[36] T.F. Soules, J. Non-Cryst. Solids 73 (1985) 315.

[37] (a) R. Ochoa, T.P. Swiler, J.H. Simmons, J. Non-Cryst. Solids 128 (1991) 57;
(b) J.H. Simmons, J. Non-Cryst. Solids 239 (1998) 1.

[38] D. Liao, PhD thesis, MIT, 2001, p. 136.

[39] G.W. Scherer, Relaxation in Glass and Composites, Wiley, 1986.