

# Intrinsic strength and the structure of glass

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*Intrinsic strength is the strength of a glass without extrinsic flaws. Knowledge of the composition dependence of the intrinsic strength is important both technologically for the development of high strength glass compositions and theoretically as it may provide important structural information. Intrinsic strength is easy to define but difficult to measure experimentally. In this paper we discuss intrinsic ( $\sigma^*$ ) strength measured in normal laboratory conditions as well as the inert intrinsic ( $\sigma_0^*$ ) strength. We define these terms in a rigorous manner and indicate how to gauge if they have been measured by developing a set of criteria. Based on these criteria, we tabulate those values of intrinsic strengths that have been measured to date.*

Composition dependence of an intrinsic property of glasses provides a structure based understanding of the property itself when the structure is known as well as indirect information about the glass structure when the structure is not known. Examples of intrinsic properties often employed are density, diffusion, viscosity and elastic constants. Another property that should be considered in this regard is mechanical strength. In order to study its composition dependence, it is necessary that it be intrinsic ( $\sigma^*$ ).

Over the years a large number of studies have been made of the mechanical strength of various inorganic glasses. In spite of this very little is known about their 'intrinsic' strength. In this paper we will use the terms 'intrinsic' and 'inert intrinsic' as recently defined by Gupta.<sup>(1)</sup> By intrinsic strength we mean the strength of a pristine or 'flaw free' sample. When such a sample is tested under conditions where no 'delayed failure' is possible, we term this 'inert intrinsic' strength. This strength is normally measured at liquid nitrogen temperature (77 K) or in vacuum where the activity of water is so low that stress corrosion is very small or nonexistent.

In early works it was found that attempts to measure the strength of glasses produced very large spreads in strength values. In attempting to overcome this obstacle, most investigators resorted to applying a 'stand-

ard' abrasion treatment to the glasses being studied.<sup>(2,3)</sup> In addition to providing only values of extrinsic strength, this procedure assumes that the damageability of the glasses is not a function of composition. This is now known not to be true.<sup>(3)</sup>

Thus the measurements made on the strength of oxide glasses to date, few can be considered 'intrinsic'. In the following we show how these measurements can be made and develop criteria to determine if intrinsic or inert intrinsic strengths have been measured. We then tabulate measured strength values that are intrinsic based on these criteria.

## Theory of intrinsic strength

Orowan<sup>(4)</sup> considered the theoretical strength and by making a number of approximations arrived at an equation relating the strength to more fundamental atomic scale parameters.

$$\sigma \sim (E\sigma/a_0)^{1/2} \quad (3)$$

Here  $\sigma$  is strength,  $E$  Young's modulus,  $\sigma$  the fracture surface energy and  $a_0$  is the atomic spacing. If the sample is a one component solid, the elastic modulus would indeed be expected to be a measure of the bonding in the solid and the bond distance would simply be  $a_0$ . Even if the sample is not the simple one component oxide considered above, it might be thought that since the elastic modulus is a measure of the stiffness of the network plots of  $\sigma$  vs  $E^{1/2}$  would be approximately linear. For multicomponent glasses, however, there is not a single bond strength or distance and thus the modulus is more of an average parameter. A simple equation like (3) is clearly not appropriate. It would be expected that some sort of weakest link (such as the largest bond length) would be applicable. Doremus<sup>(5)</sup> has made an interesting point in this regard. He has suggested that in the normal range of oxide glass compositions one would not expect any of these values to vary by more than a factor of four and thus the strength should vary by less than a factor of two.

Orowan's treatment is derived for crystalline materials. In glasses, the stress is distributed nonuniformly and a model of intrinsic strength involving crack nucleation should be more appropriate.<sup>(6,7)</sup>

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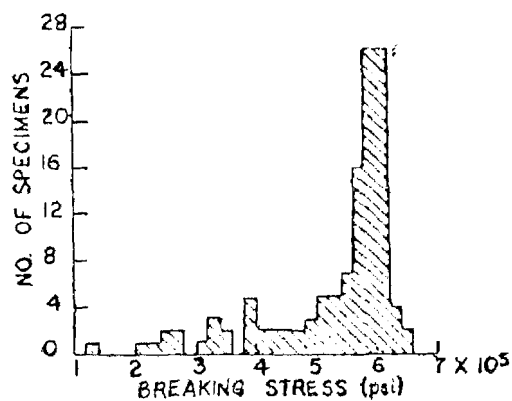


Figure 1. 3-point bending strength of E-glass fibres.  $L \sim 1.25$  mm;  $d \sim 100$   $\mu$ m (Mould<sup>(9)</sup>)

Since it is clear that no theoretical foundation exists for the prediction of the intrinsic strength of a glass, it seems worthwhile to examine the data that exist for the strength of pristine glasses and to suggest where additional experimental work is needed.

#### Evaluation of intrinsic strength

Gupta<sup>(1)</sup> has suggested the following three criteria to determine if inert intrinsic strength is being measured: 1. there should be no size dependence for the measured strength.

2. the distribution of measured strengths should be narrow. While as will be seen below, for silica the flaw-free strength is single-valued, in the case of multi-component glasses, this may not be so because of broader distribution of bond types, or perhaps the existence of some type of 'microstructure'.

3. the measured strength should be high. It is seen from a search of the literature that values for a given glass will often appear to increase as newer and newer measurements are considered. As a moderate rule of thumb we use  $E/20$  as a lower limit for the inert intrinsic strength (i.e. 5% failure strain). This may be rather conservative since for example for silica the measured value is  $\sim E/5$  (70/14).

The intrinsic strength at room temperature is influenced by fatigue. Criteria (1) and (2) still apply, the distribution, for the same sample size, is not significantly affected by fatigue. For the last criterion, we use  $E/40$  (i.e. 2% failure strain) as the lower limit. This is based on the rule of thumb (see below) that there is approximately a factor of 2.5 between the inert intrinsic and the room temperature intrinsic strengths of silicate glasses.

In his classic 1920 paper, Griffith<sup>(8)</sup> described his measurement of the strength for a large diameter (1 mm) silica 'fibre'. He was able to bend this fibre into a loop  $\sim 8$  mm diameter. This gives an estimated failure strain of  $\sim 2.5\%$  at room temperature and a corresponding failure stress of  $\sim 10^6$  lb/in<sup>2</sup> ( $\sim 7$  GPa). He commented that this was 'approximately the theoretical strength'. As indicated above there is little basis for theoretical calculations of strength of glasses. In what follows we will look at other means of assessing whether or not the intrinsic strength has been measured.

Table 1. Percentage elastic failing strain\*

Origin of fibre	8 in test length in tension	1 in test length in tension	0.025 in test length in bending
Rod	1.2	2.4	5.4
Melt	2.0	3.1	

\*Table 1 from Parratt<sup>(10)</sup>

Perhaps the first measurements of intrinsic strength were those of Mould<sup>(9)</sup> in 1958 (Figure 1). He measured the three-point bending strengths of E-glass fibres (95–100  $\mu$ m diameter). He showed that for the gauge lengths (1.25 mm) that were used, only very small surface areas were exposed to the high tensile stresses. He obtained tensile strengths of 530 k/in<sup>2</sup> (3.7 GPa) at a testing time of 10 s. The important observation was that although the overall standard deviation was  $\sim 20\%$ , the standard deviation of the high strength mode was about 1% and thus he argued that he had observed the intrinsic strength of his fibres.

A similar measurement at room temperature is illustrated by the data in Table 1. This is from the work of Parratt<sup>(10)</sup> also in 1958. She drew fibres of a commercial soda-lime-silica glass by hand from a rod and also automatically from a bushing. It can be seen from the table that the strength values obtained using a bending technique are consistently higher than those obtained in tension. She correctly concluded that the difference arose from the very different gauge lengths involved in the two different types of measurement. The tensile measurement involved a gauge length of 5 cm while she estimated the gauge length in the bending experiment at 25  $\mu$ m. As had been shown in detail by Matthewson *et al.*<sup>(11)</sup> this difference in gauge length may result in the measurement of some flaw free sections of fibre when the very short gauge length obtained in bending is employed.

A number of very important studies of the strength of E-glass as a function of many experimental parameters were carried out in the 60s starting with the classic works of Otto,<sup>(12)</sup> Thomas,<sup>(13)</sup> Holloway<sup>(14)</sup> and Cameron<sup>(15)</sup> as well as Bartenev,<sup>(16)</sup> Aslanova<sup>(17)</sup> and Pahler & Brückner.<sup>(18)</sup> Thomas was the first to show that if the experimental drawing parameters were controlled, no variation in measured tensile strength was found over the diameter range initially studied by Griffith.<sup>(8)</sup> He and most others who followed found standard deviations in the measured strengths to be 1–2%. Studies by many other investigators around the world followed during this time period.

The 'proof' by Mould<sup>(9)</sup> that he had measured the intrinsic strength of E-glass fibres was followed much later by detailed work on silica by Kurkjian & Paek.<sup>(19)</sup> They obtained values for the tensile strength of 0.5 m long samples measured at room temperature that were consistent with those obtained earlier by a number of workers. More importantly they were able to show that the variance which they observed in strength was just twice that for the variance in fibre diameter ( $n_s = 2n_d$ ). This dependence on variation in diameter then strongly suggests that the variation which is observed in the measured strength is not intrinsic but is the result of diameter variations (see Figure 2). The conclusion they reached from this was that there was no actual varia-

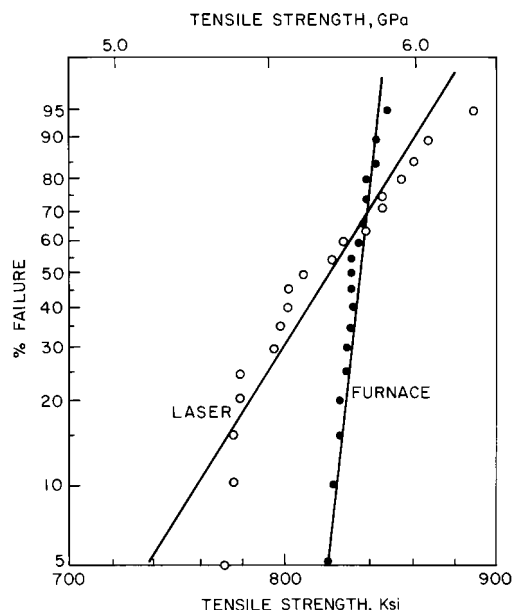


Figure 2. Tensile strength of silica fibres.  $2n_d = n_s$  (Kurkjian & Paek<sup>(19)</sup>)

tion in the fibre strength i.e. that the fibre strength was essentially single valued. This further suggests that either the flaws in the samples tested were all of the same size (severity) or perhaps more likely that there were no flaws in the sample tested. Since the measured strengths were high (>10% failure strain at room temperature corresponding to about 20% failure strain under inert conditions) we consider these measurements intrinsic. If these silica fibres were indeed flaw free, we might make the constraint ( $n_s = 2n_d$ ) a necessary condition for the measurement of the intrinsic strength. This is however only possible when all experimental variables are eliminated from consideration. In most cases where attempts have been made to measure either the intrinsic or the inert intrinsic strength, the combined experimental errors are much greater than the ~1% seen by Mould,<sup>(9)</sup> Thomas,<sup>(13)</sup> Cameron,<sup>(15)</sup> etc. In some cases the magnitude of the experimental errors can be assessed and can be shown to leave the strength values essentially single valued as suggested by Kurkjian & Paek.<sup>(19)</sup> In other cases such evaluations are not possible.

While Kurkjian & Paek<sup>(19)</sup> found that the tensile strength of 0.5 m long fibres of silica was single valued, a more recent study by Smith & Michalske<sup>(20)</sup> is also interesting. They drew and tested (in tension in high vacuum  $<10^{-8}$  torr) samples ~30  $\mu\text{m}$  in diameter and 3 mm in length. Overall for their data, they found  $n_s \sim 15n_d$  for both synthetic and natural starting materials. Consequently they separated their data into bimodal distributions with high strength modes ~14.4 and 14 GPa and low strength modes of 10.1 and 9 GPa, respectively for the two materials. These high strength mode values are approximately the same as that estimated from the Kurkjian & Paek<sup>(19)</sup> data for inert conditions.

This issue of the observed and real value of the variation of strength can be addressed by looking further at the literature. Pahler & Bruckner<sup>(18)</sup> made impor-

tant studies on the effect of drawing conditions on the mechanical properties of commercial fibreglass (E-glass) as well as several simple phosphate glasses. They studied the effects of varying the drawing conditions: draw temperature, draw rate, etc. and found that although there is an apparent dependence of strength on  $1/r$  (in the diameter range 5–15 microns) this is a second order effect in  $1/r$ . A very interesting result of these studies is that he observed variance in strengths of ~25%. Extremely precise diameter measurements must be made on fibre of this size in order to eliminate its variation from affecting the measured variation in strength.

While most recent investigators quote the total variability of their data, often no Weibull plot or other detailed description is given. Two sets of studies have however given such plots. Data from Baikova *et al.*<sup>(21)</sup> (3-point bend) and Kurkjian<sup>(22)</sup> (2-point bend) are both on phosphate glasses. The Weibull slopes are rather constant with  $m \sim 10$  consistent with their variation in diameter. However, in each case one glass was found to show a substantially tighter distribution. The glasses of Pukh are listed in Table 5 and are numbered from the start of his glasses in the table. Glass number 3 shows a tighter distribution, and is the  $20\text{K}_2\text{O} \cdot 10\text{La}_2\text{O}_3 \cdot 70\text{P}_2\text{O}_5$  glass. In the case of Kurkjian's data the tight distribution is found for the  $\text{NaPO}_3$  glass. Are these distributions real, i.e. are they due to a distribution of glass structures or are they extrinsic; somehow due to experimental effects such as the ease of drawing uniform fibres? The only way to answer this is by precisely measuring the fibre diameters and diameter distribution.

Another issue with regard to strength distributions should be mentioned here. Figure 2 shows the strength distribution as a familiar Weibull plot. The Weibull equation is developed by considering a random distribution of noninteracting flaws. It is assumed that the stress dependence of the failure probability is a power law, with the power being represented by the Weibull parameter,  $m$ . Thus for equal failure probabilities,

$$\ln s_1 / \ln s_2 = 1/m (\ln L_2 / \ln L_1) \quad (4)$$

where the mean strengths are determined at two gauge lengths,  $L_1$  and  $L_2$ . It is thus clear that if the strength distributions at a given gauge length are narrow (high  $m$ ) there will be very little (or no) dependence of strength on gauge length.

The tensile strengths that Kurkjian & Paek<sup>(19)</sup> measured were clearly not values of intrinsic inert strength. They were measured at ambient conditions and therefore as shown by Proctor *et al.*<sup>(23)</sup> were subject to delayed fracture or fatigue. Thus in order to measure the inert intrinsic strength, precautions must be taken to avoid the action of water. It has been shown that testing at low temperature or in vacuum may do this. This will be discussed in more detail below.

#### Preparation conditions

An important part of the measurement of intrinsic strengths is the preparation of pristine or flaw free samples. Thus preparation conditions play a key role. Although mostly overlooked, Griffith<sup>(8)</sup> outlined

**Table 2.** Inert intrinsic strength of silica and multi-component silicate glasses

Glass	$\sigma$ ( $IN_2$ )/GPa ( $10^6$ lb/in <sup>2</sup> )	$\epsilon$ ( $IN_2$ ) (%)	Comments	Group <sup>ref</sup>
SiO <sub>2</sub>	[17.5] [2.5]	[25]	estimated from $\epsilon_{RT} \sim 12.5\%$ (bending)RT	Griffith <sup>(4)</sup>
		est. E*		
	8.1 (1.15)	11.5	tension, 77K	Hillig <sup>(42)</sup>
	13.2 (1.9)	19	tension, 77K	Proctor <sup>(23)</sup>
	[12.7] [1.8]	17.6	2pb, est. E	France <sup>(30)</sup>
	11-14 (1.6-2)		drawn and tested in tension at $10^{-8}$ Torr RT, not 77K	Michalske <sup>(20)</sup>
	11.9 (1.7)	16.5	$10^{-8}$ Torr RT, 2pb, est. E, not 77K	Griffioen <sup>(27)</sup>
NMAZS <sup>1</sup>	10.5 (1.5)	15	2pb, est.E	France <sup>(26)</sup>
RR'BS <sup>2</sup>	[8.75]		tensile tested at RT	Shibata <sup>(46)</sup>
E-glass <sup>3</sup>	5.8		tension, 77K	Gupta <sup>(48)</sup>
AlBSiO <sub>2</sub> <sup>4</sup>	5.5		3pb, as drawn	Pukh <sup>(42)</sup>
AlBSiO <sub>2</sub> <sup>4</sup>	7.5		3pb, etched	Pukh <sup>(42)</sup>
S-glass <sup>5</sup>	8.4		tension, 77K	Gupta <sup>(49)</sup>
NaAlSi <sup>6</sup>	8.4		Na <sub>2</sub> O=Al <sub>2</sub> O <sub>3</sub>	Pukh <sup>(43)</sup>
Soda-lime-silica	7.7		oblate bubble	Ernsberger <sup>(28)</sup>
Soda-lime-silica	2.4		3pb, as drawn	Pukh <sup>(42)</sup>
Soda-lime-silica	7.5		3pb, etched	Pukh <sup>(42)</sup>

<sup>1</sup> 'Na<sub>2</sub>O.MgO.Al<sub>2</sub>O<sub>3</sub>.ZnO.SiO<sub>2</sub>'

<sup>2</sup> 14.5RO.6.9RO.13B<sub>2</sub>O<sub>3</sub>.65.6SiO<sub>2</sub> (mol%)

<sup>3</sup> 19CaO.7MgO.8.7Al<sub>2</sub>O<sub>3</sub>.8.9B<sub>2</sub>O<sub>3</sub>.56SiO<sub>2</sub> (wt%)

<sup>4</sup> 16.5CaO.4MgO.14.5Al<sub>2</sub>O<sub>3</sub>.10B<sub>2</sub>O<sub>3</sub>.54SiO<sub>2</sub> (wt%)

<sup>5</sup> 15.6 Al<sub>2</sub>O<sub>3</sub>.15.9MgO.68.5SiO<sub>2</sub> (wt)

<sup>6</sup> 50, 67 and 75% SiO<sub>2</sub> (mol%)

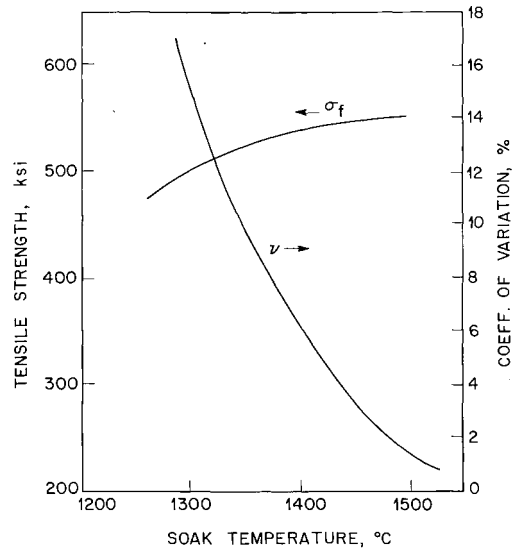
\* in order to calculate  $\sigma$  from  $\epsilon$ , E is taken as the zero stress value, i.e. 72 GPa

conditions for the production of high strength glass fibres. In addition he gave the following recipe for the production of uniformly strong fibres.

'It was found that the irregularities were due to the dependence of the strength on the following factors': (1) the maximum melting or 'cook-out' temperature of the glass; (2) the temperature during drawing; (3) the presence of impurities and foreign bodies; (4) the age of the fibre.

In the early works of Otto,<sup>(12)</sup> Thomas<sup>(13)</sup> and Cameron<sup>(15)</sup> it was rediscovered that the conditions of formation are very important. Otto<sup>(12)</sup> first indicated, and Thomas<sup>(13)</sup> and/Cameron<sup>(15)</sup> confirmed in detail, that multicomponent glasses must be heated to sufficiently high temperature (greater than the liquidus temperature) for a reasonable duration before lowering the temperature for fibre drawing. On the other hand as will be shown in Table 2, the measured strength of fused silica has remained remarkably constant since the early work of Griffith<sup>(8)</sup> in 1920. This suggests that the conditions of formation may not be of major importance in a single component glass like silica i.e. the possibility of the complications from the formation of unmelted remnants may not be a problem in a single component good glass former. Some measurements made by one of the present authors<sup>(22)</sup> on fused germania indicate that this is also the case with germania. These single component glasses may not require heating to any minimum temperature so long as crystallisation is avoided.

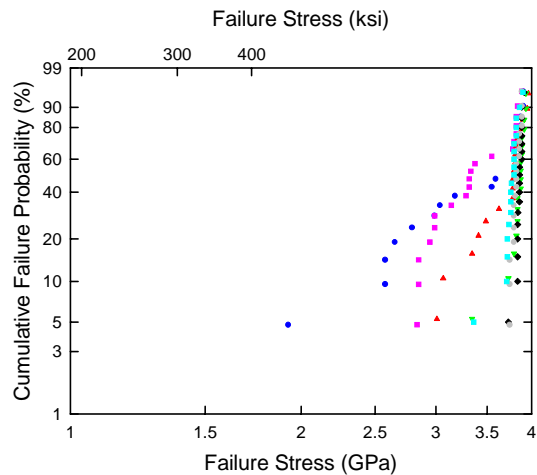
Cameron<sup>(15)</sup> gave the most striking illustration of this minimum temperature effect. These data are reproduced in Figure 3 as discussed above. Although the mean strength is not much affected by the melting temperature, the coefficient of variation is drastically reduced as the temperature is increased. Holloway<sup>(24)</sup>



**Figure 3.** Tensile strength and coefficient of variation of E glass fibres as a function of maximum melting temperature (Cameron<sup>(15)</sup>)

showed that high strength fibres could be drawn from a rod as well as from a bushing provided the minimum temperature requirement was met. While this can be done, very often when drawing from a rod especially in a continuous operation, this is not the case. It was also shown above, in the data of Parratt,<sup>(10)</sup> that by measuring short enough gauge lengths, the extrinsic flaws might be avoided. Figure 4 is a Weibull plot of the data of Cameron<sup>(15)</sup> at various 'cookout' temperatures. While at every temperature there are some samples that have the maximum strength, at lower temperatures, more and more of a low strength mode is developed. While this explains the effects seen by Mould<sup>(9)</sup> and Parratt<sup>(10)</sup> the result of Pukh<sup>(21)</sup> and co-workers (see below) on the etching of E-glass are not.

Thomas<sup>(13)</sup> studied the effects of fibre/rod diameter on strength. He found that while maximum strength was maintained, the mean value for the large diameters was much lower than that for the thinner fibres. His supposition was that the thicker fibres/rods were



**Figure 4.** Weibull distribution of E glass strength as a function of 'soak' temperature. The lowest temperatures, 2366, 2492 and 2580F show a low strength mode, Cameron<sup>(15)</sup>

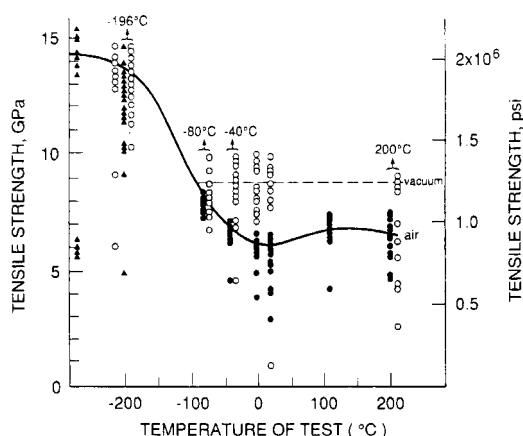


Figure 5. Tensile strength of silica fibres as a function of testing temperature (Proctor<sup>(23)</sup>)

more likely to contain more serious bubbles. Another factor that was found by Sproull & Rindone<sup>(25)</sup> to produce low fibre strengths was the presence of Pt particles in the glass. While this was found to be the case only in glasses melted for very long times, this will clearly depend on the glass composition and the level of strength being measured. A third possibility is one that we have not yet considered, that the fibre surface has aged in the time after drawing and before testing. Such effects will be discussed below.

### Testing

In order to make measurements of inert intrinsic strength it is desirable to test short gauge lengths at low temperature (77 K). It has been found that in general the simplest way to do this is in bending rather than tension. Tension requires gripping the sample. This may involve additional stresses but more importantly, measurements at low temperature involve additional gripping difficulties. Both 2 and 3 point bending techniques have been employed<sup>(11,21)</sup> but there are experimental difficulties in testing very thin strong fibres in this way. Thus for very thin fibres tension may be necessary. Overall, the 2 point technique may be preferred but in this case knowledge of the Young's modulus is necessary. This is especially the case of silica where it is known that the modulus is a strong function of the applied strain.<sup>(11)</sup> While this is not the case for 3 point bending, there is a risk of damage from the supports and some knowledge of the friction between the fibre and the support is necessary.

In earlier sections we indicated that reductions in strength could occur by stress assisted corrosion or fatigue during the measurements. As indicated, in order to reduce the effect of fatigue, inert strength measurements are made in the absence of water. Very careful measurements have been performed in 2 point bending by France *et al.*<sup>(26)</sup>, by Griffioen *et al.*<sup>(27)</sup> and by Smith & Michalske.<sup>(20)</sup> These results listed in Table 2 show clearly that a value for the inert intrinsic strength of silica glass from all these investigations is ~14 GPa or  $\sim 2 \times 10^6$  lb/in<sup>2</sup>. This is approximately  $E/5$  (72/5 ~ 14 GPa).

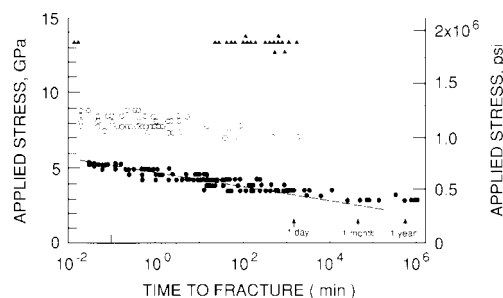


Figure 6. Tensile static fatigue of silica fibres at room temperature as a function of atmosphere (Proctor *et al.*<sup>(23)</sup>)

As indicated above, a strength measurement of a 'perfect' pristine fibre at room temperature, at ambient humidity (~50%) and reasonable testing times (s) will result in a strength which is not the 'inert' strength. This is because this strength is affected by the reaction of the fibre with the ambient moisture. This is clearly indicated in Figures 5 and 6 from Proctor *et al.*<sup>(23)</sup> for silica fibres. This reduces the impact of stress induced corrosion. In the case of silica, the ratio of the strength at 77 K to that at room temperature, 300 K, is ~2.5. Figure 7 from Ernsberger<sup>(28)</sup> shows a similar increase for a commercial soda-lime-silica glass. Thus, in those cases for which only room temperature strengths have been obtained, we may estimate the inert strength from this by multiplying by a factor of 2.5. This is clearly an approximation. In cases where stress corrosion is very serious, it might be expected that the ratio of these strengths might be higher although this is perhaps not the only factor to be considered. While E and S glasses show ratios less than this, the sodium borosilicate glasses studied by Imaoka *et al.*<sup>(33)</sup> indicate this ratio must be greater than 3.

Obviously, even in the absence of stress, corrosion by liquid water is possible. This corrosion can produce surface changes that may behave as stress concentrators. This has been found to be the case with high strength silica fibres. It would be expected to be even

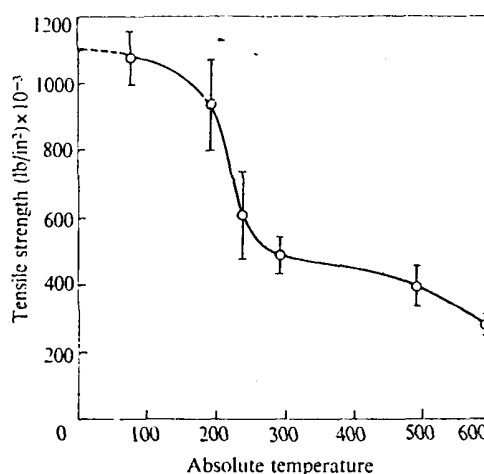


Figure 7. Tensile strength of a commercial soda-lime-silica glass as a function of temperature using the oblate bubble technique (Ernsberger<sup>(28)</sup>)

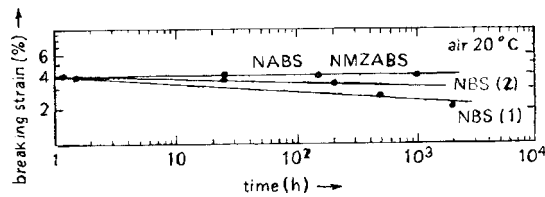


Figure 8. Ageing of experimental alkali/alkaline earth borosilicate glasses in air at room temperature. (France et al<sup>(6)</sup>)

more significant in the case of alkali containing glasses, borate glasses and other chemically nondurable glasses. This is illustrated in Figure 8 for a relatively stable multi-component borosilicate glass.<sup>(30)</sup> It has recently been shown<sup>(31)</sup> that this decrease in strength during aging can be understood on the basis of the corrosion or pitting of the glass surface. In fact this pitting may be a function of the fundamental structure of the glass.<sup>(32,33)</sup> Thus the structure and its relation to the chemical stability of the glass especially in contact with water is important to the understanding the strength as well as the stability of the strength upon ageing. Therefore, an important parameter in determining the strength of a sample is the length of time the sample has been in contact with water or water vapour before being tested. Indeed the entire thermal/chemical/mechanical history of the sample since its last exposure to high temperature is important.

#### Composition dependence of intrinsic strength

In this section we discuss those experiments which we think meet the criteria established in the third section. These data have been collected in a series of tables (Tables 2-5). These tables list the glass composition, failure stress (strength) and failure strain at 77 K as well as any clarifying comments. In addition the 'group' that conducted the research is indicated with a reference to the publication involved. Where estimates have been made, they are indicated by means of brackets []. Such estimates are primarily the calculation of values at 77 K from those carried out at room temperature (multiplying by a factor of 2.5). In cases where testing is done in 2 point bending, Young's modulus ( $E$ ) is used to calculate strength from failure strain. Although it is known that for silica,  $E=f(\epsilon)$ , we have used the zero strain value (72 GPa) for both room temperature and 77 K measurements. Another example involves measurements of Imaoka and co-workers<sup>(29,34,35)</sup> described below. In this case measurements made at low humidity (~10%) and in short times (0.001 s) have been adjusted to ambient conditions<sup>(36)</sup> and then to 77 K.

#### 1968. Aslanova<sup>(17)</sup>

These may be the first studies of the composition dependence of the tensile strength of 'pristine' fibres. Although few experimental details are given, a very interesting set of glass composition studies was made (silica, a magnesium aluminosilicate, a sodium aluminosilicate glass, a zinc titanium magnesium aluminosilicate, E-glass, probably something approaching S-glass and a soda-silica glass with 3% alumina). Studies were made on fibres that had been collected on a drum as well as fibres that had never been touched.

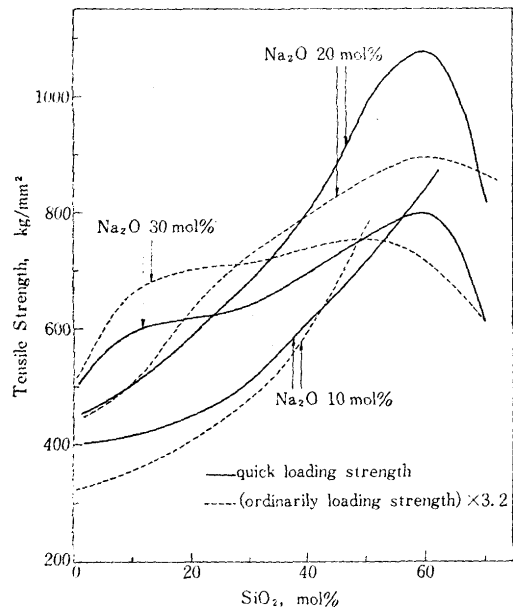


Figure 9. Tensile strength at high testing rate ( $t \sim 0.001$ s) and at ordinary rate ( $t \sim 10$ s) (Hasegawa et al<sup>(29)</sup>)

In addition, tests were carried out at room temperature as well as at 77 K. While the mean strengths were low, very high maximum values were also included. Unfortunately no follow-up, improved work was published. None of these values is listed in the tables.

#### 1971. Imaoka

This group has studied glasses in the  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  system. They developed a series of techniques that allowed them to draw and test in low humidity or vacuum environments<sup>(29,38,39)</sup> and at high strain rates (testing times of  $\sim 0.001$  s). The maximum strength measured was 10 GPa for a  $20\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 60\text{SiO}_2$  glass. Making approximate corrections for both testing time and humidity, we have estimated the inert strength of this glass to be  $\sim 5.8$ - $8.4$  GPa. The measured tensile strength as a function of composition is shown in Figure 9. The overall trends are interesting and seem to show some correlation with the expected structure of these glasses. While the trends may be qualitatively correct, in all cases, adjustments need to be made for the time and humidity of testing. In addition, as indicated above, the possibility of aging before the tests were carried out may be a problem.

#### 1974. Rindone

Starting with the study of simple mixed alkali silicate glass, in 1974<sup>(27)</sup> Rindone and his co-workers made studies of simple silicate glasses.<sup>(2)</sup> Glasses were carefully melted, drawn into pristine cane  $\sim 2$  mm in diameter and tested in three-point bending at 77 K. Most of these values now seem too low. Other measurements on simple silicates are the recent ones of LaCourse & co-workers.<sup>(37)</sup> They found that the measured strength is a function of the draw velocity. Again, while the measurements were not made at 77 K, we have estimated this value by multiplying by a factor of 2.5. In addition, one of the present authors<sup>(38)</sup> has recently

**Table 3.** Borate glasses

*Glass	$\sigma_s (IN_2)/GPa$ $\epsilon (IN_2)/\%$	$\sigma_s (10^8 \text{ lb/in}^2)$	Comments	Group <sup>ref</sup>
B <sub>2</sub> O <sub>3</sub>	1-15		3pb, 77K	Pukh <sup>(41)</sup>
B <sub>2</sub> O <sub>3</sub>		0.6	tension, 10 secs., ambient RT	Imaoka <sup>(29)</sup>
B <sub>2</sub> O <sub>3</sub>		1.2	t=10 <sup>-3</sup> s, 7%RH/RT	Imaoka <sup>(29)</sup>
B <sub>2</sub> O <sub>3</sub> <sup>4</sup>	>5.5	>25	2 pb, 77K	Kurkjian <sup>(38)</sup>
10Na <sub>2</sub> O.90B <sub>2</sub> O <sub>3</sub>		4	t=10 <sup>-3</sup> s, 7%RH/RT	Imaoka <sup>(29)</sup>
15Na <sub>2</sub> O.85B <sub>2</sub> O <sub>3</sub>	2.65		3pb, 77K	Pukh <sup>(41)</sup>
20Na <sub>2</sub> O.80B <sub>2</sub> O <sub>3</sub>		4.5	t=10 <sup>-3</sup> s, 7%RH/RT	Imaoka <sup>(29)</sup>
30Na <sub>2</sub> O.70B <sub>2</sub> O <sub>3</sub>		4.8	t=10 <sup>-3</sup> s, 7%RH/RT	Imaoka <sup>(29)</sup>
33Na <sub>2</sub> O.67B <sub>2</sub> O <sub>3</sub>	3.0		3pb, 77K	Pukh <sup>(41)</sup>
33Na <sub>2</sub> O.67B <sub>2</sub> O <sub>3</sub>	6	>8	2pb, 77K	Kurkjian <sup>(38)</sup>

estimated the strength of a Na<sub>2</sub>O.3SiO<sub>2</sub> glass at 77 K to be ~7.5 GPa. A more complete study of such glasses is important in developing a model for the composition dependence of silicate glass strength.

1978. Pukh

This group made some of the first studies and certainly the most complete studies on the strengths of simple oxide glasses.<sup>(21, 39-46)</sup> They employed a 3-point bending technique similar to that of Mould.<sup>(9)</sup> They used 100–200 μm diameter fibrers and a gauge length of ~1.2 mm. They have analysed<sup>(41)</sup> the large deflection situation applicable in such a case. Alkali borates, a variety of silicates and a large number of phosphates were studied usually at room temperature and 77 K. Some care must be taken in using these data, however. In their early studies they found the strength of silica showed a diameter dependence.<sup>(42)</sup> Because of this they were forced to use fibres ~100 μm or less in diameter. In the case of silica with its strength at 77 K of ~12–14 GPa, the deflection is extreme for this diameter fibre and the chosen gauge length. Thus they show no experimental values of their own for silica at 77 K. The extensive data at 77 K of this group are given in Tables 2–5. The effects of different network modifiers can be seen. Several things of special importance should be noted in their data in Table 2. First, while the strength of their as-drawn soda-lime-silica glass is low (2.4 GPa), chemical etching increases this to 7.5 GPa in agreement with that of Ernsberger.<sup>(28)</sup> Similarly, their data for an AlBSi glass (essentially an E-glass composition) are remarkable. The as-drawn value is the ‘accepted’ value ~5.5 GPa. After etching however, the value is substantially greater than the ‘accepted’ value ~7.5 GPa. Earlier Bartenev<sup>(16)</sup> had shown that E-glass strengths of pristine fibres decreased after etching. Also, from the work of Parratt<sup>(10)</sup> and Mould,<sup>(9)</sup> with the gauge lengths employed in the work of Pukh *et al*<sup>(40)</sup> draw conditions should not be of such great importance. The second measurements of interest are the strengths for a series of NaAlSi<sup>(43)</sup> glasses of different silica content but with equal amounts of sodium and alumina. The strengths of these glasses are essentially the same and the same as that ‘accepted’ for S-glass. S-glass is a ternary eutectic glass in the Al<sub>2</sub>O<sub>3</sub>/MgO/SiO<sub>2</sub> system, with approximately equal Al<sub>2</sub>O<sub>3</sub> and MgO contents.

Table 3 lists data on borate glasses. As perhaps expected there are large variations in values for B<sub>2</sub>O<sub>3</sub> and simple sodium borate glasses. This is probably due to aging prior to the strength measurement. It is interest-

**Table 4.** Simple silicate glasses

Glass	$\sigma_s (IN_2)/GPa$ $\epsilon (IN_2)/\%$	$\sigma_s (10^8 \text{ psi})$	Comments	Group <sup>ref</sup>
SiO <sub>2</sub>	12–14 GPa			Average lit. Rindone <sup>(25)</sup>
16.5Li <sub>2</sub> O.16.5Na <sub>2</sub> O.67SiO <sub>2</sub>	7(1)		Max. $\sigma_s = f(\text{melting})$	
33Na <sub>2</sub> O.67SiO <sub>2</sub>	3.8			Pukh <sup>(39)</sup>
25Na <sub>2</sub> O.75SiO <sub>2</sub>	2.75			Rindone <sup>(25)</sup>
25Na <sub>2</sub> O.75SiO <sub>2</sub>	[7]		tension = f(v)	LaCourse <sup>(37)</sup>
25Na <sub>2</sub> O.75SiO <sub>2</sub>	[7.5]		2pb@RT/est.@77K	Kurkjian <sup>(38)</sup>
30Na <sub>2</sub> O.10Zn.60SiO <sub>2</sub>	5-4			Pukh <sup>(39)</sup>
18Na <sub>2</sub> O.20ZnO.62SiO <sub>2</sub>	2.6			Pukh <sup>(39)</sup>
10Na <sub>2</sub> O.30ZnO.60SiO <sub>2</sub>	2.7			Pukh <sup>(39)</sup>
20Na <sub>2</sub> O.B <sub>2</sub> O <sub>3</sub> .60SiO <sub>2</sub>	[5-6-8-4]		tension, 10-3-secs, 10%RH/est.RH/77K	Imaoka <sup>(29)</sup>
60SiO <sub>2</sub>	(0.8-1.2)			

ing to see the very large values for failure strain obtained by one of the present authors<sup>(38)</sup> for pure B<sub>2</sub>O<sub>3</sub> glass. This may be the result of the more ‘planar’ structure of this glass that allows for ‘sliding’ of triangles relative to one another.

A large number of phosphate glass compositions has been studied by this group<sup>(21,48)</sup> and are listed in Table 4. The most dramatic data in this table are those for the 40Fe.60Fe glass<sup>(22)</sup> (actually ~10%Fe<sup>2+</sup>.30%Fe<sup>3+</sup>.60P<sub>2</sub>O<sub>5</sub>) and the ‘similar’ ZnO.Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub> glass. The measured strengths are unexpectedly high.

Clearly Pukh’s group has made impressive studies of the effects of composition on strength. This work needs to be studied carefully and decisions about additional studies made.

1980. France

This group from British Telecom studied silica and a series of alkali-alkaline earth borosilicates glasses<sup>(26)</sup> for optical fibre use. They used high quality raw materials as well as the high quality draw procedures used for lightguide fibres. These multicomponent glasses were drawn from a Pt bushing. The measurements were made in 2 point bending at 77 K. Since the results of this group on silica are the base line for the inert intrinsic strength of silica, it is presumed that these values can also be taken as inert intrinsic values.

**Table 5.** Phosphate glasses

Glass	$\sigma_s (IN_2)/GPa$ $\epsilon (IN_2)/\%$	$\sigma_s (10^8 \text{ lb/in}^2)$	Group <sup>ref</sup>
NaPO <sub>3</sub>	1.8 (0.26)	5	Kurkjian <sup>(22)</sup>
Zn(PO <sub>3</sub> ) <sub>2</sub>	2.4 (0.34)	5.7	Kurkjian <sup>(22)</sup>
‘laser glass’ ~20K <sub>2</sub> O.10MgO.10Al <sub>2</sub> O <sub>3</sub> .60P <sub>2</sub> O <sub>5</sub>	2.3 (0.33)	4.9	Kurkjian <sup>(22)</sup>
40Fe <sub>2</sub> O <sub>3</sub> .60P <sub>2</sub> O <sub>5</sub>	5.9 (0.84)	8.5	Kurkjian <sup>(22)</sup>
20SrO.10La <sub>2</sub> O <sub>3</sub> .70P <sub>2</sub> O <sub>5</sub>	3.4 (0.485)		Pukh <sup>(21)</sup>
25Li <sub>2</sub> O.9La <sub>2</sub> O <sub>3</sub> .66P <sub>2</sub> O <sub>5</sub>	2.7 (0.385)		Pukh <sup>(21)</sup>
20K <sub>2</sub> O.10La <sub>2</sub> O <sub>3</sub> .70P <sub>2</sub> O <sub>5</sub>	2.4 (0.34)		Pukh <sup>(21)</sup>
15K <sub>2</sub> O.5SrO.10La <sub>2</sub> O <sub>3</sub> .70P <sub>2</sub> O <sub>5</sub>	2.4 (0.34)		Pukh <sup>(21)</sup>
25(Li <sub>2</sub> O.K <sub>2</sub> O).10CaO.5Al <sub>2</sub> O <sub>3</sub> .70P <sub>2</sub> O <sub>5</sub>	1.8 (0.26)		Pukh <sup>(21)</sup>
20(Na <sub>2</sub> O.K <sub>2</sub> O)10Al <sub>2</sub> O <sub>3</sub> .50P <sub>2</sub> O <sub>5</sub>	2.4 (0.34)		Pukh <sup>(21)</sup>
35(BaO.SrO.CaO)5La <sub>2</sub> O <sub>3</sub> .50P <sub>2</sub> O <sub>5</sub>	3.3 (0.47)		Pukh <sup>(21)</sup>
15ZnO.17.5Al <sub>2</sub> O <sub>3</sub> .67.5P <sub>2</sub> O <sub>5</sub>	5.7 (0.815)		Pukh <sup>(21)</sup>
16.7Cs <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	1.64 (0.235)		Pukh <sup>(45)</sup>
16.7Rb <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	2.4 (0.34)		Pukh <sup>(45)</sup>
16.7K <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	2.46 (0.35)		Pukh <sup>(45)</sup>
16.7Na <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	3.03 (0.43)		Pukh <sup>(45)</sup>
16.7Li <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	3.4 (0.485)		Pukh <sup>(45)</sup>
33.3K <sub>2</sub> O.83.3P <sub>2</sub> O <sub>5</sub>	1.20 (0.17)		Pukh <sup>(45)</sup>
Na <sub>2</sub> Li(PO <sub>3</sub> ) <sub>2</sub>	[-1.9] (0.27)		Brückner <sup>(50)</sup>
Ca <sub>2</sub> Ba(PO <sub>3</sub> ) <sub>2</sub>	[-2.2] (0.31)		Brückner <sup>(50)</sup>

1981. Shibata<sup>(46)</sup>

This group from Nippon Telephone and Telegraph also applied their lightguide fibre preparation techniques to their glasses. They studied a series of alkali-alkaline earth silicate glasses with alumina, boron and germania substitutions. Measurements were made only at room temperature and thus the values in the table have been adjusted to 77 K. It is interesting that this group also encountered problems from Pt inclusions as did Sproull & Rindone.<sup>(25)</sup>

### Summary and conclusions

In this work we have tried to outline the conditions necessary for obtaining samples with, and measuring values of, intrinsic and inert intrinsic strength of glasses. In addition we have listed those literature values that we believe are intrinsic. While there are no absolute criteria for making judgments about the intrinsic strengths, some guidelines have been proposed. Early measurements by several groups have indicated the importance of studies of strength and composition. The particular work of the group of Pukh<sup>(21,39-45)</sup> has shown several important effects. More such measurements, perhaps in 2 or 3 point bending would be useful in understanding the nature of the strength and could shed additional light on the structure of these glasses. They would also be valuable in the design of more mechanically useful glasses.

Although our study has indicated that there are a reasonable number of glasses for which measurements of inert intrinsic strength have been measured, no complete study of a glass system has been made. With more data of this type, not only may we hope to develop a detailed theory of the strength of glasses but also correlations with other physical/chemical properties could be made. Correlation with such parameters as hardness, 'brittleness', glass transition temperature, fragility, etc. would provide valuable insights into all of these phenomena.

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