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Structure and the Intrinsic Strength of Glass

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Abstract

Pristine glass fibers have been drawn from aluminosilicate and aluminophosphate melts and their strengths determined in liquid nitrogen and in air at different humidities using a two-point bending technique. 'Inert intrinsic strength' ranges from >11 GPa for fused silica to <2GPa for alkali aluminophosphate glasses and depends on the extent of the cross-linking of the glass-forming network and the field strength of modifying cations. Fatigue effects control the 'intrinsic strengths' of fibers tested in ambient conditions.

Introduction

A variety of mechanical properties, including elastic modulus and hardness, are sensitive to glass composition and can be related to the nature of the glass structure. (See, for example, the changes in elastic moduli reported for series of sodium silicate, borate, and germanate glasses reported by Krause and Kurkjian /1/). The intrinsic strength of glass, in principle, will also depend on the composition and structure. Orowan /2/ developed a model in which the theoretical strength (σ) depends on atomic scale properties according to:

$$\sigma = (E\gamma/a_0)^{1/2} \quad (1)$$

where E is the Young's modulus, γ is the fracture surface energy and a_0 is the atomic spacing. Thus, glasses with stiffer bonds and higher elastic moduli would generally be expected to possess greater strengths. Kurkjian and Gupta /3/ recently reviewed studies of the intrinsic strengths of oxide glasses and showed that strength decreases in the order silica > aluminosilicates > alkali silicates > phosphates > borates. They note, however, that the usefulness of equation (1) for predicting the strengths of multicomponent glasses that possess a variety of atomic configurations is not clear.

Under most conditions, the mechanical strength of glass will depend on extrinsic effects, including the extent of surface damage and the ambient conditions in which the glass is tested. 'Intrinsic strength' measurements require pristine or flaw-free surfaces and 'inert intrinsic strength' measurements must be made under conditions where fatigue (or delayed failure) effects are excluded /3/. The latter measurements are done either in liquid nitrogen (77 K) or in vacuum where the activity of water is so low that the effects of stress corrosion are negligible.

In the present study, the strengths of pristine glass fibers, drawn from a variety of aluminosilicate and aluminophosphate glass melts, have been characterized in liquid nitrogen (σ_{LN}) and at room temperature (σ_{RT}) in controlled humidity using a two-point bend technique. The effects of glass composition on both σ_{LN} and σ_{RT} are discussed.

Experimental Procedures

Several series of glass compositions were prepared and characterized for this study. Calcium aluminosilicate glasses were prepared from batches of reagent grade CaCO_3 , Al_2O_3 , and SiO_2 that were heated to 1500-1650°C (depending on composition) for several hours in a platinum crucible. Alkali and alkaline earth aluminophosphate glasses were prepared from batches of reagent grade alkali (or alkaline earth) carbonates, Al_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, melted in alumina crucibles at 1000-1200°C for several hours. When homogeneous, bubble-free melts were obtained, the crucibles containing the melts were transferred to a second furnace heated to a temperature best suited for fiber-pulling. Glass fibers, approximately 100 μm in diameter, were pulled upward from melt surfaces onto a collection apparatus that yields several thousand pristine (untouched) samples, approximately 10 cm long, for strength testing.

Glass strengths were determined using a two-point bending technique that strains a U-shaped fiber (diameter= d) between two polished plates that are driven together at a fixed rate (100 to 4000 $\mu\text{m}/\text{sec}$) until the fiber fails at some faceplate separation distance (D). The fiber strength (σ) is calculated from the failure strain (ϵ) according to /4/

$$\sigma = \epsilon \cdot E = 1.198 \cdot E \cdot d / (D - d) \quad (2)$$

The Young's modulus (E) was determined using an acoustic pulse technique (at 200 kHz) on glass samples approximately 10 cm long and 1 mm in diameter that were hand-drawn from the same melts as the fibers. Strength tests were performed on fresh fibers immediately after drawing, either in liquid nitrogen or at room temperature (22°C) at known humidities. In general, at least twenty fibers were tested for each set of experimental conditions and the results are presented as a probability of failure versus applied stress using Weibull statistics.

The strengths of the test glasses were compared to those determined for two commercial glasses. E-glass fibers were drawn as described above from commercially available marbles. (The approximate composition of E glass is (mole%) 19.5 CaO ·7.0 MgO ·8.5 Al_2O_3 ·9.0 B_2O_3 ·56.0 SiO_2). Standard fused silica optical fibers (125 μm diameter) were tested after stripping the polymer coating in acetone.

Results

Figure 1 shows strength distributions for silica and E-glass fibers fractured in liquid nitrogen and at room temperature in different humidities. The Weibull modulus (m) for each data set is indicated on the plot. The inert intrinsic strengths of the silica (average σ_{LN} =11.2 GPa, E =70 GPa) and E-glass (average σ_{LN} =10.0 GPa, E =78 GPa) fibers are about twice as great as the respective room temperature strengths, a ratio that has been discussed elsewhere /3/. The difference in the room temperature

results and those at 77K indicate the important effects of stress-corrosion on the intrinsic strength of glass. The average room temperature strength of E-glass decreases with increasing ambient humidity (Figure 1, inset). The average strength in liquid nitrogen for silica is somewhat lower than that reported elsewhere (11.2 GPa vs. 14 GPa) but the room temperature strengths are similar [3].

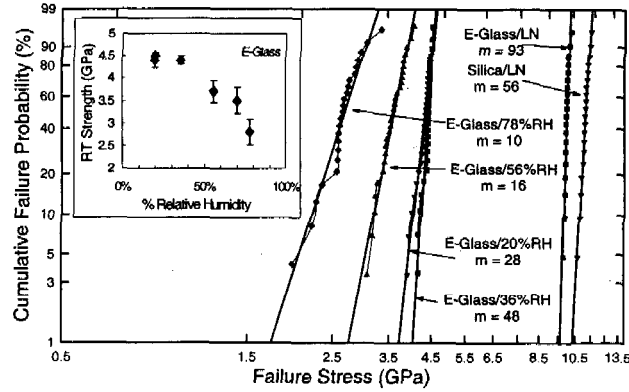


Figure 1: Weibull distributions of the failure strengths of silica and E-glass fibers tested in liquid nitrogen and in air as a function of humidity. The inset shows the average failure strength of E-glass fibers at room temperature as a function of relative humidity.

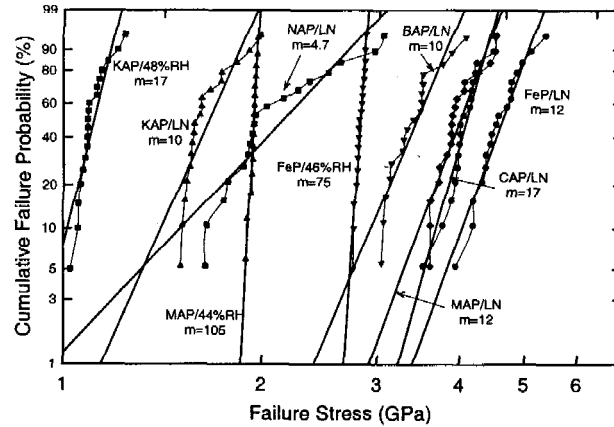


Figure 2: Weibull distributions of phosphate glass fibers tested in liquid nitrogen and in air at room temperature and known humidity.

Figure 2 shows strength distributions for fibers drawn from alkali (or alkaline earth) aluminometaphosphate glass melts with the nominal composition (mole%) $30RO \cdot 10Al_2O_3 \cdot 60P_2O_5$, where $RO = Na_2O, K_2O, MgO, CaO$ and BaO . Also shown is a data set collected from fibers pulled from a $40Fe_2O_3$

60P₂O₅ melt. (Certain iron phosphate glass compositions have unusually good chemical durabilities and have been developed for vitrifying nuclear wastes /5/.) Failure strength distributions were also collected for the Ca-aluminosilicate fibers. Those results are summarized in Table 1.

Glass	Young's Modulus	Avg. σ_{LN}	m
SiO ₂	70 GPa	11.2 GPa	56
E-glass	78 GPa	10.0 GPa	93
35CaO-5Al ₂ O ₃ -60SiO ₂	75 GPa	8.9 GPa	33
30CaO-10Al ₂ O ₃ -60SiO ₂	75 GPa	8.9 GPa	28
25CaO-15Al ₂ O ₃ -60SiO ₂	77 GPa	8.6 GPa	34
20CaO-20Al ₂ O ₃ -60SiO ₂	79 GPa	9.8 GPa	28
30Na ₂ O-10Al ₂ O ₃ -60P ₂ O ₅	47 GPa	2.3 GPa	4.7
30K ₂ O-10Al ₂ O ₃ -60P ₂ O ₅	32 GPa	1.7 GPa	9.9
30MgO-10Al ₂ O ₃ -60P ₂ O ₅	55 GPa	4.1 GPa	12
30CaO-10Al ₂ O ₃ -60P ₂ O ₅	54 GPa	4.2 GPa	17
30BaO-10Al ₂ O ₃ -60P ₂ O ₅	47 GPa	3.6 GPa	11
40Fe ₂ O ₃ -60P ₂ O ₅	58 GPa	4.8 GPa	12

Table 1: Summary of the strength measurements on glass fibers tested in liquid nitrogen; 'm' represents the Weibull modulus of the particular test.

Discussion

Kurkjian and Gupta /3/ have proposed some guidelines for judging studies of 'intrinsic strength', including narrow distributions of relatively high measured strengths. The first criterion can be evaluated by the Weibull moduli calculated from the slopes of the strength distribution plots, like those shown in Figure 1 and Figure 2. 'High strengths' are judged relative to the Young's modulus, with 'inert intrinsic strengths' reported to fall in the E/σ_{LN} range of 5 to 20 /3/.

Table 1 summarizes the liquid nitrogen results from the individual fiber failure experiments. The Weibull moduli for silica (m=56) and E-glass (m=93) are quite high, representing strength variances of 1-2%. The Weibull moduli for the phosphate and Ca-aluminosilicate glasses are lower (m ranging from ~10 to 30), representing strength variances of ~3-10%, and likely due to the poorer quality of these fibers. The phosphate melt viscosities were more sensitive to small changes in temperature, producing greater variability in fiber diameter and several of the Ca-aluminosilicate melts, particularly the 25-15-60 and 20-20-60 compositions, showed signs of crystallization at the conclusion of the fiber-drawing experiment. In fact about half of the fibers from these latter two data sets failed at low strengths and were not considered when determining the strength data in Table 1.

The average 'inert intrinsic strengths' of the glasses in this study also meet the Kurkjian-Gupta strength criterion relative to the Young's modulus; the ratio E/σ_{LN} is equal to ~6 for silica, ~8 for the aluminosilicate glasses and between ~12 and 18 for the phosphate glasses. The intrinsic strength, relative to E, increases with an increase in the extent of cross-linking of the glass-forming network, from the 'chain-like' metaphosphate structures to the 3-dimensional framework of silica.

The high failure strengths and relatively tight failure distributions make it possible to discern strength dependencies on glass composition and structure. For example, Figure 3 shows the failure strengths of the alumino-metaphosphate glass fibers increasing with the field strength of the modifying cation (z/a^2 ,

where z is the ion charge and a is the ion-oxygen bond distance). Baikova et al. /6,7/ reported similar trends for alkali aluminophosphate glasses. The structures of aluminophosphate glasses consist of phosphate anionic chains that are linked through the modifying cations and the Al-polyhedra /8/. Increasing the field strength of the modifying cations increases the 'inert intrinsic strength' of the glass by forming stronger linkages between the phosphate anions. Similar explanations have been offered to explain the effects of increasing modifier field strength on other metaphosphate glass properties, including elastic modulus and hardness /6,7/. Table 1 offers a second example of the dependence of inert intrinsic strength on structure. In the Ca-aluminosilicate series, replacing CaO with Al_2O_3 reduces the number of nonbridging oxygens as Al-tetrahedra are added to the structure. The fraction of oxygens in the $(40-x)CaO-xAl_2O_3-60SiO_2$ series that are nonbridging is given by $f_{NBO} = (40-2x)/(80+x)$. The 20-20-60 composition will have a completely cross-linked (framework) structure with no nonbridging oxygens. These compositional changes produce an increase in the inert intrinsic strength of the fibers, from 8.9 GPa for the 35-5-60 composition ($f_{NBO}=0.353$) to 9.8 GPa for the 20-20-60 sample ($f_{NBO}=0.00$).

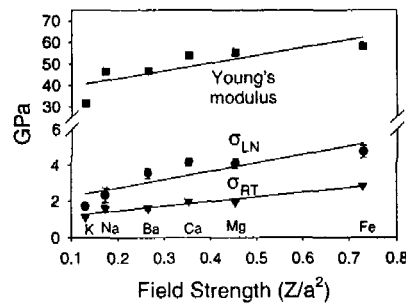


Figure 3: Young's moduli and average failure strengths of alkali and alkaline earth aluminophosphate fibers and iron phosphate fibers fractured in liquid nitrogen and at room temperature (~50% RH). The lines are linear least squares fits to the respective data.

Figure 1 and Figure 2 show that at room temperature, the intrinsic strength of a fiber is dependent on the humidity of the ambient in which the test is performed. Dynamic fatigue effects are illustrated in Figure 4, which shows strength distributions of E-glass fibers, fractured at room temperature using different faceplate velocities (v) and at different humidities. Fibers fractured with slower faceplate velocities (or lower applied strain rates) are weaker because longer times are available for stress-corrosion enhanced crack growth to occur /9/. The inset to Figure 4 shows a logarithmic plot of the average failure strength against the faceplate velocity. The inverse of the slope of each plot is related to the dynamic fatigue parameter, N , according to /9/:

$$\log(\sigma) \sim (N-1)^{-1} \cdot \log(v) \quad (3)$$

The E-glass fibers become slightly more susceptible to dynamic fatigue effects (N decreases) with increasing humidity, a trend reported elsewhere for alkali borosilicate fibers /9/.

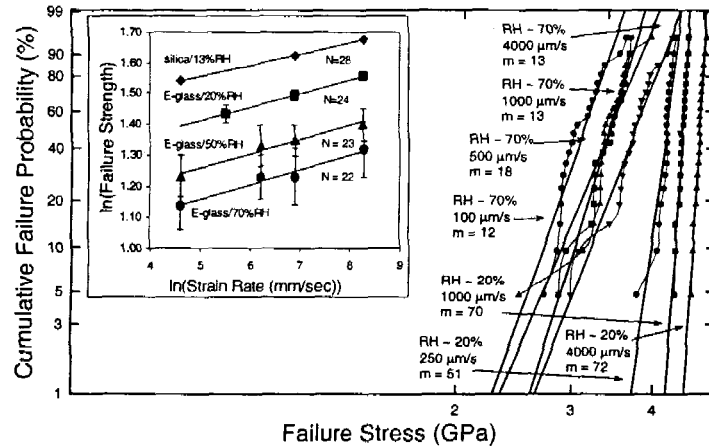


Figure 4: Weibull distributions of E-glass fibers fractured at room temperature using different faceplate velocities and under different relative humidities. The inset is a plot of fracture strength against faceplate velocity, as described by equation 3.

Acknowledgments

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