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NATIONAL BUREAU OF STANDARDS REPORT

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ENVIRONMENTAL STRESS CORROSION CRACKING OF GLASS

April 1971

Third Technical Report

Prepared for

Office of Naval Research

Department of the Navy

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ENVIRONMENTAL STRESS CORROSION CRACKING OF GLASS

by
S. M. Wiederhorn
Inorganic Materials Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

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Third Technical Report

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ABSTRACT

A review is presented on the effect of environment on the strength of glass. The structure of glass and its strength in the absence of environment are discussed briefly. Experimental results on environmental cracking of glass are presented. Finally, theoretical treatments are given and discussed with respect to available experimental data.

1. INTRODUCTION

Glass is an inert material that is used where chemical resistance is needed. Despite this resistance, glass is susceptible to stress corrosion cracking known as static fatigue. This phenomenon is caused by water in the environment, and because of its practical importance, a large body of knowledge has been accumulated on the subject. This paper briefly reviews the phenomenon of static fatigue. The structure of glass and its strength in the absence of corrosive environments are discussed. The experimental facts of static fatigue are reviewed and, finally, theoretical treatments are given. This paper supplements previous review papers on the subject[1-7] and concentrates on more recent work in the field.

2. STRUCTURE OF GLASS[2,8]

Unlike crystalline materials, glass contains no long-range order. Evidence for this conclusion comes from x-ray investigations which reveal only broad diffuse diffraction spectra.[9] These patterns differ from those obtained on crystals, but are similar to patterns obtained on liquids and amorphous gels, figure 1. They are consistent with the interpretation that glass contains silicon atoms located at the center of oxygen tetrahedra which are connected at their corners and arranged in space in a random continuous network,[10,11] figure 2. Cations such as Si^{+4}, Al^{+3}, and B^{+3} that tend to form tetrahedra or other coordinated units with oxygen are known as network formers. Other cations, such as alkali or alkaline earth ions, are called network modifiers, and lie in open spaces in the network structure. Glass normally forms a loosely packed structure as a result of the random arrangement of the silicon-oxygen tetrahedra. Its density may be increased by slow cooling from the melt or by application of high pressures.[12-14] Most glasses used in strength studies have silica as the major constituent, table 1.

At low temperatures, glass behaves as a rigid solid, since its thermal expansion coefficient is close in magnitude to that of a crystalline solid[8], figure 3. The temperature at which the transition from super-cooled liquid to solid occurs is called the fictive temperature. At the fictive temperature, relaxation processes in the glass become so slow that the structure of the glass becomes frozen. Physical properties of glass can be characterized by the fictive temperature which depends on the composition of the glass and on its thermal history.

Not all silicate glasses are mutually soluble. Consequently, many glasses are not homogeneous and consist of multicomponent structures[15, 16], figure 4. Second phase formation in glass is believed to occur by both nucleation and growth and by spinoidal decomposition. The effect of two phase structure on strength or stress corrosion is not well known.

3. STRENGTH OF GLASS[4-7]

It has been stated that in measuring the strength of glass, one is actually measuring the weakness of its surface.[17] This weakness is caused by cracks normally present in the surface of the glass. Phenomenal increases in strength can be obtained by removal of surface flaws. For example, the strength of bulk glass can easily be increased from approximately 5,000 to 500,000 psi by chemically polishing it with hydrofluoric acid solutions.[6] The highest strength to be achieved was

2×10^6 psi on small flame polished silica rods.[4] High strength is not related to the size of the specimen, as was once believed, but to the perfection of the specimen surface.

Glass at room temperature is one of the most brittle substances know. The yield stress, as estimated from hardness indentations, is greater than 10^6 psi.[18] The fracture energy in the absence of water has been shown to range from 3.5 to 4.8 J/m^2, depending on the glass composition[19] and is insensitive to temperatures from -196°C to 25°C. These energy values are two to four times that expected theoretically and are four orders of magnitude less than those obtained on ductile metals.

The extent of plasticity at crack tips in glass can be estimated from the Dugdale[20] model of plastic flow at a crack tip. The length of the plastic zones for soda-lime silicate and silica glass are calculated to be 2.6×10^{-9}m and 6.4×10^{-10}m respectively, while the crack tip displacements prior to fracture are calculated to be 4.5×10^{-10}m and 2.2×10^{-10}m, respectively.[19] Other plastic flow models give similar results.[18,21] These dimensions are not much larger than the silicon-oxygen bond distance, 1.6×10^{-10}m, or the oxygen-oxygen bond distance, 2.6×10^{-10}m in silicate glass and, consequently, the amount of plastic deformation from crack tips in these glasses is small. The very small plastic zone size is responsible for the very brittle nature of glass.

The nature of plastic deformation in silicate glass is a matter of controversy. Plastic deformation has not been observed in silicate glasses tested in tension, bending or compression. Glass is elastic and failure occurs without evidence of a yield stress. In contrast, glass can be deformed during the placement of hardness indentations or by scratching with hard materials.[18,23] Some have accepted these observations as evidence of plastic deformation. Others[24, 25] have noted that deformation at hardness-indentations results primarily from densification of the glass and not from volume conserving shear deformation. The relationship between this type of deformation and that which occurs at crack tips is not understood and remains a subject for future investigation.

Stress fields and stress gradients at crack tips are very high as a direct consequence of the brittle nature of glass. These stress fields and gradients give rise to enhanced chemical activity of the glass surface and to enhanced ionic transport through the network structure, both of which are important to static fatigue. Stress enhanced chemical activity results in crack elongation and ultimately failure, while stress enhanced transport results in parasitic stresses at the crack tip and chemical modification of crack tip solutions. Thus, the rigid network structure that makes glass so brittle also contributes to static fatigue.

4. EXPERIMENTAL ASPECTS OF STRESS CORROSION

A number of experimental techniques have been used to investigate the static fatigue of glass. By far, the largest amount of data has been obtained from flexural studies in which the time to failure is measured as a function of variables such as environment, temperature, glass composition and surface structure. Tensile tests on glass fibers and crack growth studies also have yielded a large body of knowledge on the subject of static fatigue.

4.1 FLEXURAL STUDIES

The static fatigue of glass can be characterized by a time delay to failure, figure 5. Glass becomes weaker as the required duration of load increases. For very long durations, there appears to be a threshold stress below which failure will not occur. This threshold stress, called the fatigue limit,[1,26] is approximately 20 percent of the environment-free strength.

Static fatigue is caused by water in the environment.[27-30] Glass that is baked out and tested in vacuum shows little fatigue.[28,29] Similar results are obtained for tests conducted in liquid nitrogen which reduces the chemical activity of water. In contrast, when tested in water or air, static fatigue occurs within time intervals as short as 10 milliseconds.[30] Comparison of cyclic and static tests demonstrate that the time to failure depends on the magnitude and total duration of the load, but not on its cyclic nature.[31] Permanent weakening has been reported due to temporary pre-stressing of glass.[1] Finally, in the absence of stress, glass left immersed in water, steam, or air tends to gain strength.[30,32,33] Glass is weakened by water at stresses above the fatigue limit, but strengthed at stresses below the fatigue limit.

Previous investigations on the effect of temperature, load duration and environment on the strength of glass, are summarized in figure 6.[34] The strength of glass as a function of temperature can be divided into four regions.[34] At low temperatures, region A, water is chemically inactive and strength is independent of temperature, loading rate and environment. At higher temperatures, region B, water becomes chemically active and static fatigue is observed. At still higher temperatures, region C, water desorbs from the crack surface, plastic flow may occur at the crack tip and the strength increases with temperature. Finally, strength decreases rapidly as glass approaches its softening point, region D.

Static fatigue has been shown to be an activated process[35] by Charles who conducted studies in which fatigue curves were obtained at temperatures ranging from -170°C to 242°C. A plot of the logarithm of the time to failure versus reciprocal absolute temperature gave a straight line whose slope corresponded to an apparent activation energy of 18.8 Kcal per mole, figure 7. This value was close to that obtained for the corrosion of the same glass,[36] 20 Kcal per mole, and was also close to the activation energy for sodium ion diffusion in glass,[37] 17-23 Kcal/mole. Charles suggested that the three processes were related and that static fatigue resulted from a corrosive attack of water on the silica network at the crack tip in which sodium ion diffusion was the rate limiting step for the reaction.

One of the most definitive studies on the static fatigue of glass was performed by Mould and Southwick.[38] Four point bend tests were conducted on soda-lime silicate glass slides that had received various surface abrasion treatments. The load duration ranged from 2 x 10^{-3} to 600 seconds. Strength, time to failure plots gave a distinct curve for each abrasive treatment. A single curve fitting all of the data was obtained by plotting the relative strength, σ/σ_N, as a function of the logarithm of the reduced time to failure, $\log_{10}(t/t_{0.5})$, figure 8, where σ_N is that measured in liquid nitrogen, t is the time to failure and $t_{0.5}$, the characteristic duration, is the time to failure of a specimen loaded at half its liquid nitrogen strength. The strength of glass in liquid nitrogen characterizes its flaw structure, since static fatigue is inoperative at liquid nitrogen temperatures. The characteristic duration and the slope of the curve give a measure of the rate of static fatigue. For the two different types of abrasive treatment, classed as "point" and "linear," the characteristic duration was found to be related to the liquid nitrogen strength by $\ln t_{0.5} = A + B/\sigma_N^2$. This relationship implies that flaws of greater severity fatigue more slowly under stress than do less severe ones. This type of curve, termed the universal fatigue curve, is valuable for theoretical and engineering purposes.

The strength and static fatigue of soda-lime silicate glass were also studied in environments other than air or water.[39,40] The characteristic duration, $t_{0.5}$, increased dramatically when tests were conducted in relatively dry nitrogen gas,[39] however the slope of the universal fatigue curve was unaffected by the water content of the gas. The difference in fatigue behavior was attributed to a decrease in concentration of water at the tip of a growing crack, and not to a change in mechanism.

Organic liquids also affect the fatigue properties of soda-lime silicate glass. Strength measurements made in dry alcohols were observed by Moorthy and Tooley[40] to be 19 to 36 percent greater than those made in water. Smaller increases in strength were found in tests made in heptane, benzene and toluene while a decrease in strength was observed in tests conducted in nitrobenzene. Fatigue curves obtained on specimens immersed in methyl or isopropyl alcohol do not fit the universal fatigue curve for tests conducted in water.[39] No satisfactory explanation for the fatigue behavior of soda-lime silicate glass in organic liquids has been presented.

The effect of electrolyte pH on the strength of glass has been investigated by Mould.[39] He found the strength to be constant for test solution pH ranging from 1 to 13, figure 9. Strength increases were observed at high pH and decreases were observed at lower pH. These results cannot be interpreted easily in terms of a stress corrosion mechanism because high pH solutions would be expected to weaken rather than strengthen the glass. Sodium-hydrogen ion exchange at the crack tip however could explain the experimental observation. In contrast to Mould's results, Hillig[41] observed that 10 percent NaOH solutions greatly reduced the fatigue resistance of fused silica rods. This difference in behavior may be a result of compositional differences or the fact that Hillig studied flame polished rather than abraded specimens.

Static fatigue can be studied by measuring strength as a function of loading rate,[42-44] figure 10. The slope of the curve can be related theoretically to the motion of cracks that cause failure. Results are in good agreement with those obtained by direct measurement of crack velocity, and suggest that crack growth is an important part of the fatigue process. The technique can be used to select compositions having high resistance to static fatigue, since the slope of the strength versus loading rate correlates with fatigue resistance.

The static fatigue behavior of glass can be altered by chemical polishing. Ritter and Sherburne[44] have observed that data from chemically polished soda-lime silicate glass does not agree with the universal fatigue curve obtained on abraded soda-lime silicate glass. Fatigue behavior is closer to that of silica and alumino-silicate glass fibers, figure 11, and may result from the relative perfection of the glass surfaces. The kinetics of the fracture process and the local environment at relatively perfect surfaces may differ considerably from those found at the roots of surface cracks.

4.2 TENSILE STRENGTH STUDIES ON GLASS FIBERS

The most extensive study of the static fatigue of silica glass fibers was conducted by Proctor, Whitney and Johnson.[45] Studies were conducted in liquid helium, liquid nitrogen, and in vacuum and air at temperatures ranging from -196°C to 500°C. In liquid helium and nitrogen, strengths were found to be approximately 2 x 10^6 psi, confirming findings of other authors.[41,46] This high strength value is close to the theoretical cohesive strength of silica glass 2-4 x 10^6 psi[19] and suggests that the glass fiber surfaces were relatively perfect. Imperfections that might be present were probably the size of the open spaces of the silica network.

Static fatigue of silica fibers was observed in air, but not in liquid nitrogen, figure 12. The fatigue limit was approximately 20 percent of the liquid nitrogen strength. The slope of the universal fatigue curve differed from that of abraded soda-lime silicate glass, figure 11, possibly due to differences in glass composition or surface condition. Static fatigue was attributed to water adsorbed on the glass surface. It was suggested that water diffuses on the glass surface to a site at which breakdown of the silica network is initiated.

Once reaction has started at a particular site, rupture of the network throws extra load on the surrounding structure, making further reaction probable. Strength reductions of silica fibers tested in vacuum was attributed to residual moisture adsorbed in the glass surface.

Some studies of dynamic effects were conducted by Proctor et al. with mixed results. When silica fibers were subjected to square pulse stresses, static fatigue resulting from each pulse was additive, suggesting no effect of cyclic loading. Earlier studies by Whitney, Johnston and Proctor[47] do indicate a weakening effect in excess of that expected from static fatigue when cyclic loads were applied to silica rods and fibers. It was also suggested that high prestressing may influence the subsequent fatigue life, greatly extending it in some cases.[45]

Studies on glasses of the compositions used commercially for the production of glass fibers, principally E-glass, table I, have been reported by a number of authors.[48-54] As in the case of fused silica, very high strengths were found at liquid nitrogen temperatures,[48,50] 8×10^5 psi. At room temperature, the strength in air is reduced to much lower values due to the presence of water in the environment. Static fatigue has been observed, but there is disagreement as to the exact shape and position of the fatigue curve.[44] A fatigue limit has not been obtained for E-glass. The slope of a static fatigue curve derived by Ritter from data by Hollinger et al.[54] is close to that for silica glass fibers and chemically polished soda-lime silicate glass, figure 11, but differs from that obtained from surface abraded soda-lime silicate glass. This difference may reflect differences in reaction mechanism between relatively perfect and severly damaged glass surfaces. The weakening process in E-glass is believed to involve surface adsorption of water from the environment.[49]

Strength degradation of E-glass fiber is observed even in the absence of stress and is attributed to water in the environment. Thomas[48] has shown that fibers tested in air after exposure to 100 percent relative humidity experience a strength reduction of approximately 30 percent over a period of 128 days storage, and 15 percent during a 32 day storage. Storage in vacuum for a 28 day period does not result in strength degeneration. Similar studies on fused silica fibers[45] give no indication of strength reduction due to stress-free storage in moist environments. In contrast, strength increases are observed when abraded soda-lime silicate glasses are stored in water.[33]

Insight into the stress-free weakening process has recently been obtained by Metcalfe et al.[53] It had been demonstrated earlier that hydrochloric acid is detrimental to the strength of E-glass.[48] Using modified E-glass that contained 5 percent Na_2O or K_2O, Metcalfe et al. demonstrated that glass fibers will crack spontaneously when exposed to hydrochloric acid of pH 2. It was clearly demonstrated that the cracking resulted from stresses due to ion exchange between the alkali ions in the glass and the hydrogen ions in solution. This process is the reverse of that commonly used to chemically strengthen glass. The weakening mechanism occurs more slowly in neutral solutions, can be retarded by the addition of alkali ions to the test solution and can be reversed by reducing the hydrogen ion concentration of the test solution after exposure to HCl. The requirement of mobile alkali ions explains the absence of stress-free strength degradation in fused silica. Ion exchange may be the dominant factor influencing the strength of glass fibers containing alkali ions.

4.3 INDENTATION STUDIES

If a sphere is loaded normally on a flat surface of glass, a conical crack will initiate and grow from a point just outside of the circle of contact between the sphere and glass surface. This phenomenon was observed first by Hertz in 1881 and is known as Hertzian fracture.[55] This technique may be used to study the influence of environment on the fracture of glass.[56-58]

Results from indentation studies are in good agreement with other studies of the effect of environment on the fracture of glass. Roesler[56] and Culf[57] used flat-ended indenters to demonstrate a severe weakening effect of water. The critical load for crack formation and the fracture energy calculated from it were reduced by a factor of two when water was present. Tests in other environments also suggested a weakening effect, however, the possible presence of small amounts of water could not be eliminated.

More recent studies by Langitan and Lawn[58] clearly demonstrate a static fatigue effect caused by water. In agreement with Charles[35] the effect has a demonstrable temperature dependence, although the apparent activation energy for the process has not been determined. The effect of acidity on the fracture process was clearly demonstrated and results were similar to those obtained by Mould.[39] Strengthening was observed in strong sodium hydroxide solutions while weakening was observed in hydrochloric acid.

4.4 FRACTURE MECHANICS STUDIES

The first fracture mechanics studies on the effect of environment on the fracture of glass were conducted by Berdennikov[59] who measured the load to initiate crack motion in center cracked tensile specimens. Results were expressed in terms of the fracture energy of glass in various environments. Unfortunately, the equation relating surface energy to load was in error, giving results too low by a factor of approximately 3.2.[60] Corrected values of Berdennikov show that water reduced the fracture energy of glass from 4.06 J/m^2 in vacuum to 0.966 in water. Organic environments were also found to reduce the energy required for fracture, and Berdennikov was able to demonstrate a relationship between the dielectric constant of the test medium and the fracture energy.

Later experiments were carried out using edge notched, center notched and double cantilever type specimens.[60-67] Crack velocities were measured as a function of stress intensity factor or fracture energy and studies were conducted in vacuum, in gases containing varying percentages of water vapor and in distilled water. Variation of temperature permitted the evaluation of activation energies for the process.

Crack velocity studies, conducted in vacuum,[66] indicate that the logarithm of the crack velocity can be expressed as a linear function of the stress intensity factor or the fracture energy, figure 13. Fracture is an activated process with a zero load activation energy of 80 Kcal/mole. This activation energy is close to the Si-0 bond energy and suggests that fracture of silicate glass in vacuum is due to thermal fluctuations.[66]

Crack propagation studies in air or nitrogen gas containing varying amounts of water indicate at least three modes of behavior,[63,64] figure 14. At low stress intensities, the crack velocity depends exponentially on the stress intensity factor and also on the relative humidity of the gas. At medium stress intensities, the crack velocity depends on the relative humidity, but is nearly independent of the stress intensity factor. At high stress intensity, the results are independent of environment. The first two modes of behavior have been attributed to stress corrosion cracking at the crack tip.[63] In mode I, the rate of crack propagation is reaction rate limited while in mode II the rate of propagation is transport rate limited. Detailed calculations give good support of the suggested mechanism.[63] The temperature dependence of the crack velocity in mode III is the same as that obtained in vacuum[64] suggesting that the fracture mechanism is also controlled by thermal fluctuations of Si-O bonds.

Fracture mechanics studies conducted in distilled water indicate a dependence of crack velocity on glass composition,[67] figure 15. At high crack velocity, all glasses exhibit an exponential dependence of crack velocity on stress intensity factor. At lower velocities, the crack velocity decreases at a greater than exponential rate for soda-lime silicate and borosilicate glasses suggesting a fatigue limit. Fused silica and aluminosilicate glasses exhibit exponential behavior over the entire range of variables studied. There is no evidence of a static fatigue limit, though presumably one exists at a lower stress intensity factor. At velocities greater than those indicated in figure 15, the increase in crack velocity with stress intensity factor is less than exponential[64] for soda-lime silicate glass. Other glasses have not been investigated in the high velocity range. In the exponential region, the glasses are found to fit the following empirical equation,

$$v = v_o \exp(-E^* + bK_I)/RT, \qquad (1)$$

where v_o, E^* and b are empirical constants, see table II.

A relationship between crack velocity data and static fatigue data can be demonstrated by calculating universal fatigue curves from the crack velocity data.[67] Calculated curves, figure 16, are found to agree with those obtained for abraded soda-lime silicate glass[38] and fused silica fibers.[45] This agreement suggests that crack growth is an important part of the static fatigue process.

5. THEORIES OF STATIC FATIGUE

5.1 THE ROLE OF PLASTIC DEFORMATION

One of the first explanations of static fatigue was given by Murgatroyd,[69] who assumed that weakening occurred because of a viscous process in the glass. One of the reasons that the theory was not accepted was that its quantitative aspects did not satisfy the universal fatigue curve.[4] More recently, the possibility of viscous processes playing a role in fracture has been reconsidered by Marsh.

Marsh[18,70] has assumed that the failure of glass is entirely due to plastic yielding, the yield stress being less than that required for tensile fracture. The fact that a macroscopic yield stress has never been observed is explained by the assumption that plastic flow in glass is not of a strain hardening type. Therefore, no mechanism exists for stabilization of the plastic flow. Water is thought to play a role by penetrating the glass and softening it.

Marsh's assumptions are based largely on his experiments on the hardness of glass and the relationship of hardness to tensile strength. He and others[23] noted that hardness indentations and scratches in glass give the appearance that plastic flow has occurred. By revising the yield stress-hardness relationship, he was able to demonstrate that the calculated yield stress was equal to the fracture strength of glass. Both the fracture stress and yield strength depended on moisture in the environment. Glass was softer at higher relative humidities and the hardness was time dependent. Observations of environmental softening by Westbrook and Jorgensen[71] and by Westwood et al.[72] add support to Marsh's observations.

Additional evidence for plastic flow is the high fracture energies obtained on glass, which Marsh attributes to plastic blunting of crack tips. Unfortunately, the theoretical aspects of Marsh's ideas have not been developed and, until they are, a closer comparison of his ideas and the available data on static fatigue cannot be made.

5.2 THE ROLE OF ALKALI IONS

The motion of alkali ions through the glass structure may play an important part in the fatigue process. Ion transport may raise the stress at glass surfaces, thus increasing the probability of fracture, or it may enhance the chemical reaction rate at crack tips by either modifying the corrosive environment or changing the chemical potential at the surface.

The theory recently proposed by Cox[73] ascribes to alkali ions a local bond weakening influence due to the elastic strain that accompanies the ions as they migrate through the glass. Fracture occurs when a number of ions cooperate to initiate a self generating flaw. The theory is based on statistical arguments and relates parameters such as time to failure, failure stress, temperature, area of loading, bond strength, probability of failure, flaw structure and activation energies for the formation and motion of interstitial alkali ions.

A serious objection to Cox's theory is its failure to account for the charges carried by the alkali ions.[7] The electrostatic energy created by the clustering of alkali ions depends on the size and density of ions in the cluster and is of the same order of magnitude as other energy terms used to calculate the probability of failure. Cox did not consider the energy of cluster formation in his calculation, but recognized its importance and suggested that excess positive charges are neutralized by others in the environment. Although alkali ions play an important role in the fracture process, the equations developed by Cox are quite insensitive to the absolute concentration of alkali ions.

Comparison of Cox's theory and experiment leads to mixed results. The theory is specific in relating strength to area under load and good agreement is found between this prediction and the strength values obtained by Griffith[74] on soda-lime silicate glass fibers. Agreement may be fortuitous since Loewenstein and Dowd[75] have recently shown that the strength of A-glass, a soda-lime silicate composition, was constant over a fiber diameter size range of from 1.5 to 4 x 10^{-4} inches. In contrast, a factor of 2 change in strength was observed by Griffith over the same size range. Furthermore, the size predictions are not in accord with the relative strength insensitivity to dimensions of E-glass fibers[48] and silica rods and fibers.[41,45] Other aspects of the theory seem to agree with experimental observations.

Metcalfe, Gulden and Schmitz[53] have given evidence of the effect of ion exchange on the strength of glass fibers. The exchange of sodium ions in the glass with hydrogen ions in solution undoubtedly accounts for the stresses that cause spontaneous fracture of sodium modified E-glass and for the observed decrease in glass fiber strength with time in moist environments.[48] The lack of sodium ions in fused silica also accounts for the lack of stress-free strength degradation in silica fibers[45] The occurrence of ion exchange at crack tips of abraded glass may account for the relative weakening of abraded glass in low pH solutions and the relative strengthening in solutions of high pH.[39] Finally, the observation that the loading rate dependence of strength is an activated process is in agreement with ion exchange as a mechanism, since diffusion of sodium in glass is known to be an activated process. A more detailed commentary on the work of Metcalfe, Gulden and Schmitz will have to await the application of the theory of ion exchange to the sodium-hydrogen exchange process, and possibly the collection of additional data on the process. Nevertheless, their observations mark a significant development in understanding the static fatigue process.

5.3 THE ROLE OF CHEMICAL INTERACTION

Water is known to react chemically with glass, resulting in dissolution of the silicon-oxygen network.[76,77] This process is slow, depending on temperature, hydroxyl ion concentration and glass composition. Glasses containing large amounts of sodium ions dissolve more easily than those containing small amounts. Considering these facts and those presented earlier on static fatigue, it is logical to assume that water behaves as a chemical agent that controls the strength of glass.

The concept of water as a stress-corrosion agent originated with Guerney[31] who suggested that a corrosive environment would preferentially attack a crack at its root where bonds are severely stretched. The elastic energy of the bond would aid the chemical reaction and chemical corrosion would occur preferentially at the crack tip. The time to failure would be equal to the time necessary for a crack to grow from subcritical to critical Griffith size. The particular theory derived by Guerney did not fit the available experimental data.

Charles[42] made the assumption that the rate of flaw growth was a power function of the crack tip stress, $v = (v_o\sigma^n)(\exp A/RT)$, and derived relationships that adequately fit the existing experimental data. n was found to be a function of the glass composition.[43] Recently, Ritter and Sherburne[44] used Charles's treatment to describe the loading rate dependence of the strength of glass and showed that exponents obtained were consistent with crack velocity data obtained by Wiederhorn,[67] suggesting the important role of crack propagation in the failure of glass, table III.

Another theory of crack propagation was developed by Charles and Hillig[68,78] who assumed that crack propagation was an activated process in which the activation energy was stress dependent. Their basic equation for crack velocity can be developed from the absolute rate theory of chemical reactions.[79] If the rate limiting step for crack propagation is assumed to be an attack on the silicon-oxygen bonds by hydroxyl ions, then the crack propagation equation is,

$$v = v_o\ [OH^-]\ [A_g]\ \exp\ [(-\Delta E^{\ddagger} + \sigma \Delta V^{\ddagger}/3 - V_M\ \gamma/\rho)/RT], \qquad (2)$$

where $[OH^-]$ is the hydroxyl ion activity at the crack surface. $[A_g]$ represents the chemical activity of a flat glass surface in contact with the corrosive environment. The first term in the exponential, $\Delta E^{\ddagger}$, represents the activation energy for the chemical reaction. σ gives the stress at the glass-liquid interface and $\Delta V^{\ddagger}$ the activation volume for the chemical reaction. The final term in the exponential accounts for the changing chemical activity of the glass surface with surface curvature. V_M is the molar volume of the glass. γ is the interfacial surface tension at the glass medium interface and ρ is the radius of curvature of the crack surface. Charles and Hillig used Eq. (2) as a starting point to develop the relationship between the rate of crack propagation and the geometry of the crack surface. For a given glass composition and chemical environment, the radius of curvature and stress at the crack surface are the only variables in Eq. (2) and therefore control crack geometry and the rate of crack motion. Changes in flaw geometry due to chemical attack could be demonstrated by considering the relationship between ρ and σ in Eq. (2) and the Ingles stress concentration equation, $\sigma = S\ [1 + 2\ (L/\rho)^{\frac{1}{2}}]$, where S is the applied stress and L is the half length of an elliptical crack. At stresses greater than a characteristic threshold value, flaw sharpening occurred, and ρ decreased as the crack advanced, figure 17. Conversely, below the threshold stress, crack blunting occurred. The threshold stress was interpreted to be the static fatigue limit. The chemical theory of static fatigue is in agreement with most experimental observations on the subject.

Several aspects of the chemical theroy of static fatigue should be discussed further. The theory as developed is applicable only to glass containing cracks. In a number of cases, flaw-free glasses have been studied.[45] Attack of flaw-free surfaces is believed to initiate from preferential sites on the glass surface where bonds are most severely stretched. The rate of attack is governed by the kinetics of the chemical reaction, but the details of the fatigue process may differ from that given for specimens containing flaws because of geometrical considerations. This, in part, may explain the difference in results for abraded and chemically polished soda-lime silicate specimens.

The theory derived by Charles and Hillig does not account specifically for environment at crack tips. Other kinetic processes may occur which control the crack tip environment and the crack propagation rate. Results on the propagation of cracks in gaseous nitrogen[63] indicate a region of crack propagation that is limited by the rate of water transport to the crack tip. The hydroxyl ion concentration at crack tips may be governed by chemical reactions at the glass surface, thus accounting for gross differences in behavior among glasses of different composition.[67] Control of the crack tip environment by surface chemical reactions may be more important for deep cracks than for shallow cracks or for relatively flaw-free surfaces because of the small volume of solution at the crack tip and the long diffusion distance necessary to equalize bulk and crack tip environment. Thus, differences in behavior for specimens containing abraded versus relatively flaw-free surfaces may be attributed to differences in surface environment. Similar suggestions have been made recently for stress corrosion cracking of metals.[80-82]

An early theory of static fatigue, developed by Orowan,[83] attributed the phenomenon to a decrease in surface energy caused by water adsorption at the glass surface. Orowan noted that the fracture energy of mica measured in vacuum was ten times that found in air and suggested that this relative difference in fracture energy would lead to a strength reduction of approximately one-third, agreeing quite well with experimental observation. The kinetics of the fracture process can be described by absolute rate theory provided that the adsorption process involves chemisorption. The assumption of a chemisorption process is reasonable because surface water is known to be strongly bound to glass surfaces. Thus, an equation identical in form to Eq. (2) can be derived for a chemisorption process. The static fatigue limit would be defined by the minimum stress level compatible with glass surface energy and the Griffith condition for failure.

The occurrence of chemical attack at crack tips or glass surfaces does not preclude the possibility of other simultaneous processes. Thus, the changes in strength of abraded glass specimens tested in high and low pH solutions may indicate that sodium-hydrogen ion exchange is accompanying crack growth caused primarily by chemical attack. Because water-induced weakening is observed even in sodium-free glass fibers, it is possible that chemical corrosion accompanies sodium-hydrogen ion exchange at glass fiber surfaces. Therefore, while stress enhanced chemical corrosion may appear to be the most probable explanation of static fatigue, it may not be the only process involved.

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FIGURE CAPTIONS

1. X-ray diffraction patterns of cristobalite, silica gel, and vitreous silica. (after Kingery [8])
2. Schematic representation of a sodium silicate glass. (after Warren [10])
3. Relation between liquid, crystalline, and vitreous state. (after Kingery [8])
4. Two phase glass structure. This electron micrograph shows a sodium borate glass that has separated on cooling into two continuous and interpenetrating phases, each of them a glass. (after Charles [84])
5. Static fatigue curve for annealed soda-lime glass rods, 1/4 in. diameter, tested in bending. (after Shand [1])
6. Relative strength of glass tested in air as a function of temperature and load duration. Semi-quantitative composition curves from several investigations. The relative strength is the ratio of the applied stress, σ, to the strength in liquid nitrogen, σ_N. (after Mould [34])
7. Temperature dependence of delayed fracture process. The applied stress was 7 Kg/mm^2. (after Charles [35])
8. Universal fatigue curve. Symbols represent various abrasion treatments. The error bar gives the uncertainty for individual points. (after Mould and Southwick [38])
9. Strength at 0.82 - second load duration vs. pH for specimens immersed in HCl, in NaOH, and in buffer solutions. (after Mould [39])
10. Effect of loading rate at room temperature on the most probable

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11. Static fatigue of silicate glasses. 1) acid etched soda-lime glass, 2) E-glass fibers, 3) silica fibers, 4) abraded soda-lime glass. (after Ritter [44])

12. Static fatigue data for silica fibers. x in vacuum at -196°C, o in vacuum at room temperature, ● in air at room temperature. (after Proctor et al. [45])

13. Crack propagation in vacuum. Average crack growth curves in vacuum of 10^{-3} torr at various temperatures after preheating at 330°C: 1) 330°C; 2) 200°C. (after V. P. Pukh et al. [66])

14. Crack propagation in gaseous nitrogen containing varying concentrations of water. The percent relative humidity for each set of runs is given on the right-hand side of the diagram. The Roman numerals identify the different modes of crack propagation. (after Wiederhorn [63])

15. Effect of glass composition on crack propagation rate. Tested in water at 25°C. (after Wiederhorn [67])

16. Crack velocity data compared with the universal fatigue curve. Open circles and squares were obtained from crack velocity data on soda-lime glass. Closed circles and squares were obtained from fused silica crack velocity data. Curve labeled Mould and Southwick was taken from ref. 39. Error bar gives standard derivation of data associated with this curve. Curve labeled Proctor et al. was calculated from data in ref. 46. (after Wiederhorn [67])

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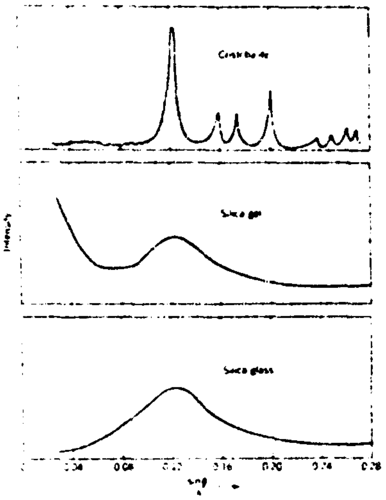

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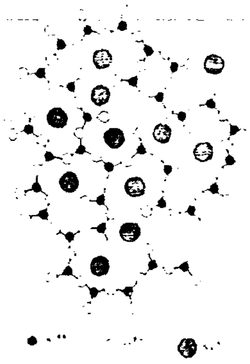

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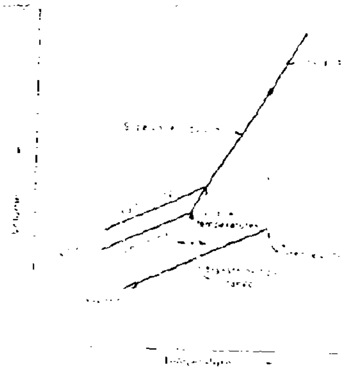

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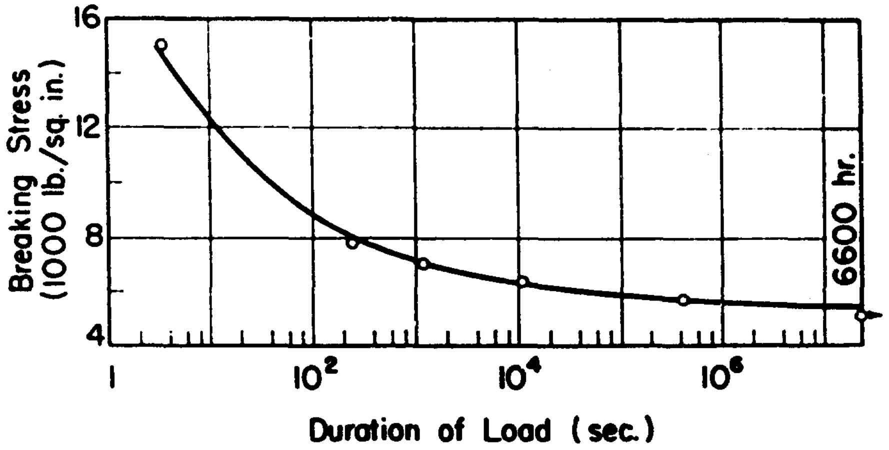

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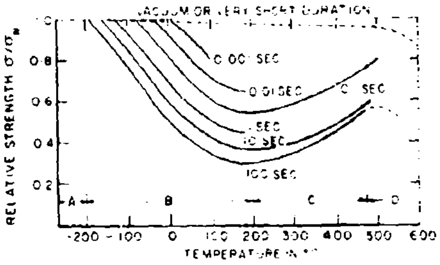

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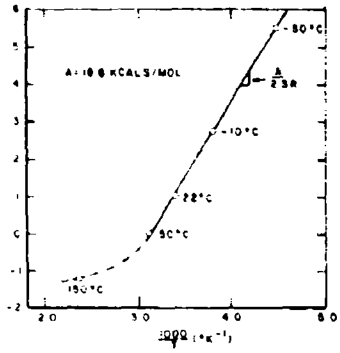

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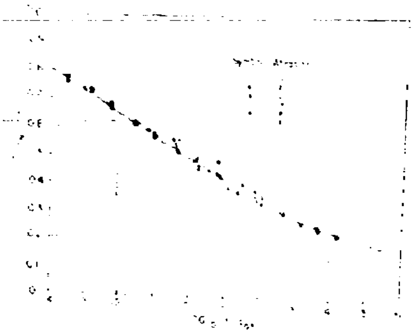

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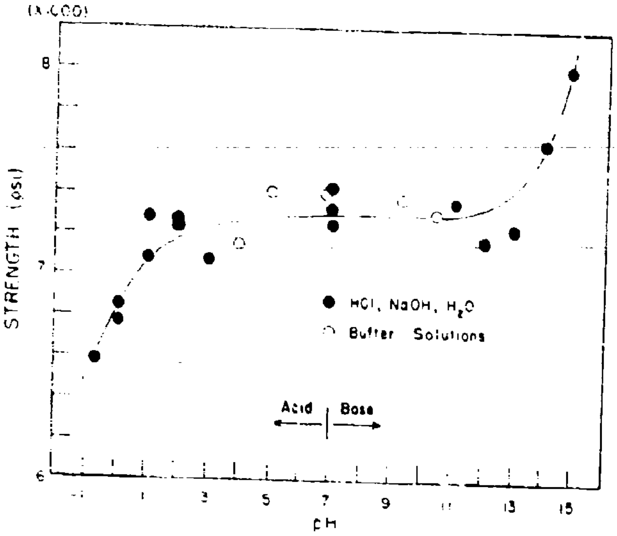

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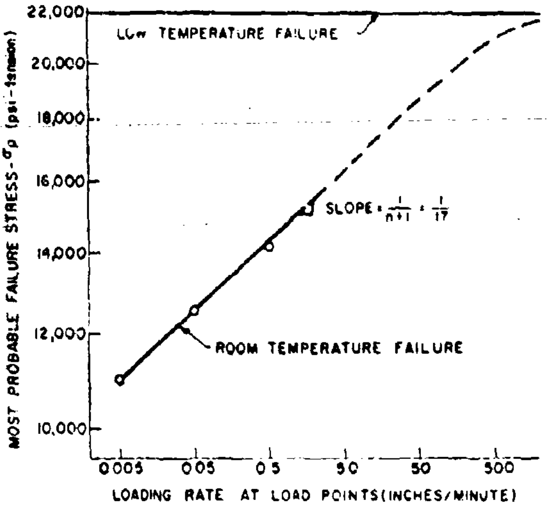

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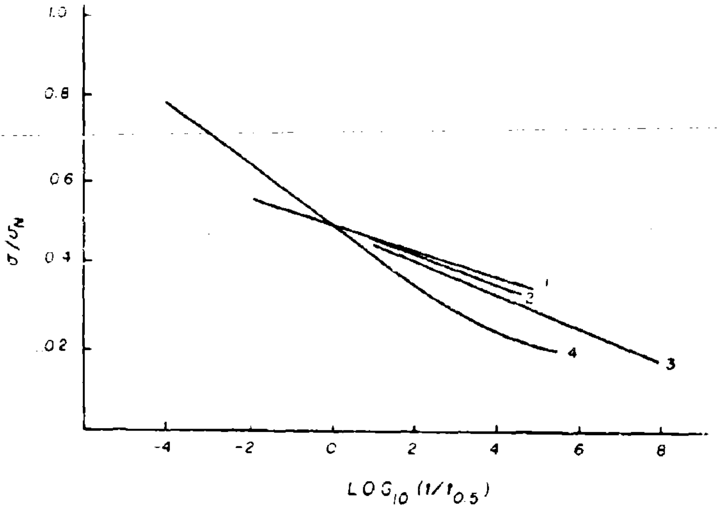

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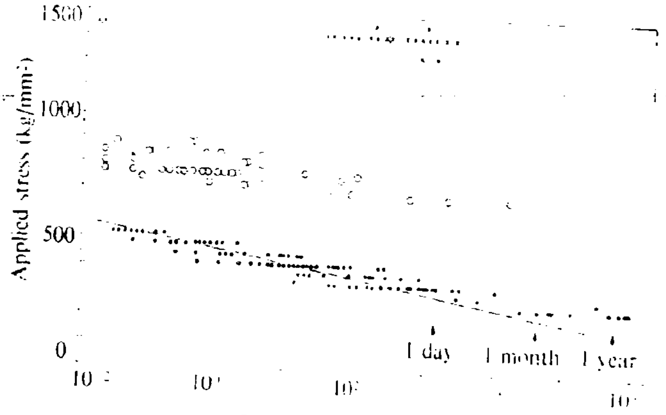

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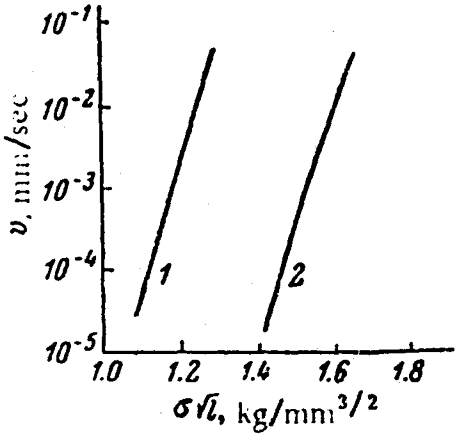

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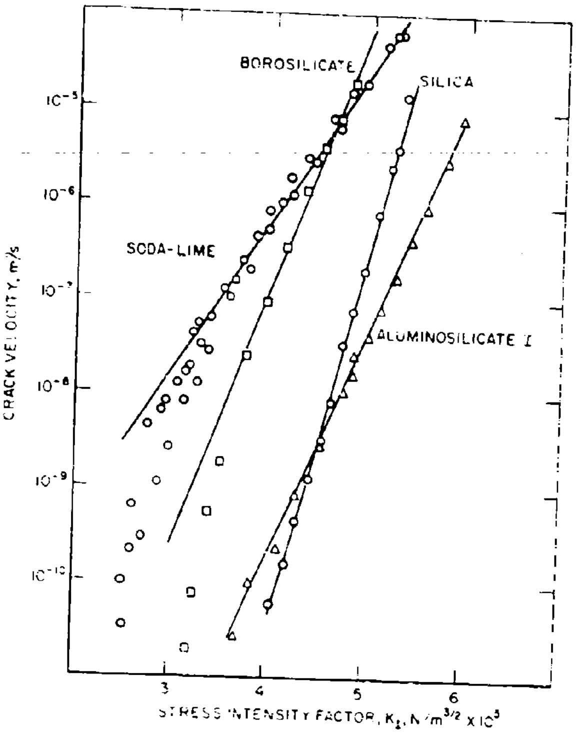

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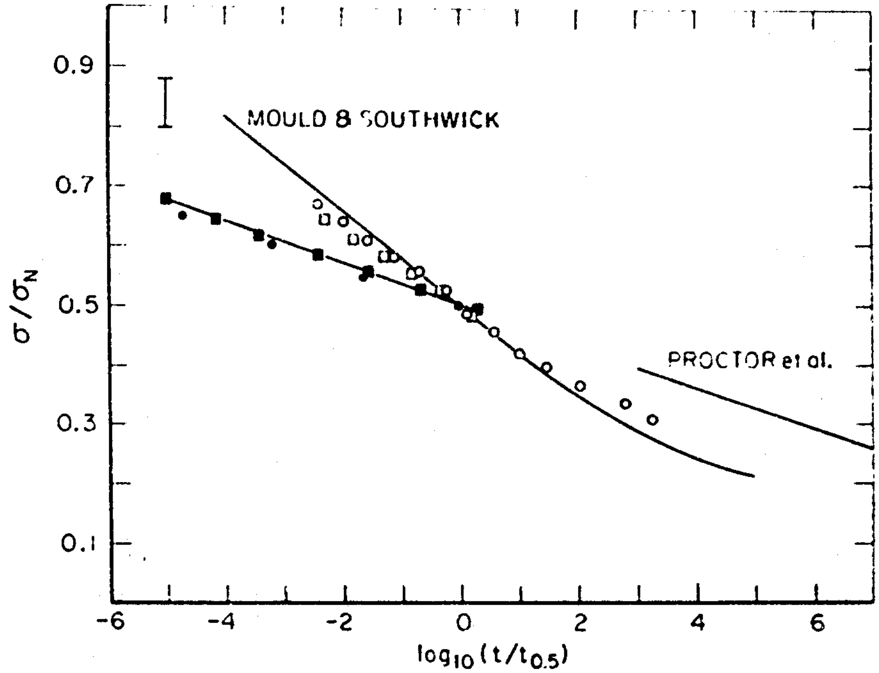

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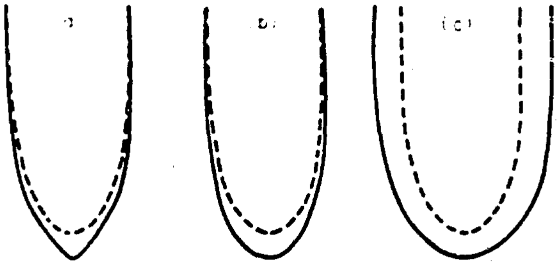

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TABLE I

Glass Composition, Weight Fraction

Glass	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	MgO	CaO	PbO	Use
Silica	0.998								Ultrasonic
Alumino-silicate I	0.57	0.04	0.20	0.01		0.12	0.06		Ignition Tubes
Alumino-silicate II	0.618		0.17	0.125	0.034	0.036	0.004		Auto Windshields After Ion Exchange
Borosilicate	0.80	0.14	0.02	0.04					General, Chemical
Lead-Alkali	0.60		0.04	0.10	0.02			0.24	Lamp Tubing
Soda-Lime	0.72		0.02	0.14	0.01	0.04	0.07		Windows
E-Glass	0.544	0.08	0.144	0.005		0.045	0.175		Fiber Reinforcement

TABLE II

Summary of Crack Velocity Data

Glass	E^*, Kcal/mole (J/mole)	b, MKS Units	$\ln v_c$
Silica	33.1 ± 1.0 (1.391 E5)	0.216 ± 0.0006	-1.32 ± 0.6
Aluminosilicate I	29.0 ± 0.7 (1.212 E5)	0.138 ± 0.003	5.5 ± 0.4
Aluminosilicate II	30.1 ± 0.6 (1.262 E5)	0.164 ± 0.003	7.9 ± 0.3
Borosilicate	30.8 ± 0.8 (1.288 E5)	0.200 ± 0.005	3.5 ± 0.5
Lead-Alkali	25.2 ± 1.2 (1.056 E5)	0.144 ± 0.006	6.7 ± 0.6
Soda-Lime	26.2 ± 1.1 (1.088 E5)	0.110 ± 0.004	10.3 ± 0.5

TABLE III

Comparison of Crack Velocity and Dynamic Fatigue Data[45]

A. Dynamic Fatigue Data

Glass	Surface Condition	"n"
Soda-Lime	Acid-etched	13.0
Soda-Lime	Abraded	16.0
E-glass*	Pristine fiber	27.0
Silica	Abraded	37.8
Borosilicate	Abraded	27.4

B. Crack Velocity Data[67]

Glass	"n"
Soda-Lime	16.6
Aluminosilicate I*	27.4
Silica	36.1
Borosilicate	34.1

*E-glass and Aluminosilicate I can be compared because they have similar compositions.