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ORIGINAL ARTICLE

Effects of acid leaching treatment of soda-lime silicate glass on crack initiation and fracture

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Abstract

Water or acid soaking surface treatments have been shown to increase the mechanical strength of soda-lime silicate (SLS) glasses. This increase in strength has traditionally been attributed to effects related to residual stress or changes in fracture resistance. In this work, we report experimental data that cannot be explained based on the existing knowledge of glass surface mechanics. In dry environments, annealed and acid-leached SLS surfaces have comparable crack initiation stress and fracture stress as measured by Hertzian indentation and biaxial bending tests, respectively. Yet, in the presence of humidity, acid-leached surfaces have higher failure stress than the annealed surfaces. This apparent enhancement in the crack resistance of the acid-leached surface of SLS glass in humid environments supports the hypothesis that acid-leached surface chemistry can lower the transport kinetics of molecular water to critical flaws.

KEYWORDS

fracture, glass, mechanical properties, surface modification

1 | INTRODUCTION

Modern advancements in manufacturing have enabled glasses to have greater chemical durability and mechanical strength, as well as more precise geometric forms such as fibers or flat monoliths. Such developments made it possible to manufacture functional glasses for use as optical fibers, display panels, architectural glazing, solar panels, nuclear waste deposit forms, etc. However, the low usable strength of glass is a major limitation for many glass products. Stronger glass may improve production yields for manufacturers, address durability and safety concerns, and increase the strength-to-weight ratio, which may lead to the reduction of transportation costs associated with glass materials. To increase the usable strength of glass, it is then crucial to understand factors controlling mechanical failures.

Modern theory attributes the low usable strength of glass largely to surface defects that are often introduced during handling.[1–6] According to Griffith–Irwin's fracture criterion, only flaws of a critical size can grow under a load exceeding the static fatigue limit.[1,3,7] Yet, the presence of water in the environment extends otherwise stable, microscopic

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flaws that are smaller than the critical size.[3] It is theorized that these strength-controlling defects in glasses are thermodynamically unstable and chemically reactive surface sites such as strained bonds or over- or under-coordinated sites that become activated in the presence of water.[8] Identifying and pacifying these strength-controlling structural defects remains a challenge in glass science. Studying the effects of such molecular-level structural flaws on the mechanical response is difficult since the presence of microscopic and macroscopic flaws often overwhelms the effects of the submicron scale structural flaws.

The activation of surface flaws at low loads in the presence of water in the environment can be manifested as sub-critical crack growth. Commonly referred to as stress-corrosion in the glass community, sub-critical crack growth is a mechanochemical event that involves a chemically assisted crack propagation under applied loads greater than the static fatigue limit.[9–13] These loads may be much lower than the fracture strength of the material in the inert (water-free) environment. The contribution of sub-critical crack growth to fracture becomes large when the load is applied slowly in a humid environment.[3,14-16] At a slower loading rate, more time is allowed for the corrosive effects of water to take place, resulting in the reduction of the measured fracture strength.[14,15]

Since stress-corrosion depends on the diffusion of water to the crack tip, it is also important to consider the diffusivity of water in addition to the size and distribution of defects. Recent works have indicated that the diffusivity of water through the glass is altered by applied stress.[17–19] Applied tensile stress enhances the diffusion of water through the glass, while applied compressive stress has the opposite effect.[18] During diffusion, however, water can react with the glass. Three reactions can occur simultaneously: (a) hydration, (b) hydrolysis, and (c) leaching.[20] Hydration involves molecular water penetration into the glass network. Hydrolysis reaction involves the breakage of the Si-O-Si network. Leaching is an ion exchange process during which modifier cations like sodium diffuse out of the glass, while water or other hydrous species diffuse into the glass hydrating and hydroxylating the surface.[20] Since leaching selectively depletes modifier cations, especially alkali ions, a layer that resembles a silica-like gel forms, which may extend up to a few hundred nanometers.[21–23]

While water in the environment compromises glass strength, surface treatments that involve soaking glass in water or acid have been shown to have a strengthening effect.[11,13,18,24–29] However, the origin of this strengthening effect is open to debate. The mechanisms proposed in the literature can be categorized into four groups: (a) introduction of compressive stresses in the hydrated layer,[11,18,24–28] (b) passivation of tensile stresses around flaws,[13,30,31] (c) alteration of the fracture resistance of the surface,[32] and (d) blunting of crack tips.[29,33] These hypotheses are based on fracture mechanics models, where the fracture strength of a material depends on its fracture toughness, the length of the critical flaw (or crack), the geometry and location of the defect, and eventually the presence of residual stresses.

The details for each of these strengthening hypotheses are summarized below. The high compressive stress of the leached layer has been ascribed to the swelling of the network.[11,18,24–28] The network swelling hypothesis seems plausible considering the larger radii of the hydronium species diffusing into the glass compared to the smaller radii of the sodium—similar to the effects of chemical tempering.[27] Note that the hydronium is not necessarily H_3O^+ only; compositionally, it is equivalent to proton converting non-bridging oxygen ($Si\text{-}O^-$) to Si-OH and additional water molecule hydrogen bonded to it. Others have considered the possibility that the acid-leached layer has a lower elastic modulus,[34] which may allow for greater compliance of the treated layer. Some have claimed that this layer dissipates the mechanical energy and prevents the formation and expansion of strength-limiting flaws.[32] But it is unclear how a surface treatment that influences only a hundred nanometers of the surface can have such drastic influence on the mechanical response on the micro- and macro-scale. It has also been proposed that the increase in strength after water soaking may be due to flaw alteration including crack tip blunting due to the reprecipitation of dissolved glass.[13,30,31] Because flaws act as stress concentrators, the crack tip blunting could induce the strengthening effect.[29,33] Although this hypothesis makes sense conceptually, it does not fully explain how precipitates at the crack tip reduce the stress intensity factor of the crack. These previous hypotheses as to why aqueous soaking increases the fracture strength of glasses are rooted in fracture mechanics derived from force balance for homogenous bulk material.

The strengthening effect of water or acid soaking surface treatments is distinct from water-containing glass compositions that have high crack resistance. Water dissolved into bulk glass alters bulk properties such as glass transition temperature or the inert mechanical response.[35,36] Meanwhile, surface treatments do not alter bulk glass properties. Instead, acid leaching surface treatment results in a silica-rich, gel-like layer in which molecular water can easily be absorbed and desorbed from the pores revealing silanol absorption sites.[21]

The goal of this paper is to investigate an alternative hypothesis explaining how structural changes associated with acid-leaching influence the mechanical response of soda-lime silicate (SLS) glass under different loading and humidity conditions. Hertzian indentation (Figure 1A) and ball-on-three-balls (B3B) biaxial strength tests (Figure 1B) showed that differences in surface chemistry between the annealed and acid-leached SLS surfaces have negligible impact on crack initiation stress and fracture stress in dry nitrogen (inert) environments. Yet, in the presence of humidity, significant differences in crack initiation stress and fracture stress between annealed and acid-leached SLS were observed. These results

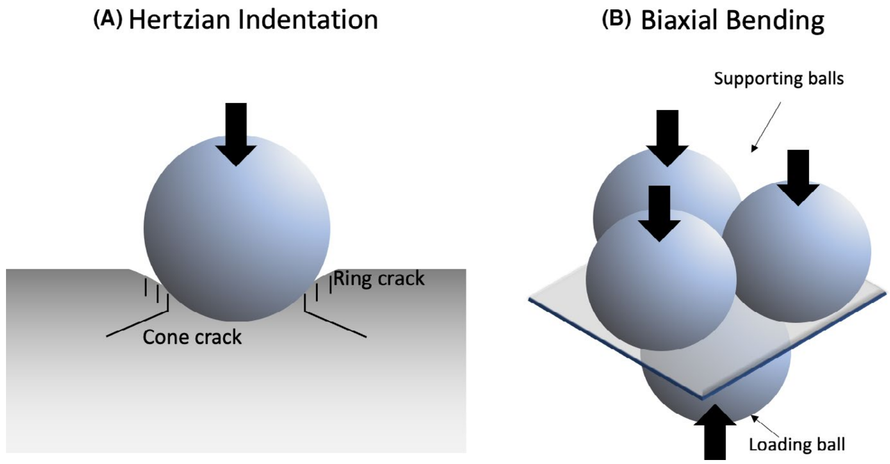

FIGURE 1 Illustration of (A) Hertzian indentation and (B) ball-on-three-balls biaxial bending

support the hypothesis which considers the transport of water through the leached layer to rationalize why acid-leaching surface treatments can increase the apparent fracture strength of SLS glass in the presence of water.[37]

2 | METHODS

2.1 | Materials and sample preparation

SLS float glass panels of (a) 5 mm and (b) 0.7 mm thickness were provided by AGC Inc. (Japan). The bulk composition for these SLS float glasses (weight %) is 72% SiO_2, 13% Na_2O, 8% CaO, 4% MgO, 2% Al_2O_3, and traces of K_2O and Fe_2O_3.[38] Acid-leached samples were then prepared by immersing the glass in a perfluoroalkoxy (PFA) jar containing pH1 hydrochloric acid solution at 90°C for a specified time (e.g., 24 hours). Samples were then rinsed with water and blown dry.

2.2 | Hertzian indentation

Hertzian indentation was used to assess the different responses to crack initiation and fracture of the glasses with surface treatments loaded at different humidity levels. Hertzian indentation is a blunt micro-indentation technique used to measure the crack initiation load of acid leaching surface treatment at different humidity levels (Figure 1A). It is important to clarify that Hertzian indentation was not used to measure the fracture toughness. The spherical indenter tip used in this work was 0.5 mm in radius and was made of tungsten carbide. The indenter was loaded onto the sample at a 1 N/s loading rate until a crack event was detected using an acoustic sensor (MISTRAS Group, Inc.; PIC-2 acoustic emission system with a PICO HF1.2 sensor). Hertzian indentation generates a tensile stress field at the glass surface around the indenter (at the perimeter of the contact with the loading ball), which is responsible for crack initiation. A number of specimens, n, ranging from 30 to 56 was tested for each sample. The tensile stress resulting from the contact loading is maximum at the surface of the material near the contact circumference of the indenter.[39,40] For Hertzian indentation, four SLS glass samples with various treatments were tested: (a) annealed (0% RH, $n = 50$), (30% RH, $n = 50$), (90% RH, $n = 47$), (b) acid-leached for 20 hours (0% RH, $n = 50$), (30% RH, $n = 50$), (90% RH, $n = 48$), (c) acid-leached for 80 hours (0% RH, $n = 50$), (30% RH, $n = 55$), (90% RH, $n = 50$), (d) acid-leached for 320 hours (0% RH, $n = 30$), (30% RH, $n = 96$), (90% RH, $n = 56$). More information about the evaluation of Hertzian indentation data can be found in the Supplemental Information.

2.3 | Biaxial bending using the ball-on-three-balls method

The ball-on-three-balls (B3B) technique is a biaxial bending method that is commonly used to measure the mechanical strength of brittle materials and components (Figure 1B).[41–44] In this loading situation, the rectangular plates (or eventually discs) are symmetrically supported by three balls on one face and loaded by a fourth ball in the center of the opposite face (see Figure 1B); this guarantees well-defined three-point contacts. At the midpoint of the plate surface, opposite to the loading ball, biaxial tensile stress is generated. When the stress intensity factor overcomes the toughness of the glass (Griffith criterion), assuming linear elastic behavior of the glass, fracture will occur. One of the main advantages of this method is that the maximal stress developed during the test is located far from the edges (corners) of the sample. Compared to uniaxial bending tests, such as three- or four-point bending, the B3B does not require rigorous sample preparation such as edge polishing or beveling which may introduce new flaws. In addition, due to the biaxial stress state at the loading surface, defects with different orientations have the same probability of becoming critical during testing.

The loading ball pressed the tin side of the float glass while the air side was in contact with the three supporting balls. The four balls had a diameter of 13.0 mm giving a support radius of 7.51 mm. A pre-load of 10 N was applied to hold the sample between the four balls. The glass was tested under compression extension and the load upon fracture was recorded. The displacement rate during testing in dry N_2 and in 30% RH was 1 mm/min (~50 MPa/s loading rate), while the displacement rate during testing in liquid water was 0.01 mm/min (~0.5 MPa/s loading rate). For biaxial bending, three SLS glass samples (containing between 9 and 11 specimens, n) with various treatments were tested: (a) annealed (0% RH, n = 11), (30% RH, n = 10), (liquid water, n = 10), (b) acid-leached for 24 hours (0% RH, n = 9), (30% RH, n = 11), (liquid water, n = 11), (c) acid-leached for 72 hours (0% RH, n = 11), (30% RH, n = 11), (liquid water, n = 9). More information about the evaluation of biaxial strength data can be found in Supplemental Information.

2.4 | Statistical analysis of data

Mechanical events such as crack initiation or fracture often result from surface flaws that have a broad distribution in size and chemistry.[2–4] These events then depend on the largest or most critical flaw in the probed region which may vary between locations within the tested specimen and samples. As a result, mechanical strength or crack initiation load should be described as a probability distribution function. In many brittle materials like ceramics and glasses, this probability function commonly follows a Weibull distribution that is associated with the underlying defect size density distribution function in the material.[45] A survival analysis of the data can be performed to represent the probability of failure or crack initiation as a function of applied load or stress. In this work, Weibull analyses of the Hertzian and the B3B tests were performed following the EN 843-5 standards.[46] The fit of the distribution function was carried out using the maximum likelihood method. The corresponding Weibull parameters, that is, characteristic strength and Weibull modulus, were determined. The characteristic strength represents the stress at which the probability of failure (or crack initiation) is ≈63% (for the volume of specimens equal to the reference volume).[45] The Weibull modulus (m) is the shape constant of the distribution function and describes scattering within the data. Larger modulus indicates less scatter within the data set, which can be interpreted as narrower size distribution of strength-limiting defects in the specific test conditions.

3 | RESULTS

In general, acid leaching treatments result in a silica-rich surface layer with increased amounts of hydrous species (Si-OH and molecular water) and with an increased void volume fraction.[21,22,37,47,48] Water can easily absorb into and desorb from this newly formed porous surface layer.[21,48] Previous work showed that acid-leaching (in pH 1, 90 ºC) SLS for 24-hours results in a leached layer thickness of ~120 nm which increases to ~150 nm after 72-hour of acid-leaching.[37]

3.1 | Crack initiation from Hertzian Indentation

The effects of water on the crack initiation for annealed and acid-leached SLS were probed using a humidity-controlled Hertzian indentation system. Hertzian indentation was performed on 5-mm thick float glasses. Figure 2 shows the Weibull diagram of the probability of crack initiation as a function of applied stress in 0%, 30%, and 90% RH conditions and compares glasses that have been annealed or acid-leached for various durations. The Weibull parameters including the characteristic crack initiation stress ($\sigma_{0,CIS}$) and Weibull modulus (m) with the respective 90% confidence interval are calculated following the EN 843-5 standards are shown in Table 1.[46] The characteristic crack initiation stress, $\sigma_{0,CIS}$, represents the applied stress that corresponds to a ~63% probability of initiating a crack in the glass sample.

At 0% RH, the annealed and acid-leached SLS samples have comparable $\sigma_{0,CIS}$ (~1.9 GPa) and crack initiation stress distribution (Figure 2A). At higher relative humidities (Figure 2B,C), the crack initiation stress decreases for all treatments indicating that molecular water absorbed from the gas phase facilities crack initiation. Yet, the detrimental effects of humidity on $\sigma_{0,CIS}$ are less severe for acid-leached glasses, especially those that have been acid-leached for a longer duration. Furthermore, annealed and acid-leached glasses have comparable Weibull moduli at all relative humidities (Table 1).

3.2 | Biaxial strength distributions

The mechanical fracture strength of 0.7-mm thick SLS float glass was determined from a biaxial bending test using the B3B technique. Figure 3 represents the strength distribution in a Weibull plot for annealed and acid-leached glasses in 0% RH, 30% RH, and liquid water environments. The Weibull parameters including the characteristic fracture strengths (the applied stress with a ~63.2% failure probability) and Weibull moduli are reported in Table 2 with the respective 90% confidence interval.

Samples tested at 0% RH were kept in dry nitrogen environment for 5 minutes before being fractured at a 1 mm/min displacement rate. As seen in both Figure 3A and Table 2, the fracture stress and Weibull moduli are comparable for both annealed and acid-leached glasses at 0% RH environmental

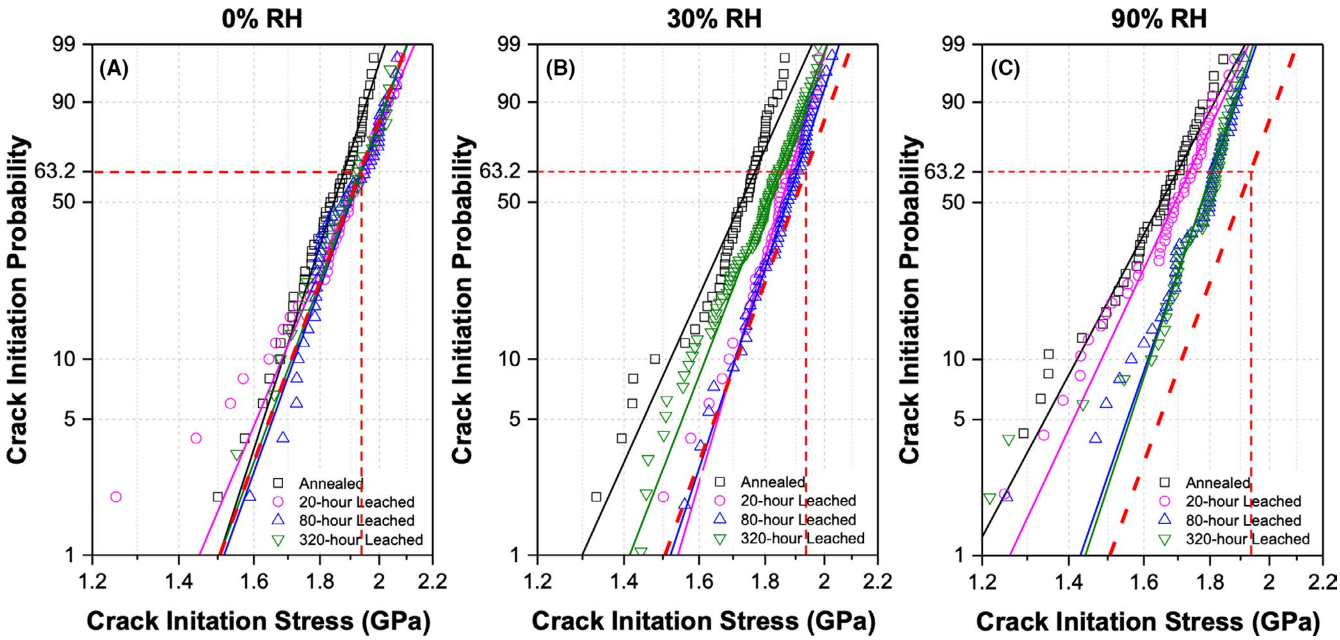

FIGURE 2 Weibull plots of probability of crack initiation as a function of applied stress for Hertzian indentation for annealed and acid-leached glasses: (A) 0% RH (B) 30% RH (C) 90% RH. The solid line represents the best-fit trend of the fracture data set described by the Weibull distribution. The red dashed line represents the inert crack initiation stress for 320-hour acid-leached SLS at 0% RH and is included as a reference

TABLE 1 Hertzian indentation characteristic crack initiation stress ($\sigma_{0,CIS}$) and Weibull modulus (m) for annealed and acid-leached glasses at 0% RH, 30% RH, and 90% RH. The 90% confidence intervals are given in square brackets

	0% RH		30% RH		90% RH	
Sample	$\sigma_{0,CIS}$ (GPa)	m	$\sigma_{0,CIS}$ (GPa)	m	$\sigma_{0,CIS}$ (GPa)	m
Annealed	1.88 [1.86–1.90]	21 [17–24]	1.77 [1.74–1.80]	15 [12–18]	1.70 [1.66–1.73]	13 [10–15]
20-hour Acid Leached	1.94 [1.91–1.97]	16 [13–19]	1.88 [1.86–1.90]	23 [19–27]	1.73 [1.70–1.77]	14 [12–17]
80-hour Acid Leached	1.94 [1.91–1.96]	19 [15–22]	1.91 [1.88–1.93]	20 [17–24]	1.81 [1.78–1.83]	20 [16–23]
320-hour Acid Leached	1.93 [1.90–1.97]	18 [14–22]	1.84 [1.82–1.86]	17 [15–20]	1.80 [1.78–1.83]	20 [17–24]

conditions. This indicates that the acid leaching does not have a significant influence on the flaw size, flaw shape, fracture toughness, or residual stress.

Figure 3B shows the Weibull diagram for tests performed at 30% RH at a 1 mm/min displacement rate. The Weibull distribution shifts to much lower fracture strength values for the annealed glass compared to the acid-leached glasses. Figure 3C displays the Weibull diagram for tests performed in liquid water at a 0.01 mm/min displacement rate. In this test, the compressive displacement rate was reduced so that the effects of sub-critical crack growth, if any, would be manifested with a larger difference in the measured fracture strengths. Here, the Weibull distribution for both annealed and acid-leached glasses shifts to lower values compared to fracture performed at 0% RH or 30% RH conditions indicating that sub-critical crack growth is promoting failure. The Weibull distribution shifts to a lower value for the annealed glass compared to the 24 and 72-hour acid-leached glasses. Since sub-critical crack growth is a thermally activated bond dissociation event during which water diffuses to the crack tip, a lower fracture strength value may be associated with water reaching the crack tip more easily. In summary, (consistent with the $\sigma_{0,CIS}$ data shown in Section 3.1), the fracture strength results suggest that the presence of the acid-leached layer can mitigate the detrimental effects of stress corrosion which eventually may lead to failure of the glass.

4 | DISCUSSION

The increase in the apparent fracture strength of the water-soaked or acid-leached glass surfaces has previously been

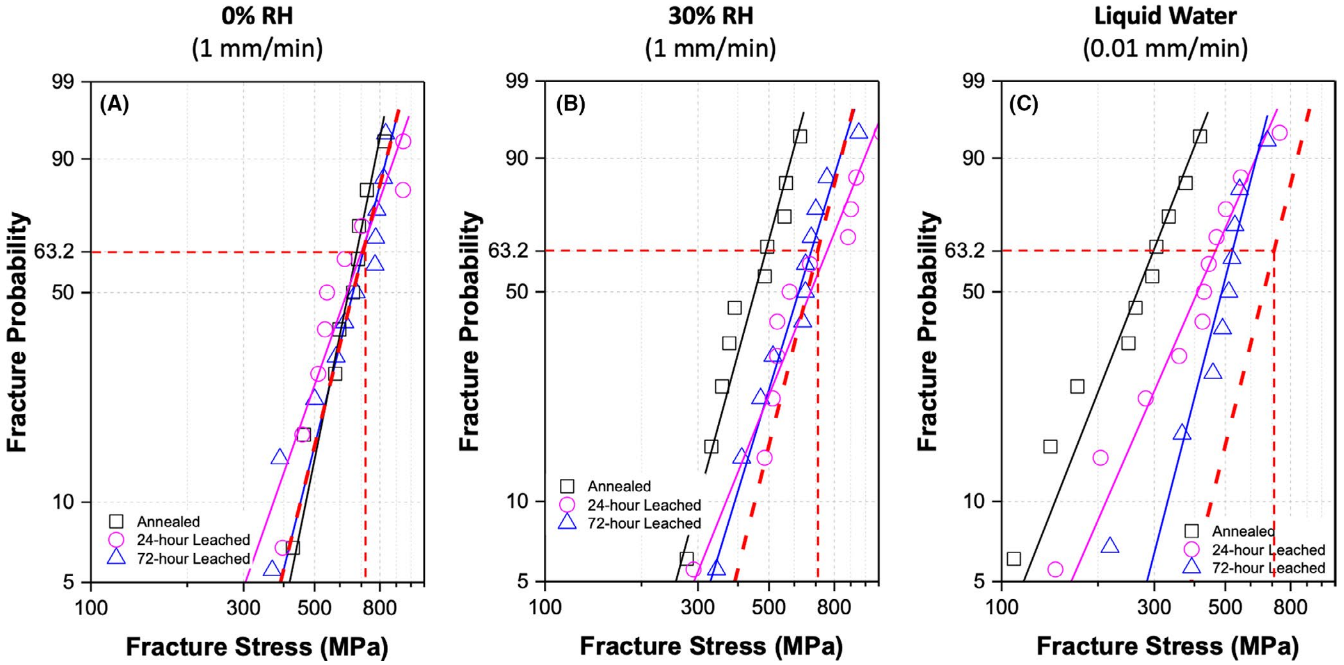

FIGURE 3 Weibull plot of the failure probability as a function of fracture stress for annealed, 24 and 72 h acid-leached SLS float glasses. Fracture in liquid water was performed at a 0.01 mm/min displacement rate. Fracture at 0% RH and 30% RH was performed at a 1 mm/min displacement rate. The red dotted line represents the inert fracture strength of 72 h acid-leached SLS at 0% RH and is included as a reference

TABLE 2 Characteristic fracture strength ($\sigma_{0,\,Fracture}$) and Weibull modulus (m) of samples tested at 0% RH (1 mm/min displacement), 30% RH (1 mm/min displacement), and in liquid water (0.01 mm/min displacement). The 90% confidence intervals are listed in brackets

	0% RH (Displacement rate 1 mm/min)		30% RH (Displacement rate 1 mm/min)		Liquid Water (Displacement rate 0.01 mm/min)	
Sample	$\sigma_{0,\,Fracture}$ (MPa)	m	$\sigma_{0,\,Fracture}$ (MPa)	m	$\sigma_{0,\,Fracture}$ (MPa)	m
Annealed	677 [606–761]	6 [3–8]	489 [426–566]	5 [3–6]	298 [244–367]	3 [2–4]
24-hour Acid Leached	700 [577–856]	4 [2–5]	759 [625–927]	3 [2–4]	466 [377–579]	3 [2-4]
72-hour Acid Leached	709 [629–803]	5 [3–7]	678 [585–789]	4 [2–6]	526 [456–611]	5 [3–7]

attributed to compressive residual stresses,[11,18,24–28] changes in the fracture resistance of the surface,[32] changes in the flaw size,[13,30,31] or crack tip blunting.[29,33] Yet, the experimental results reported in this work cannot be explained with such hypotheses. In this section, we provide a surface science-driven hypothesis as to why acid-leaching surface treatments can increase the fracture strength of soda-lime silicate (SLS) glass in the presence of water vapor or liquid water.

4.1 | Comparison with the previous hypotheses

According to the Weibull plots of crack initiation stress and fracture stress shown in Figures 2A and 3A, the annealed and acid-leached glasses have comparable mechanical response in dry environments. The comparable fracture strengths for annealed and acid-leached glasses at 0% RH indicate that acid-leaching does not have a significant influence on the flaw size, flaw shape, fracture toughness, nor residual stress. The comparable Weibull moduli for both annealed and acid-leached glasses indicate that they have comparable flaw size distributions (Figures 2A and 3A).[45] As a result, without a supply of water molecules from the gas or liquid phase, the difference in surface chemistry and structure between the annealed and acid-leached surfaces have negligible impacts on crack initiation and fracture strength. The crack initiation stress measured by Hertzian indentation shows a high Weibull modulus (m~20) indicating low scatter in defect size (Table 1). Meanwhile, the biaxial fracture strength measured using B3B biaxial bending results in relatively lower Weibull modulus (m~5) indicating greater scatter in defect size. The differences between the Weibull moduli for Hertzian and B3B can be attributed to the effective area being tested. The applied tensile stress from B3B covers a much larger effective area than Hertzian indentation and, as a result, may capture a greater range of the flaw size and chemistry distribution compared to the Hertzian indentation test.

A major issue with the hypotheses proposed in the past as to why aqueous soaking increases the fracture strength of glasses is that they were rooted in the use of Linear Elastic Fracture Mechanics (LEFM) to rationalize fracture. According to LEFM, a defect of a given size may grow when the stress intensity factor, K, upon externally applied load, overcomes the fracture toughness of the material. Typical critical defects in glass have been found to be "handling" flaws, with an order of magnitude of ~5 to ~10 μm or even larger (if corresponding to defects introduced during sample preparation, e.g. cutting or chamfering process).[3] Under such premises, an acid-leached layer of ~100 nm might have negligible impact on the fracture process, since the thickness of this altered layer is considerably smaller than the typical size of a handling flaw.

If one uses the Griffith theory and assumes the critical fracture toughness (K_{Ic}) and shape factor (Y) are 0.7 $MPa \cdot m^{1/2}$ and 1, respectively,[37,49] then the $\sigma_{0,CIS}$ values of the Hertzian indentation (Table 1) may imply that the critical defect grows to ~130 nm in 0% RH and ~170 nm in 90% RH during the test of the annealed glass. Then, the question here is why this growth is suppressed to ~50 nm upon the acid treatment before the mechanical test. If the $\sigma_{0,Fracture}$ values of the B3B test (Table 2) are used, then the critical defect size can be said to grow during the test in liquid water to ~5 μm for the annealed glass and ~2 μm for the acid-leached glass, although both glasses have the same and small growth to only ~1 μm in the 0% RH condition. Again, what needs to be addressed is why the defect growth in water is so fast for the annealed glass and much slower for the acid-treated glass which has the ~100 nm thick leached layer.[37]

4.2 | New hypothesis—responsive or adaptive nature of the leached layer

In this paper, we discuss an acid-leaching surface treatment that creates a silica-rich, porous, hydrated surface layer that is ~100 nm thick. The significant difference between the observed crack initiation and fracture strength of annealed and acid-leached glasses only in humid or liquid water environments, but not in dry conditions, (Figures 2B,C, 3B,C) indicates that sub-critical crack growth-promoting failure involves water molecules supplied from the environment (outside the glass). Since sub-critical crack growth is a mechanochemically driven phenomenon that depends on the transport of molecular water from the gas or liquid phase to the flaw or crack tip,[11,26,50,51] the presence of acid-leached surface layer is likely to alter transport of molecular water to the flaw. Given that there are both compositional as well as nano-scale and atomic-scale structural changes, it is difficult to deconvolute individual contributions of these changes in the transport of water through the leached layer. Alkali-free glasses have a higher crack growth exponent.[9,52] This has been attributed to the differences in water transport to the flaw between alkali-free and alkali-containing bulk compositions. Based on this concept, bulk composition has been shown to influence water transport (and as a result, crack growth exponent). The surface treatment produces an alkali-depleted layer whose composition is different from the bulk composition. However, the layer is so thin that it has not been possible to assess the crack growth exponent of this layer. In addition, the leached surface layer is porous; thus, the relationship between the bulk composition and the crack growth exponent found from measurements of pristine glasses may not be applicable to the surface layer formed by acid leaching even if their nominal compositions may be the same. Furthermore, ReaxFF simulations show that this leached layer is susceptible to structural rearrangement under applied stress.[37] This structural rearrangement of the leached layer under applied load is an additional confounding factor. All these variables (composition, atomic-scale structure, nano-scale structure, and restructuring under applied load) may have influenced water transport through the leached layer and identifying a single dominant variable may not be possible at this time.

Spectroscopic analysis of the acid-leached surface has revealed that the silica-rich surface is enriched with hydrous species and voids.[21–23,37,48] The combination of both structural and chemical changes may alter the transport of molecular water through the leached layer, which may manifest itself through changes in mechanochemical reactions such as sub-critical crack growth. This suggests that while acid leaching treatments do not alter the mechanical response of the glass in dry (inert) conditions, it may influence mechanochemical behaviors such as sub-critical crack growth in humid environments.

A previous study on aqueous corrosion of boroaluminosilicate glass showed that not all pores are fully connected and accessible by gas-phase water molecules.[48,53] If the pore connectivity is suppressed by dynamic rearrangement of glass network under mechanical stress resulting in reducing the connectivity of pores and trapping the water species in the isolated pores, then the water transport through such layers would be suppressed significantly. In such cases, the corresponding diffusion coefficient of water molecules could be estimated as low as 10^{-21} m^2/s.[53] Unfortunately, the current study could not measure or estimate the diffusivity of water species through the leached surface layer that would undergo dynamic rearrangement under applied mechanical stress.

Simultaneously, a previous study performed by Sheth et al. showed that acid-leached surfaces appear to impede the propagation of sub-surface cracks to the surface during Vickers indentation.[37] Molecular dynamics simulation with ReaxFF reactive force field suggested that the leached layer can undergo structural rearrangement under applied load.[37] This silica-rich structure of the leached layer becomes more silica-like after mechanochemically induced structural rearrangement.[37] Since the hydroxylation kinetics as well as transport behavior vary significantly depending on the network structure,[8,54,55] structural rearrangement in the acid-leached layer under applied load may reduce the rate of molecular water transport from the environment to the crack tip. These previous findings are in agreement with the results in this work and should be considered in tailoring surfaces of engineering glasses, in particular for applications where the glass material is exposed to corrosive environments.

5 | CONCLUSIONS

The effects of acid-leaching on the mechanical response of SLS glasses in dry and humid conditions were studied. In dry conditions, annealed and acid-leached glasses have comparable crack initiation and fracture strength indicating that the differences in surface chemistry between the annealed and acid-leached surfaces have negligible impacts on the mechanical response of glass in the absence of water molecules in the environment (inert environment). Yet, significant differences between annealed and acid-leached glasses were observed under humid or wet conditions. This implies that while differences in surface chemistry do not alter the mechanical response of the glass, as interpreted by brittle fracture described by Griffith's theory, they may influence mechanochemical process involved in sub-critical crack growth in humid environments. Pressure-induced mechanochemical restructuring may also occur in the acid-leached layer during applied load. It is hypothesized that the restructuring of the acid-leached layer under applied stress may reduce the transport kinetics of molecular water to critical flaws, thereby retarding crack initiation and growth in engineering glasses.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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