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Crucial effect of angular flexibility on the fracture toughness and nano-ductility of aluminosilicate glasses

Mengyi Wang [a], Bu Wang [a], Tobias K. Bechgaard [b], John C. Mauro [c], Sylwester J. Rzoska [d], Michal Bockowski [d], Morten M. Smedskjaer [b], Mathieu Bauchy [a,*]

[a] Physics of AmoRphous and Inorganic Solids Laboratory (PARISlab), University of California, Los Angeles, CA 90095, USA
[b] Department of Chemistry and Bioscience, Aalborg University, Aalborg 9220, Denmark
[c] Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA
[d] Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw 00-142, Poland

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ABSTRACT

Understanding and controlling materials' resistance to fracture is critical for various applications. However, the structural origin of toughness, brittleness, and ductility remains poorly understood. Here, based on the experimental testing and atomistic simulations of a series of aluminosilicate glasses with varying thermal and pressure histories, we investigate the role of structure in controlling fracture toughness at fixed composition. We show that fracture toughness decreases with density, but strongly depends on the details of the temperature and pressure histories of the glass. This behavior is found to arise from a loss of nano-ductility rather than a loss of cohesion. Finally, we demonstrate that the propensity for nano-ductility is primarily controlled by the extent of angular flexibility between the rigid polytopes of the network. Tuning the extent of nano-ductility in silicate glasses would permit the design of ultra-tough glasses.

1. Introduction

Despite recent advances in the development high performance glasses – like Corning® Gorilla® Glass [1–3], a scratch- and damage-resistant glass used on >4 billion smartphone and tablet screens – glass still breaks. Developing novel glasses featuring higher resistance to cracking while retaining transparency would greatly extend the range of applications of glasses, e.g., for fiber optics, flexible substrates, or protective screens in extreme conditions [4]. In turn, the use of glasses with improved mechanical properties would also permit the use of thinner material while achieving similar performances. This would reduce the weight of glass panels, which, in the case of car windshields, would result in significant gas savings. Although extrinsic treatments like compositing [5], inclusion of holes [6], or surface treatments [7] can enhance glass toughness, they often result in undesirable side effects like a loss of transparency [4]. Alternatively, the recent observation that glass can feature some ductility at the nanoscale despite being brittle at the macroscale [8–10] offers a new degree of freedom to improve the intrinsic toughness of glasses.

However, our ability to enhance the intrinsic resistance to fracture of glasses is presently limited by a lack of understanding in the influence of composition and atomic structure on strength, fracture toughness, and brittleness. In fact, this gap of knowledge has recently been identified as a "Grand Challenge" in glass science [11–13]. Understanding such linkages is complicated by the difficulty of precisely isolating the effects of composition, packing density, short-range, medium-range, and long-range order structure on toughness.

Here, we consider a series of glasses of similar composition with differing temperature and pressure histories to isolate the effect of *only* structure on fracture toughness, that is, the fact that temperature and pressure histories each impact the short- and medium-range structure differently allows us to isolate the relative influence of each scale on fracture toughness. In detail, by combining experimental indentation tests and atomistic molecular dynamics (MD) simulations, we show that thermal annealing and pressure quenching treatments both affect fracture toughness, but in a drastically different fashion. The detailed investigation of the differing structural modifications induced by varying temperature and pressure histories reveals that the degree of brittleness of glass fracture is primarily controlled by the short-range order structure and, specifically, the extent of inter-tetrahedral motion in the atomic network. This emphasizes the important role of angular flexibility in controlling glasses' resistance to fracture.

2. Experimental and computational methods

2.1. Sample preparation

The glass used herein is a commercial alkaline earth aluminosilicate glass, i.e., Corning Jade® glass with a patented composition given in Ref.

* Corresponding author.
E-mail address: bauchy@ucla.edu (M. Bauchy).

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[14] and a glass transition temperature $T_g = 1055$ K. Due to its high thermal and chemical stability, this glass is typically used for pSi liquid crystal display substrates. The glass was manufactured using the fusion draw process, which yields a high initial fictive temperature $T_f = 1125$ K. Such high initial T_f allows us to investigate a wide range of thermal histories through annealing. We also point out that the fusion draw process ensures a high level of homogeneity, which is required to meaningfully compare the subtle effects of varying thermal and pressure histories [15].

Glass sheets with dimensions of approximately $25 \times 25 \times 0.7$ mm^3 were prepared, and subsequently (1) annealed for times t_a varying from 5 min to 88 h at a temperature $T_a = 1034$ K (0.98 T_g) or (2) isostatically compressed at T_g for 30 min at pressures P varying from 0.1 and 1.0 GPa. Annealing was performed by placing the samples in a furnace at the temperature T_a for a pre-determined annealing time, before rapidly quenching the glass. Isostatic compression was achieved using a nitrogen gas pressure chamber, as described in details in Ref. [16]. The resulting glass densities were determined using Archimedes' principle with water as the immersion medium. Each measurement of sample weight was repeated ten times.

2.2. Indentation fracture toughness

The indentation fracture toughness K_c of the samples were determined using a Vickers micro-indenter (Duramin 5, Struers A/S) at a load of 9.8 N. The indent diagonal a and length c of radial/median corner cracks were measured using optical microscopy. From the measured value of a, Vickers hardness H_V was determined. To calculate the indentation fracture toughness K_c, Young's modulus E is also required, which was determined based on measured sound velocities (ultrasonic pulse-echo technique) and densities. K_c was then subsequently determined by measuring the crack-to-indent size (c/a) ratio (see details in Ref. [17]). The measured c/a ratio was larger than 2.5 for all investigated samples, thus satisfying the condition of a semi-elliptical median-radial crack system and enabling K_c to be calculated based on the equation given in Refs. [18,19]. We note that the fracture toughness values obtained through Vickers indentation differ from those determined using other standardized tests [20], and can therefore only be used for relative internal comparisons. Nevertheless, determining fracture toughness using standard techniques like chevron notch beam (CNB) or V-notched beam (SEVNB) requires larger quantities of each sample, which, in the present case, were not available due to the limited volume of the utilized pressure vessel. As such, we rely here on Vickers indentation to determine the relative effects of varying thermal and pressure histories on fracture toughness, but remain fully aware that the results will not be quantitatively comparable to those obtained using the above-mentioned CNB or SEVNB techniques.

2.3. Molecular dynamics simulations

To gain deeper insights into the experimental trends observed herein, a $30CaO–10Al_2O_3–60SiO_2$ glass (in mol %) of 2995 atoms was simulated through classical MD. This composition was chosen to be similar – in terms of types and ratio of the major oxides – to that of the experimental glass, while remaining simple enough to be well documented, which is a necessary condition to validate the outcomes of the simulations. Note that, as the exact composition of the simulated glass differs from that of the glass synthesized herein, we do not expect an absolute agreement between simulations and experiments. Nevertheless, as shown below and in Ref. [21], the experimental and simulated glasses show similar trends in density, hardness, fracture toughness, and brittleness and, as such, can be compared on a relative basis. For this study, we relied on a two-body Born-Mayer-Huggins potential, recently parameterized by Jakse [22]. The details of the simulation parameters, as well as multiple structural, mechanical, and vibrational validations can be found in Refs. [9,23]. It is worth noting that the Jakse potential used herein was shown to offer the best agreement with available experimental structural data, as compared to various alternative potentials [23]. Note that the ability of the potential to predict a realistic structure is of primary importance here as we aim to understand the structural origin of toughness and brittleness. In particular, this potential was found to yield the best prediction of the Si–O–Si angle, with an improved level of agreement as compared to an alternative 3-body potential [23].

Following the synthesis protocol, the simulated systems were subsequently quenched under pressure or thermally annealed. As a starting configuration, a liquid was relaxed at 5000 K and zero pressure in the *NPT* ensemble for 1 ns. First, to study the effect of quenching under pressure only, i.e., without any annealing, several glasses were prepared by compressing during 1 ns the liquid in the *NPT* ensemble at 5000 K under a pressure varying from 0.5 to 2.5 GPa. Such duration was found to be long enough to ensure a full relaxation of the melt. The samples were then subjected to an instantaneous quenching down to 300 K. Each glass was eventually relaxed for 1 ns in the *NPT* ensemble at zero pressure. Second, to study the effect of annealing only, the liquid was instantly quenched down to 1500 K, a temperature that is slightly lower than the simulated T_g. The system was then annealed in the *NPT* ensemble at 1500 K and zero pressure, with intermediate configurations being saved after 0 ps ("as-prepared" glass), 1 ps, 10 ps, and 1 ns of annealing. Each configuration was then instantly quenched down to 300 K and relaxed in the *NPT* ensemble at zero pressure for 1 ns. Finally, all systems were further sampled in the *NVT* ensemble at 300 K during 200 ps for statistical averaging. Pair distribution functions, interatomic distances, neutron structure factors, and angular distributions were computed and can be found in Refs. [21,23].

It is worth pointing out that, upon annealing, samples exchange heat through their surfaces [24]. As such, note that, although the simulated annealing durations are extremely small as compared to those reached experimentally, the simulated systems also feature a much smaller surface and, as such, exchange heat significantly faster with the thermostat. Altogether, as shown below, the simulated annealing used herein yields variations of density that are comparable to those observed experimentally, which allows us to make qualitative comparisons between the experimental and simulation results presented herein.

2.4. Simulations of fracture

The influence of the temperature and pressure histories on the mode I fracture (i.e., under a tensile stress orthogonal to the plane in which the crack propagates) of the studied glasses was then simulated by MD. To compute fracture toughness, we relied on the energetic approach of fracture mechanics [25–27]. We first manually inserted a sharp initial crack in the (x, y) plane. After a relaxation to zero pressure, the system was elongated step-wise in the direction z by small increments (1%) of tensile strain. During each step, the system was relaxed for 50 ps, followed by another 50 ps for statistical averaging of the properties. Note that we examined the effect of the strain rate and found that, provided it is sufficiently low (<0.5 ns^{-1}), no significant influence on the obtained stress–strain curve is observed. Once the system is broken, the stress goes back to zero, so that the fracture energy G_c can be estimated by integrating the stress over the strain. The relationship between K_c and G_c is then given by the Irwin formula [28]. This methodology, whose details can be found in Refs. [9,29–31], was shown to offer realistic values of fracture toughness for various silicate glasses [9]. In complement, the surface energy γ_s of the glasses was roughly estimated by cutting the system into two parts, letting it relax for 25 ps, and computing the resulting change of the potential energy of the system (see Ref. [30]).