EMSE-290
Materials Laboratory III

Brittle Fracture of Glass

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1 Overview

Silicate glass is an ideally brittle material. Under mechanical loading, it behaves ideally elastic. There is no plastic deformation, the deformation energy is entirely stored as elastic strain, and all the strain energy is dissipated during fracture. This ideal behavior is a direct consequence of its structural perfection. Modern, liquid-based glass fabrication methods enable efficient removal of inclusions or bubbles by diffusion or mechanical means. Moreover, the transparency of glass permits a very effective quality control, so that defective parts are rarely put in service. The only region where a piece of glass can typically have a high concentration of defects is its *surface*.

Therefore, the fracture behavior of a piece of glass is usually dominated by the properties of its surface. In particular, it is important to what extent defects in the surface, "surface flaws," can concentrate applied mechanical stress. "One does not measure the strength of glass, one measures the strength of the surface of glass."

On one hand, the accumulation of surface flaws during service can severely limit the lifetime of class under mechanical load. On the other hand, the surface of glass is accessible to Engineering. The strength of glass can be improved, for example, by tempering it to retain residual stresses countering the opening of cracks at the surface.

Commercial glasses all contain at least 50 % silica (SiO_2, which forms the glassy network and is known as a "glass *former*." the properties of silica can be greatly modified by adding oxides of aluminum, sodium, calcium, barium, boron, magnesium, titanium, lithium, lead, and potassium. Depending on their function, these oxides are known as *intermediates* or *modifiers*. Soda-lime glass, the most widely produced glass, contains approximately 74 % SiO_2, 10 % CaO, 14 % Na_2O, and 2 % MgO. The elastic modulus of silicate glass ranges from 55 to 90 GPa, while the Poisson ratio ranges from 0.16 to 0.28.

In bulk form, silica glass typically has a strength of no more than 140 MPa. The reason why the strength is so low can be explained by the presence of small flaws and microcracks on the surface, some or all of which are introduced by inadvertent abrasion during normal handling of the material. These defects reduce the intrinsic strength of the materials strength by two or three orders of magnitude! The intrinsic or theoretical strength of glass is as high as 35 GPa, and freshly drawn fibers possess a tensile strength as high as 7 GPa, perhaps the highest strength of any tested material. Average values for glass fibers are on the order of 2 GPa. This is much stronger than steel (!), and therefore, glass is widely used as a high-strength/low-density reinforcement for polymeric materials (fiberglass).

Except for fibers, the strength of glass is usually measured in bending or "flexure." To improve the bending strength, there are two common strategies: (i) removal of the flaws from the surface prior to testing, and (ii) tempering.

To remove the flaws in the surface of a piece of glass, one can e. g. polish it with a flame or chemically etch it. Flame polishing is accomplished by heating the work piece (e. g. a glass rod) in a flame until it reaches a temperature at which the glass can flow. Owing to its surface tension, the glass will flow to close the flaws and round off any sharp edges. Chemical etching, in contrast, can entirely remove the thin surface layer that contains the flaws (or at least blunt them). In this experiment, we examine the effectiveness of chemical etching.

Tempering of glass aims to generate compressive stresses in the surface layer containing the flaws. If the layer that is left under compression remains sufficiently thin, the compressive stresses can be balanced by a relatively low, safe level of tensile stresses in the flaw free interior volume. Three strategies are widely used for this purpose: (i) thermal quenching, (ii) ion exchange, and (iii) cladding. The goal of each method is to achieve the equivalent of a union between a glass sheath that would like to be larger and an internal core that would like to be smaller. Mechanical incompatibility then requests the sheath to remain in compression and the core to remain in tension.

In thermal quenching, the surface sees a higher cooling rate than the interior. Therefore, the resulting room-temperature molar volume is larger than that of the interior of the workpiece, which is the the desired condition. In addition, the core remains warm enough to flow during some of the cooling period, while the outer sheath shrinks. This allows to relieve some of the transient stress. Further cooling causes the interior to shrink and add to the compressive load in the sheath. For thick pieces of glass, appropriate thermal gradients are readily obtained with gas jets. Thin pieces of glass require more aggressive quenching.

Ion exchange, or "ion stuffing," is obtained by tempering at low temperature. For this treatment, the glass is immersed in a molten salt containing monovalent ions with a large radius and a high activity. The high diffusion coefficient of monovalent ions in glass enables their diffusive mixing with the ions of the molten salt. Thus, sodium diffuses out of the glass to be replaced by potassium. Since the ionic radius of potassium (0.138 nm) substantially exceeds that of sodium (0.102 nm), the glass in which such ion exchange takes place will attempt to swell. As it is prevented from swelling, it will develop compressive stresses.

"Cladding" means to laminate two glasses with different thermal expansion coefficients at high temperature, such that the resulting glass composite features compressive stresses at the surface, balanced by tensile stress in the interior.

In the present experiment, we investigate the use of tempering and ion exchange.

In order to understand the mechanical properties of glass, is also important to recognize that interaction with the environment can change (*increase*) the flaw population on a glass surface. Water, in particular, affects glass by decreasing the connectivity of the network via the following chemical reaction:

$$\text{—Si—Si—} + \mathrm{H_2O} \longrightarrow \text{—Si—OH HO—Si—} \qquad (1)$$

This means that covalent chemical bonds are replaced with "physical" hydrogen bonds. The reaction (1) is promoted by mechanical stress. Thus, it preferentially occurs at crack tips under stress and so assists crack propagation. In our experiments, we explore this phenomenon by bend testing glass rods if submerged in water.

2 Experimental Procedure

2.1 Preparation of Glass Specimens

In addition to as-received to be used as reference, the following specimens will be tested:

2.1.1 Etched

A group of 10 SLS-glass rods will be aged for 1 h in an acid solution of 5 % HF. After etching, the samples must be rinsed thoroughly in flowing water and dried. Be careful not to scratch the sample surface after etching.

2.1.2 Etched and Abraded

As above, a group of 10 SLS-glass rods will be aged for 1 h in an acid solution of 5 % HF. Subsequently, when the samples have dried, flaws will be re-introduced to their surface by grinding them with SiC paper (400 grit).

This direction of motion of the abrasive related to the loading axis can be important to the results and should be recorded.

2.1.3 Chemically Strengthened by Ion Exchange

A series of 10 commercial SLS glass rods will be heated in a molten potassium nitrate at 400 °C for 2.5 h. After removing the samples from the salt, they will be allowed to cool slowly and then be washed from residual salt using water.

2.1.4 Thermally Strengthened

A series of 10 commercial SLS glass rods will be heated in a furnace at 650 °C, which roughly corresponds to the softening part of the glass. The tempering will continue for sufficient time to allow thermal equilibration (15 min). Subsequently, the samples will be quenched in warm oil and then slowly cooled to room temperature.

2.2 Bend Testing

All bend testing will be carried out in four-point bending with the Instron testing machine in the second floor laboratory of our Department. Test the following materials:

- 10 as-received rods.
- 10 as-received rods with the surface a saturated with water.
- 10 etched rods.
- 10 etched and abraded rods.
- 10 ion-exchanged rods.
- 10 tempered rods.

Evaluate the tests in the following way:

- For each test, compute the fracture stress and the elastic modulus of each specimen material and determine the average over all specimens.
- Plot the stress versus the deflection for “representative” examples of each class of specimens.

- For each class of specimen, plot the probability of failure versus the strength and determine the Weibull modulus.
- Discuss how and why each one of the different surface treatments affects the results.

References

[1] R Gardon. Calculations of temperature distributions in glass plates undergoing heat-treatment. *Journal of the American Ceramic Society*, 41:200, 1958.

[2] R Gardon. Evolution of theories of annealing and tempering: Historical perspective. *Ceramic Bulletin*, 66:1594, 1987.