Chapter 9: Mechanical Properties

With few exceptions (fiber-reinforced plastic or cement), glasses are not used as load bearing structural materials. Nevertheless, glass strength is still important:

- Large windows must be strong enough to withstand wind and weather
- John Hancock Building, Boston, is a noted failure
- Glass bottles that avoid over-pressurization by carbonated beverages
- Television tubes that don't implode
- Disaster? Depends on what's on…

**Glasses are brittle materials**

- No plastic deformation or ductile fracture
- Glasses fail catastrophically due to flaw growth
  - Flaws are stress intensifiers
- Brittle materials are stronger in compression:

  ![Compression closes flaws](image1) ![Tension opens flaws](image2)

US Navy deep-diving submarine design (1950’s) had spherical glass pressure hulls which would get stronger when submerged because of the hydrostatic compression.

- Brittle materials exhibit a Hookean response to applied stress. The extent of that response depends on the *Elastic Modulus*.

\[ \sigma = E \varepsilon \]

where E is the *Young’s Modulus*

Stiff materials (high E) require larger stresses to achieve minimal strains

*Poisson’s Ratio* describes the effect of longitudinal strain on transverse shrinkage:

\[ \nu = -\varepsilon_y/\varepsilon_x \]

most glasses: \(0.2 \leq \nu \leq 0.3\)

*Shear Modulus*: two dimensional response of shear strain (\(\varepsilon_{xy}\) or \(\gamma\)) to applied shear stress (\(\sigma_{xy}\) or \(\tau\)):

\[ \sigma_{xy} = G \varepsilon_{xy} \]

\[ G = E/2(1+\nu) \]
Condon-Morse description of ion-ion interactions can be used to define the elastic modulus. Relate an *applied force* to the average ion-ion distance in a bond. Shelby’s figure 9.1 (below) is the first derivative of the Condon-Morse potential used to describe CTE (figure 7.7)

![Shelby's Figure 9.1](image)

Equilibrium distance ($r_0$) is at $F=0$; need to apply force to move ions apart from $r_0$

- The *slope* of the $dF/dr$ curve defines the modulus
  - Greater slope $\rightarrow$ more applied force to separate an ion pair $\rightarrow$ greater modulus

**Strong Bonds:**
- *deep, more symmetric potential wells (Figure 7.7)*
- *higher modulus*
- *higher transformation temperatures (and melting points)*
- *lower thermal expansion coefficients*

**Effects of structure on modulus:**
- chains $\rightarrow$ planes $\rightarrow$ 3D network: increasing modulus
- nonbridging oxygens decrease modulus
  - alumina for alkali oxides: increase modulus
    - S-glass: high strength fiber glass: alkaline earth aluminosilicate
  - SiAlON glasses have the highest moduli: $\sim 200$ GPa (vs. $\sim 70$ GPa for silica)
Table 15-1 (from Kingery) compares elastic moduli of various ceramics and glasses.

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina oxide crystal</td>
<td>35.0</td>
</tr>
<tr>
<td>Alumina oxide (99% pure)</td>
<td>165.0</td>
</tr>
<tr>
<td>Alumina oxide (95% pure)</td>
<td>130.0</td>
</tr>
<tr>
<td>Alumina oxide (90% pure)</td>
<td>110.0</td>
</tr>
<tr>
<td>Alumina oxide (85% pure)</td>
<td>95.0</td>
</tr>
<tr>
<td>Alumina oxide (80% pure)</td>
<td>80.0</td>
</tr>
<tr>
<td>Alumina oxide (75% pure)</td>
<td>65.0</td>
</tr>
<tr>
<td>Alumina oxide (70% pure)</td>
<td>50.0</td>
</tr>
<tr>
<td>Alumina oxide (65% pure)</td>
<td>35.0</td>
</tr>
<tr>
<td>Alumina oxide (60% pure)</td>
<td>25.0</td>
</tr>
<tr>
<td>Alumina oxide (55% pure)</td>
<td>10.0</td>
</tr>
<tr>
<td>Alumina oxide (50% pure)</td>
<td>5.0</td>
</tr>
<tr>
<td>Alumina oxide (45% pure)</td>
<td>2.5</td>
</tr>
<tr>
<td>Alumina oxide (40% pure)</td>
<td>1.0</td>
</tr>
<tr>
<td>Alumina oxide (30% pure)</td>
<td>0.5</td>
</tr>
<tr>
<td>Alumina oxide (20% pure)</td>
<td>0.2</td>
</tr>
<tr>
<td>Alumina oxide (10% pure)</td>
<td>0.1</td>
</tr>
<tr>
<td>Alumina oxide (0% pure)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Hardness**
- Scratch resistance: indentation hardness, Vicker's indentor
  - Oxide glasses: 5-7 on Moh's scale
    - Will scratch apatite (Moh scale hardness = 5)
    - Will not scratch crystalline quartz (Moh scale hardness = 7)
  - In general: borates, phosphates, germanates are not as hard as silicates
  - Oxynitrides are hardest glasses: watch crystals
  - Chalcogenides are very soft

**Theoretical Strength**
Amount of work required to pull two atoms apart such that two new surfaces are created

**Orowon Equation:** Theoretical strength of ideal brittle materials; based on energy balance:
- energy required to create two new surfaces 
  \(2\gamma_f\text{, fracture surface energy}\) equals
- energy required to pull the atoms apart
  (integrated area under the \(\sigma(r)\) curve):

\[
\sigma_{\text{max}} = \left(\gamma_f E/a_0\right)^{1/2}
\]

For a typical silicate glass:
\(E \sim 70 \text{ GPa}; \gamma_f \sim 3.5 \text{ J/m}^2; a_0 \sim 0.2 \text{ nm}\)

\[
\sigma_{\text{max}} \sim 35 \text{ GPa (}=\frac{E}{2}\text{)}
\]
To break a glass, must overcome the elastic modulus and the surface energy.

Practical strengths of glasses, however, are significantly less than the theoretical strengths:

- Common glass products: \( \sim 14-70 \text{ MPa} \)
- Freshly drawn glass rods: \( \sim 70-140 \text{ MPa} \)
- Abraded glass rods: \( \sim 14-35 \text{ MPa} \)
- Wet, scored glass rods: \( \sim 3-7 \text{ MPa} \)
- Armored glass: \( \sim 350-500 \text{ MPa} \)
- Handled glass fibers: \( \sim 350-700 \text{ MPa} \)
- Freshly drawn glass fibers: \( \sim 700-2100 \text{ MPa} \)
- Most metals, including steels: \( \sim 140-350 \text{ MPa} \)

Reduction in practical strength is due to flaws that act as stress concentrators, causing local stresses to exceed the theoretical stress. Described by the Griffith equation:

\[
\sigma_{\text{frac}} = \left[ \frac{2E \gamma f}{\pi c^*} \right]^{1/2}; \text{ where } c^* \text{ is the critical crack length for crack growth}
\]

- Glass strength is dependent on the largest surface flaw
- Hard glasses are less prone to scratching and so will have greater practical strengths

Where do surface flaws come from?

- Abrasion with hard materials
  - Contact with other glasses- bottles get lubricity coatings (SnO\(_2\), TiO\(_2\)) to avoid scratches during manufacturing and handling.
  - Contact with metals
  - High strength glass rods rubbed with paper will lose 20-40% of their strength
- Chemical attack- water
- Stress corrosion
- Thermal stresses; fictive temperature effects and \( \Delta \text{CTE} \)
- Dust particles or surface devitrification during processing, etc.

Polishing (mechanical, flame, acid etching) reduces surface flaws.

**Strengthening of Glass**
You can remove flaws, as noted above, but new flaws will form with subsequent normal handling

- **Prevent crack growth**: avoid tensile stresses from being generated at a crack tip by creating a surface compression layer
  - **Ion exchange** samples (as noted in chapter 8).
    - Large ion stuffing below \( T_g \) (K\(^+\) for Na\(^+\))
    - Small ion exchange, lower surface CTE
    - Surface dealkalization- leaves lower CTE surface
2. Quench to RT: decoupled center would shrink to smaller dimension (lower $T_{fic}$), but
3. Constrained by surfaces, center goes into tension and surface into compression

- **Thermal tempering** - high $T_{fic}$ surface, low $T_{fic}$ interior
  - Works best for thick samples; hard to get sufficient $\Delta T$ with thin walled samples
  - Works best for higher CTE glasses. (Hard to thermally temper fused silica, because the induced stress depends on $(\Delta T)(\Delta CTE)$.)
  - Car windshields used to be thermally tempered: surface compression creates lots of stored energy that is released catastrophically, causing the glass to ‘dice’ into small fragments: high stored lattice energy released through the creation of a large surface area.
  - Diced windshields did less damage to flying passengers than the large, dagger-like pieces of annealed (untempered) glass. (Note: inventor of tempered safety glass was killed in a car accident- sliced up by his windshield- before his car was out-fitted with his glass.)

- Modern windshields are laminated:
  - Inner window is thermally tempered to dice; absorbs some impact energy
  - Polymer layer absorbs additional energy, helps keep passengers inside the car
  - Designed to fail just below the stress that will fracture a skull

- Thermal tempering:
  1. Glass piece is heated in furnace to 750-800°C
     - Above $T_g$; must have different $T_{fic}$
  2. Cold air then blown on both surfaces (plate glass)
     - Prince Rupert’s drops??

*Thermal Shock* - stresses that arise from temperature gradients
- These are transient stresses from $\Delta T$ below $T_g$; not a fictive temp effect

$$\sigma = \frac{E\alpha\Delta T}{(1-\nu)}$$

Where $\alpha$ is CTE, $E$ is elastic modulus, $\nu$ is Poisson's ratio.

The maximum temperature gradient that a piece of glass will survive is
So, small $\alpha$, $E$ will yield large $\Delta T$ before thermal shock failure.

Note: Glasses are more prone to thermal shock damage when quenched from hot to cold (shrinking surface puts center in compression, surface into tension) than rapid heating from cold to hot (expanding surface constrained by center).

**Annealing**
- removal of residual stresses; stress relief at a constant temperature
  - related to the Maxwell relaxation time
- after equilibration, must cool at slow enough rate to avoid creating new permanent stresses (or temporary, thermal shock stresses).

Exact annealing schedule depends on glass properties and glass geometry

Typical annealing schedule:
- 30-60 minutes at $T_g (\sim 10^{11}$ Pa-s)+ 5K; (although $T_{\text{anneal}} (\sim 10^{12}$ Pa-s)+ 5K might be better)
- -1K/min through the transformation range to $T<T_{\text{strain}} (\sim 10^{13.5}$ Pa-s)
  (Fine annealing: optical glasses that demand best homogeneity not achieved by coarse annealing may be cooled more slowly)
- At $T<<T_{\text{strain}}$, faster cooling to RT (-10K/min)
  (Large, high CTE pieces might be cooled more slowly to avoid thermal shock).

Annealing creates reproducible products.
Statistical Nature of Glass Fracture
• Glass articles have distributions of fracture strengths. Why?
  • Distributions of flaw sizes/populations

Gaussian distribution of failure stresses:
\[ P = \frac{1}{d\sqrt{2\pi}} \exp\left(-\frac{(s - s_m)^2}{2d^2}\right) \]

Weibull Statistics
\[ P = \frac{1}{d\sqrt{2\pi}} \exp\left(-\frac{(s - s_m)^2}{2d^2}\right) \]
\[ \ln[-\ln(1 - F)] = m(\ln s - \ln s_0) \]

Weibull Distribution describes the fraction, F, of samples that fail at stresses < s:
\[ F = 1 - \exp\left(-\left(\frac{s}{s_0}\right)^m\right) \]

Where \( s_0 \) is a scaling factor (\( = s_m \)), \( m = d^{-1} \), describes the distribution of fracture strengths and is called the Weibull Modulus. Obtained from 'double-log' plots:
\[ \ln[-\ln(1 - F)] = m(\ln s - \ln s_0) \]

Small values for 'm' mean large distributions in fracture stress
• hard to predict lifetimes for individual pieces of a glass, even if there is a large average fracture stress.
• Better engineering predictions with large Weibull modulus populations, even if average fracture stress is lower
Fatigue of Glasses

Some Observations:
- Under normal conditions, strength of glass decreases with time:
  - Static Fatigue
- A glass will fail at greater applied stresses, if the stress is rapidly applied:
  - Dynamic Fatigue
- Static and dynamic fatigue behaviors disappear from samples tested in liquid nitrogen (-100°C)
- Strength decreases with increasing humidity and temperature
  - Glass tensile strength is significantly less under water

These observations can be explained by a 'stress-enhanced' reaction of water with the glass lattice at a crack-tip: Stress Corrosion.

- Stretching the Si-O-Si bonds at the crack tip make those bonds more reactive to water:
  \[ \text{Si-O-Si} + \text{H}_2\text{O} \rightarrow 2\text{SiOH} \]
- Result of this reaction is a lengthening of the crack
- Faster hydrolysis reaction at higher temperatures and greater humidity
- No water transport to crack tip at liquid N\textsubscript{2} temperatures
- Static Fatigue therefore due to the diffusion of water to the crack tip, lengthening the 'critical crack length, reducing the ultimate fracture stress.
- Dynamic Fatigue occurs because fast stress drives cracks faster than water can diffuse to the crack tip, resulting in a greater ultimate fracture stress than under slow loading when water can diffuse to the tip and so lengthen the crack.