Why Does Glass Break?
Some considerations of the mechanical properties of glass

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If glass was 100X stronger, what *new* applications would result?
New applications will benefit from stronger glass.....
Apple Store, 5th Ave., NYC

Glasgow, Scotland
Train Station/Strasbourg, France
Higher Strength ➞ Less Weight

~ 2.5* MJ/container

-10% Weight

~ 2.2 MJ/container

*US DoE and Bureau of Census Data

SO_x + CO_2 + NO_x

Emilio Spinosa, O-I, Vancouver, June 2009
Strong glass comes in handy for other applications
Our Outline

1. Background Information
   • Elastic modulus
   • Fracture mechanics and strength
   • Fatigue
   • Strengthening
2. Two-point bend studies of pristine glass
Some useful references:

Can we connect mechanical performance to the molecular structure of glass?
Elastic Modulus

Definitions?
Why should we care about modulus?
Elastic Modulus - resistance to deflection

Why is the elastic modulus of a glass important?
• Stiffer hard-drive disks (minimize deflection at high rpm’s)
• Stiffer glass-fiber reinforces composites (larger wind-turbine blades)
• Reduce the thickness (and weight) of architectural glass)
• Increase the stiffness of glass-bearing structures (buildings, bio-glass scaffolds, etc.)
• Design glass or glass-ceramic matrices for aerospace applications

\[ \sigma_x = E \varepsilon_x \]

Poisson’s Ratio

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Elastic Modulus Is Related To The Strength of Nearest Neighbor Bonds

\[ F = - \frac{dU}{dr} \]

Stiffness \[ S_0 = \left( \frac{dU^2}{dr^2} \right)_{r = r_0} \]

Elastic Modulus \[ E = \frac{S}{r_0} \]

Elastic Modulus: Pascals = J/m^3
a measure of the volume density of strain energy \( (E \approx U_0/V_0) \)

Bulk Modulus:

\[ K = V_0 \frac{\partial^2 U}{\partial V^2} \bigg|_{V_0} = \frac{mn}{9V_0} U_0 \]
From atomistic to continuum properties:

\[
K = V_0 \frac{\partial^2 U}{\partial V^2} \bigg|_{V_0} = \frac{mn}{9V_0} U_0
\]

**Multi-component glasses:**

\[
\left\langle \frac{U_0}{V_0} \right\rangle = \sum f_i \Delta H_{ai} / \sum f_i M_i / \rho_i
\]

\[
\Delta H_{ai} = x \Delta H_f^0 (A) + y \Delta H_f^0 (B) - \Delta H_f^0 (A_x B_y)
\]

- \( \rho_i \): density
- \( f_i \): molar fraction of \( i^{th} \) component
- \( M_i \): molar mass of \( i^{th} \) component
- \( \Delta H_{ai} \): enthalpy of \( i^{th} \) component (Born-Haber cycle)
E and $T_g$ are related within a composition class

More cross-links: greater E

![Graph showing Young's modulus vs. carbon or nitrogen content](image)

Poisson’s ratio appears to be sensitive to structure: packing density and ‘network dimensionality’

\[ \nu = \frac{\varepsilon_\text{L}}{\varepsilon_\text{L}} = -\frac{L}{D \Delta D / \Delta L} \]

\[ \Delta V / V = \text{Trace } \varepsilon = (1 - 2 \nu) \sigma / E \]

\( a\text{-SiO}_2 \)  
\( GeSe_4 \)  
\( a\text{-Se} \)  
\( Zr_{55}Cu_{30}Al_{10}Ni_5 \)

\( \nu \approx 0.16 \)  
\( \nu \approx 0.286 \)  
\( \nu \approx 0.323 \)  
\( \nu \approx 0.37 \)
The temperature-dependence of the Poisson’s ratio may indicate changes in structure through the glass transition.
Summary: Elasticity

• There is a limited correlation between $E$ and $T_g$ within compositional series, but not necessarily between compositional types
• High elastic moduli are favored by structural disorder and atomic packing seems to be more important than bond strength
• Poisson’s ratio ($\nu$) correlates with atomic packing density and with network dimensionality (polymerization)
• The temperature dependence of elastic properties above $T_g$ may be related to “fragile” and “strong” viscosity behavior.
Glass Strength

What factors determine the strength of glass?
Theoretical Strength Can Be Estimated From the Potential Energy Curve (Orowan)

\[
\sigma_m = \lambda \frac{E}{\pi a_0}
\]

\[
2\gamma_f = \sigma_m \sin\left(\frac{\pi x}{\lambda}\right) \, dx = \frac{\lambda \sigma_m}{(\pi)}
\]

\[
\sigma_m = \left[\frac{\gamma_f E}{a_0}\right]^{1/2}
\]

If \( E = 70 \text{ GPa}, \gamma_f = 3.5 \text{ J/m}^2 \) and \( a_0 = 0.2 \text{nm} \), then

\[
\sigma_m = 35 \text{ GPa}
\]
How does the addition of Na$_2$O affect the Young’s modulus and fracture surface energy of silica glass? Consider what Prof. Pantano discussed the other day....
Practical strengths are significantly less than the theoretical strengths:

- Common glass products: $\sim 14$-70 MPa
- Freshly drawn glass rods: $\sim 70$-140 MPa
- Abraded glass rods: $\sim 14$-35 MPa
- Wet, scored glass rods: $\sim 3$-7 MPa
- Armored glass: $\sim 350$-500 MPa
- Handled glass fibers: $\sim 350$-700 MPa
- Freshly drawn glass fibers: $\sim 700$-2100 MPa
- Most metals, including steels: $\sim 140$-350 MPa
C. E. Inglis (1913): flaws acted as stress concentrators
A.A Griffith (1921): critical flaws determine strength

Stress enhancement by flaws with length 2c and radius ρ:

\[ \sigma_{yy} \approx 2 \sigma_a (c/\rho)^{1/2} \]

Calculated strength with critical flaw \( c^* \):

\[ \sigma_f = \left[ 2 \gamma_f E / \pi c^* \right]^{1/2} \]

If \( E = 70 \text{ GPa} \), and \( \gamma_f = 3.5 \text{ J/m}^2 \)
Then a crack of 100 microns will result in a failure stress of \( \approx 25 \text{ MPa} \)
Fracture mechanics allow the evaluation of stresses in the vicinity of a propagating crack.

\[ \sigma_{ij} = \left[ \frac{K}{2\pi r} \right] f_{ij}(\theta) \]

Fracture criterion when stress intensity exceeds the strain energy release rate (depends on \( E, \gamma_f \))

\[ K_{lc} = \sigma_a \left( \pi c \right)^{1/2} \]
Cathodoluminescence measurements of stress distributions around crack tips (Pezzotti and Leto, 2007)
An aside: Weibull Statistics

\[ P = \left( \frac{1}{d \sqrt{2\pi}} \right) \exp \left( -\frac{(\sigma - \sigma_m)^2}{2d^2} \right) \]

\[ \ln \ln \left( \frac{1}{P_F} \right) = m \ln \sigma - \ln \sigma_0 \]

Note: same ‘average’ fracture strength, but \( m_1 < m_2 \) (broader distribution of strengths).

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Room temperature tensile tests of pristine silica fibers drawn and tested in vacuum- bimodal distribution

![Graph showing strength distributions](image)

**Figure 2** Strength distributions for T-08

Smith and Michalske, 1992

Flame-attenuation of optical fibers

![Graph showing the relationship between fiber diameter and failure strength.](image)
E-glass fibers (tensile tests, in air)

Lower soak temperatures lead to bimodal strength distributions

Cameron, 1968
Concentric ring tests, abraded Corning glass 1737, two different thicknesses.

Mechanical properties depend on glass structure

K/Al-metaphosphate glasses
Table 2. Mechanical characteristics of inorganic glasses in three oxide systems

<table>
<thead>
<tr>
<th>Glass no.</th>
<th>Chemical composition</th>
<th>Strength in liquid nitrogen $\sigma$, GPa</th>
<th>Hardness $H$, GPa</th>
<th>Young’s modulus $E$, GPa</th>
<th>Ultimate elastic strain $\varepsilon = \sigma/E$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{B}_2\text{O}_3$</td>
<td>1.2</td>
<td>1.7</td>
<td>22</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>$15\text{Na}_2\text{O} \cdot 85\text{B}_2\text{O}_3$</td>
<td>2.7</td>
<td>3.9</td>
<td>52</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>$33\text{Na}_2\text{O} \cdot 67\text{B}_2\text{O}_3$</td>
<td>3.0</td>
<td>4.9</td>
<td>73</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td><strong>Borate glasses</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\text{SiO}_2$</td>
<td>12.0</td>
<td>8.5</td>
<td>73(100*)</td>
<td>12.0*</td>
</tr>
<tr>
<td>5</td>
<td>$33\text{Na}_2\text{O} \cdot 67\text{SiO}_2$</td>
<td>3.5</td>
<td>3.7</td>
<td>60</td>
<td>5.8</td>
</tr>
<tr>
<td>6</td>
<td>$12.5\text{Na}_2\text{O} \cdot 12.5\text{Al}_2\text{O}_3 \cdot 75\text{SiO}_2$</td>
<td>8.3</td>
<td>5.4</td>
<td>72</td>
<td>11.5</td>
</tr>
<tr>
<td>7</td>
<td>$16.5\text{Na}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{SiO}_2$</td>
<td>8.4</td>
<td>5.5</td>
<td>73</td>
<td>11.6</td>
</tr>
<tr>
<td>8</td>
<td>$25\text{Na}_2\text{O} \cdot 25\text{Al}_2\text{O}_3 \cdot 50\text{SiO}_2$</td>
<td>8.5</td>
<td>6.0</td>
<td>74</td>
<td>11.4</td>
</tr>
<tr>
<td>9</td>
<td>$14.5\text{MgO} \cdot 14.5\text{Al}_2\text{O}_3 \cdot 71\text{SiO}_2$</td>
<td>10.4</td>
<td>6.4</td>
<td>95</td>
<td>10.9</td>
</tr>
<tr>
<td>10</td>
<td>$6\text{TiO}_2 \cdot 94\text{SiO}_2$</td>
<td>7.5</td>
<td>6.5</td>
<td>68</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td><strong>Silicate glasses</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$16.5\text{Cs}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{P}_2\text{O}_5$</td>
<td>1.6</td>
<td>3.5</td>
<td>50</td>
<td>3.2</td>
</tr>
<tr>
<td>12</td>
<td>$16.5\text{Rb}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{P}_2\text{O}_5$</td>
<td>2.4</td>
<td>3.8</td>
<td>55</td>
<td>4.4</td>
</tr>
<tr>
<td>13</td>
<td>$16.5\text{K}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{P}_2\text{O}_5$</td>
<td>2.5</td>
<td>4.1</td>
<td>59</td>
<td>4.2</td>
</tr>
<tr>
<td>14</td>
<td>$16.5\text{Na}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{P}_2\text{O}_5$</td>
<td>3.0</td>
<td>4.5</td>
<td>68</td>
<td>4.4</td>
</tr>
<tr>
<td>15</td>
<td>$16.5\text{Li}_2\text{O} \cdot 16.5\text{Al}_2\text{O}_3 \cdot 67\text{P}_2\text{O}_5$</td>
<td>3.4</td>
<td>4.9</td>
<td>74</td>
<td>4.6</td>
</tr>
<tr>
<td>16</td>
<td>$27.5\text{Al}_2\text{O}_3 \cdot 67.5\text{P}_2\text{O}_5$</td>
<td>4.0</td>
<td>5.7</td>
<td>89</td>
<td>4.5</td>
</tr>
<tr>
<td>17</td>
<td>$17.5\text{Al}_2\text{O}_3 \cdot 15\text{ZnO} \cdot 67.5\text{P}_2\text{O}_5$</td>
<td>5.7</td>
<td>5.5</td>
<td>81</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td><strong>Phosphate glasses</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The parameter obtained with due regard for the increase in the Young’s modulus with an increase in the strain [17].
MD Simulations of fracture reveal the development of cavities that coalesce to form the failure site

Pedone et al., 2008
Quenched and annealed soda-lime glasses at 5GPa tension

There may be experimental evidence for cavitation near the tips of slow-moving cracks

Aluminosilicate glass, $10^{-11}$ m/s, 45% RH, AFM Images

Formation of ‘nano-cavities’ interpreted as evidence for ‘nano-ductile’ fracture of glass!

‘Nano-ductility’ interpretation is not universal

‘Post-mortem’ AFM analyses of the opposing fracture surfaces show no evidence for the formation of nano-cavities

Note the relatively rough surface

Guin and Wiederhorn, PRL (2004)
Fatigue
An example of fatigue in glass

http://www.youtube.com/watch?v=r8q-R9ZlSac
Stress Corrosion: source for static fatigue - the reduction in strength with time

Fig. 1. Stress-time characteristics of glass, from bending tests on 1/4 in. diameter soda-lime-silicate rods. Taken from Shand.¹
Fatigue data on silica fibers

- Liquid nitrogen
- Room temperature, vacuum
- Room temperature, ambient conditions

Note: residual stresses increase susceptibility to static fatigue

Fig. 10. Increased susceptibility to static fatigue due to indentation residual stresses. Vickers-Indented soda-lime glass (load: 5 N), tested in water (from [25]).
Double-Cantilever Beam (DCB) used for controlled stress intensity and crack velocity experiments

\[ V = \frac{dc}{dt} \]

\[ K = \frac{P^2}{f(\text{geometry})} \]

Crack propagation kinetics depend on the stress intensity

Region I: stress-corrosion

Region II: diffusion-limited

Region III: rapid fracture ($K_{IC}$)

Region 0: propagation threshold

Fig. 1. The schematic of the $K_I-V$ curve for soda-lime-silicate glasses. $K_{IC}$ is the critical stress intensity, i.e., fracture toughness. The dashed line shows the $K_I-V$ curve in a vacuum.
Water and stress enhance crack growth in glass

Region I: stress-corrosion

\[ v = A K_I^n \]

where \( n \) is the ‘stress corrosion susceptibility factor’

SM Wiederhorn, JACerS, 50 407 (1967)
Compositional-dependence of $v$-$K$ behavior in Region I

Different glasses are more or less susceptible to fatigue effects –

*We do not understand this compositional dependence!*
Temperature-dependence of v-K behavior in Region I

Wiederhorn and Bolz, JACerS, 53, 545 (1970)
Slow crack growth is a thermally activated process

Chemical rate theory has been used to explain the exponential form of the $V - K_I$ curves:

$$V = V_0 \exp(-E + bK_I / RT)$$

where $V_0$ is a constant, $E$ is the activation energy for the reaction, $R$ is the gas constant, $T$ is the temperature, and $b$ is proportional to the activation volume for the crack growth process, $\Delta V^*$. 

Wiederhorn, et al., JACerS, 1974
Stress-corrosion in silicate glass:

a. **Adsorption** of a water molecule on a strained siloxane bond at a crack tip;

b. **Reaction** based on proton and electron transfer;

c. **Separation** of silanol groups after rupture of the hydrogen bond.

Net result: extension of the crack length by one tetrahedral unit

Stress-corrosion in silicate glass:

a. Reactive molecules can donate both protons and electrons to the ruptured siloxane bond;
b. Reactive molecules are small enough to reach the crack tip (<0.5 nm).

Water, ammonia, hydrazine (H$_2$N-NH$_2$), formamide (CH$_3$NO)

Other ‘crack-tip chemistries’ lead to strength increasing with time

- Controlled flaws (Vicker’s indents) in S-L-S
- Aging in different environments
- Tensile tests in inert conditions (silicone oil)
- May be due to stress release- not crack geometry?

Change in crack tip geometry due to corrosion: (a) Flaw sharpening for stresses greater than the fatigue limit; (b) Constant flaw sharpness for stresses equal to the fatigue stress; (c) Flaw blunting for stresses below the fatigue limit.


AFM detects significant morphological changes around the crack-tip in aged samples

- Formation of alkali-rich regions modeled by $\text{Na}^+\text{-H}_3\text{O}^+$ inter-diffusion
- Alkali depletion from crack-tip region leads to stress-relaxation
  - Crack extension threshold

$K_\text{f}=0.422\,\text{MPa.m}^{1/2}$
$v=3\,\text{nm.s}^{-1}$

$K_\text{f}=0.42\,\text{MPa.m}^{1/2}$
$v=2.2\,\text{nm.s}^{-1}$

$K_\text{f}=0.415\,\text{MPa.m}^{1/2}$
$v=1.5\,\text{nm.s}^{-1}$

$K_\text{f}=0.38\,\text{MPa.m}^{1/2}$
$v=0.5\,\text{nm.s}^{-1}$

SLS glass, 45% RH

Célarié, et al., JNCS (2007)
The ‘corrosion reactions’ at a crack tip are similar to those that occur at glass surfaces

From Prof. Jain:
A clear glass plate is made of soda lime silicate glass by pressing molten gob. It shows the following undesirable pattern upon washing in a dishwasher. Discuss this problem with your roommate. Then develop a collaborative research program to characterize and solve the problem. The proposal should be about 1500 words long.
Water plays many roles at a crack-tip

1. Chemical attack on strained bonds to extend flaws

2. Water films adsorbed on crack surfaces

3. Capillary condensation at the crack tip

4. Water diffusion into the glass network, changing elastic properties

5. Inter-diffusion with alkali ions, changing pH and attacking glass
Strengthening - What can we do to make glass stronger (or more reliable)?
• Polished surfaces
• Surface dealkalization
• Protective coatings
• Relaxation of residual stresses (annealing)
• Reduction of expansion coefficients (thermal shock)
• Thermal tempering
• Chemical tempering
• Modified compositions:
  – Increasing elastic modulus and/or surface energy
  – Reducing stress-corrosion
  – Propagation threshold
  – Crack healing
Annealed vs. chemically tempered glass

From Jill Glass, Sandia National Labs
Two-point bend studies of the failure characteristics of silicate glasses
We have produced and tested pristine fibers

- “Pristine” 10 cm length fibers
- Fiber diameters ~125 mm.
- Fibers can be tested immediately.
We have measured failure strains using a Two-Point Bend technique

- Face plate velocities: 1 – 10,000 mm/sec
- Liquid nitrogen, room temp/variable humidity.
- Small test volume (25-100mm gauge length).

\[ \varepsilon_f = \left( \frac{1.198 \cdot d}{D - d} \right) \]

The inert failure strain measurements are reproducible

Eight sets of E-glass fibers, tested in liquid nitrogen, collected over two years

Silica  
\( m = 103 \)  
\( \varepsilon_{\text{Avg}} = 17.98 \% \)

E-Glass  
\( m = 119 \)  
\( \varepsilon_{\text{Avg}} = 12.81 \% \)
The inert failure strain measurements are intrinsic

Criteria for ‘intrinsic’ failure properties*

- Narrow failure distributions: $s(\text{failure}) < s(\text{fiber diameter})$
- Failure property (strength, strain) independent of diameter


~180 E-glass fibers/LN$_2$ tests
Fibers fail at lower strains in ambient conditions

20%RH, 26°C

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Fatigue effects can be characterized.

Weibull Plot of 4A (0.0% B₂O₃)

- Tested at 24°C and different relative humidities.
- FPV = 4000 μm/s

Increasing RH

80% RH

10% RH

4A

24°C, varied RH
m_Avg = 181

Cumulative Failure Probability (%)

1
3
5
10
20
40
60
80
90
99

Failure Strain (%)
Aging effects have also been characterized.

4A Aged at 80% RH, 50°C
Tested using: LN$_2$, 4000 μm/s

Fresh
2 days
4 days
7 days
14 days
28 days

Aging of 4A
Aging of 4A2
Aging of 4C (set 1)
Aging of 4C (set 2)

B-free composition

Ca-aluminoborosilicates

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IMI-71
What might inert 2pb studies tell us about the failure characteristics of silicate glasses?
Compositions Studied

- $x\text{Na}_2\text{O} \times (100-x)\text{SiO}_2$
  - $x = 0, 7, 10, 15, 20, 25, 30, 35$

- $x\text{K}_2\text{O} \times (100-x)\text{SiO}_2$
  - $x = 0, 4.5, 7, 10, 15, 20, 25$

- $25\text{Na}_2\text{O} \times x\text{Al}_2\text{O}_3 \times (75-x)\text{SiO}_2$
  - $x = 0, 5, 10, 15, 20, 25, 30, 32.5$

- $x\text{Na}_2\text{O} \times y\text{CaO} \times (100-x-y)\text{SiO}_2$
  - *Compositions studied by Ito, et al.*
Na-silicate inert failure strains depend on composition

Avg $m \sim 259$

$x\text{Na}_2\text{O} \times (100-x)\text{SiO}_2$
Sodium silicate properties

Elastic Modulus (GPa) vs. Mole Fraction Na$_2$O

Failure Strain (%) vs. Mole Fraction Na$_2$O

Increasing NBO’s

xNa$_2$O * (1-x)SiO$_2$

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Na-Al-silicate inert failure strains depend on composition

25Na₂O * (x)Al₂O₃ * (75-x) SiO₂
Na-Al-silicate properties depend on structure

![Diagram showing the relationship between mole fraction, elastic modulus, and failure strain.]

- Greater cross-linking: “stiffer” structure

0.25Na$_2$O * (x)Al$_2$O$_3$ (0.75-x) SiO$_2$

Fully ‘cross-linked’
Inert failure strain decreases for ‘cross-linked’ structures.
Failure strain depends on elastic modulus

- NAS
- NS
- KS
- NB
- SLS
- Silica
- CABS
- TV Panel
- E-Glass
- C-0317

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Do these measurements provide information about the strength of glass?

...depends on what we know about the elastic modulus
Elastic modulus depends on strain

E-glass fibers

Na/Li-phosphate fibers

Strain dependence of modulus has been modeled

Converting failure strain to failure stress requires knowledge of $Y(\varepsilon)$: Gupta and Kurkjian, JNCS 351 (2005) 2343

\[ Y(\varepsilon) = Y_0 + Y_1 \varepsilon + \left(\frac{Y_2}{2}\right) \varepsilon^2; \sigma_f = \varepsilon_f \left[\frac{2}{3}Y_0 + \left(\frac{Y_1}{6}\right) \varepsilon_f\right] \]
Failure strengths can be calculated if $Y(\varepsilon)$ is known.
What role is played by ‘critical flaws’?

- There are no apparent surface heterogeneities.
- If Griffith flaws are responsible for low strengths, they will be in the range of 2-7 nm, depending on the flaw (stress concentrator) geometry.

\[
\sigma_f = \left( \frac{2E\gamma}{\pi c} \right)^{\frac{1}{2}}
\]

Recall processing effects
Advantex Failure Strains

Weibull distributions of fibers drawn after different melt histories. Weibull modulus \((m)\), average failure strain \(\varepsilon_{\text{Avg}}\), and melt history are reported for each data set.

Weibull modulus \((m)\), average failure strain \(\varepsilon_{\text{Avg}}\), and melt history are reported for each data set.

Advantex C2 P5
2:00 at 1180°C
\(m = 7\)
\(\varepsilon_{\text{Avg}} = 10.36\%\)

Advantex C2 P4
2:00 at 1200°C
\(m = 9\)
\(\varepsilon_{\text{Avg}} = 10.88\%\)

Advantex C2 P3
2:00 at 1250°C
\(m = 60\)
\(\varepsilon_{\text{Avg}} = 12.11\%\)

Advantex C2 P2
12:00 at 1350°C
\(m = 129\)
\(\varepsilon_{\text{Avg}} = 12.18\%\)

Advantex C2 P8
0:30 at 1350°C
\(m = 3\)
\(\varepsilon_{\text{Avg}} = 8.51\%\)

Advantex C2 P9
1:00 at 1350°C
\(m = 4\)
\(\varepsilon_{\text{Avg}} = 9.34\%\)

Advantex C2 P10
2:00 at 1350°C
\(m = 35\)
\(\varepsilon_{\text{Avg}} = 11.73\%\)

Advantex C2 P11
3:00 at 1350°C
\(m = 55\)
\(\varepsilon_{\text{Avg}} = 11.88\%\)
Some questions related to Prof. Sen’s lecture:

What type of heterogeneities might account for these distributions in failure strains?

What techniques could you use to characterize these heterogeneities?
Advantex Thermal History Summary

When the glass was melted at 1350°C, the failure strain distributions narrow with time. Failure strain distributions begin to broaden when melts are cooled to $T_L + 50°C$. 

Glass behaves strangely at $T_L - 50°C$. 

Crystallites form when the glass was melted at 1350°C, the failure strain distributions narrow with time. 

Failure strain distributions begin to broaden when melts are cooled to $T_L + 50°C$. 

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How does glass break?
Inert ‘failure rate’ studies

- 'Normal' Inert Fatigue
  - Silica
    - $m_{\text{Avg}} = 132$
  - Increasing $V_{fp}$

- Inert Delayed Failure Effect
  - 10-10-80 SLS
    - $m_{\text{Avg}} = 189$
  - Decreasing $V_{fp}$

2010 US-China Winter School
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IMI-89
Inert ‘failure rate’ studies

\[ n = 1 / \left( \frac{d \ln(\varepsilon)}{d \ln(V_{fp})} \right) \]

\[ n = 365 \]

\[
\begin{align*}
\text{ln (failure strain, %)} & \quad 10-10-80 \text{ SLS} \\
& \quad \text{Silica}
\end{align*}
\]
The inert delayed failure effect depends on structure.
Failure strain measurements also correlate with crack initiation loads.

\[ 0.25\text{Na}_2\text{O} \times (x)\text{Al}_2\text{O}_3 \times (0.75-x)\text{Si}_2\text{O}_2 \]

Satoshi Yoshida, 2003
Failure strain measurements may provide information about ‘less brittle’ glasses

Soda-lime-silica commercial window glass

Less brittle glass

Figure 4 Micrographs of surfaces scratched by steel roller cutter (a) and indented by a diamond tool (b) at (one) 1kg load for a commercial window glass and a new less brittle glass.

Setsuro Ito, 2002
“Brittleness parameter” has been determined from indentation measurements

\[ s \equiv B = 2.39 \ P^{1/4} \left( \frac{C}{a} \right)^{3/2} \]

P is applied load, C is crack length, and a is Vickers indentation diagonal length

Setsuro Ito, 2002
Soda-lime silicate glasses exhibit the ‘delayed failure’ effect

<table>
<thead>
<tr>
<th>Failure Strain (%)</th>
<th>Cumulative Failure Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>18.5</td>
<td>5</td>
</tr>
<tr>
<td>19</td>
<td>10</td>
</tr>
<tr>
<td>19.5</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
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<td>60</td>
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<tr>
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<td>80</td>
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<tr>
<td></td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>99</td>
</tr>
</tbody>
</table>

Each glass possesses a large IDFE.

Closed symbols
4000 mm/sec,
Open symbols
50 mm/sec

15-5-80 SLS
$m_{Avg} = 345$

15-10-75 SLS
$m_{Avg} = 326$

20-10-70 SLS
$m_{Avg} = 261$
‘Brittleness’ and ‘inert delayed failure’ may be related

![Graph showing correlation between IDFE (Missouri S&T) and Brittleness (lto).]

- **IDFE (Missouri S&T)**
- **Brittleness (lto)**

Soda-lime & borosilicate glasses

- **Silica**
Is IDFE related to network relaxation?

Day & Rindone, 1962

Na diffusion

NBO motion?

Day & Rindone, 1962
Is there a universal dependence of glass failure characteristics on network structure?

WOULD ‘INSTANTANEOUS’ FAILURE STRAINS ALL FALL ON A STRAIGHT LINE??

1. $\varepsilon_{\text{LN}}$ depends on $E$ (IDFE≤0)
2. Silica is anomalous
3. $\varepsilon_{\text{LN}}$ depends on network relaxation (IDFE>0)

$\text{LN}_2$ tests at 4000 μ/sec

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Summary

- Inert failure strains are sensitive to the composition/structure of glass fibers.
  - $\varepsilon_f$ increases when NBO’s replace BO’s
  - $\varepsilon_f$ increases when Young’s modulus decreases
- Inert failure strains are dependent on the applied stressing rates ($V_{fp}$).
  - Structure with non-bridging oxygens fail at larger strains with slower $V_{fp}$.
  - ‘Framework’ structures do not exhibit this ‘inert delayed failure effect’.
- Is IDFE due to relaxation of the network? What role is played by the NBO’s?
The NSF/Industry/University *Center for Glass Research* sponsored the two-point bend studies at Missouri S&T.

Nate Lower and Zhongzhi Tang collected the data.

Chuck Kurkjian (retired, AT&T) inspired the work.