

# Strength and Microscopy Analysis of Surface-modified Soda-lime-silicate Glass Rods

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## Abstract

Glass has high theoretical strength; however, microcracks on the surface of the glass greatly decrease the strength. Various methods to alleviate the effects of these cracks have been devised, including ion-exchange, mechanical abrasion, and acid etching. The goal of this experiment was to compare these methods by quantifying the strength via three-point bend testing to determine the modulus of rupture. Optical microscopy confirmed results, including the data that indicated that ion-exchange had the largest effect on strength by either widening or forcing shut cracks. Acid etching produced a moderate improvement in modulus of rupture by smoothing cracks. Finally, mechanical abrasion decreased strength but provided a more uniform strength distribution.

Keywords: soda-lime-silicate glass, glass microscopy, three-point bend testing, modulus of rupture

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## 1. Introduction

Soda-lime-silicate glass is one of the most commonly used glasses due to ease of production and high theoretical strength. Covalent bonding prevalent in glasses results in theoretical strength on the order of 7 GPa. However, glasses actually fall far short of this theoretical strength, failing at around 100 MPa.<sup>1</sup>

This large discrepancy in theoretical strength versus actual strength is believed to be the result of microcracks across the surface of the glass. Cracks act as stress multipliers, and the high number of cracks present on the surface of glasses result in the large reduction in strength observed. Additionally, these cracks are randomly distributed over the surface of the glass, making the actual failure stress varied and unpredictable. Various methods have been developed to compensate for these effects.<sup>1</sup> This experiment compares these treatment methods.

### 1.1 Ion-exchange

The presence of cracks in a material causes a reduction of strength, and ultimately brittle failure, when the material is loaded in tensile fashion. A common method for increasing the strength of a material prone to cracking is to introduce residual compressive stresses.<sup>2</sup> Soda-lime-silicate glass contains between 12 and 16% by weight sodium oxide. At elevated temperatures, ion-exchange can occur where sodium ions diffuse out of the glass to be replaced by ions from a reactive material. One common method of ion-

exchange is putting soda-lime-silicate glass in a bath of potassium nitrate. This causes ion-exchange between the sodium ions in the glass and the potassium ions in the bath. The larger potassium ions introduce residual compressive stresses on the surface of the glass, and this residual stress compensates for the presence of microcracks.<sup>2</sup>

### 1.2 Acid Etching

The effect a crack has on a material is directly related to the size of the crack. Longer crack lengths result in lowering of the stress required for fracture. Additionally, the shape of the crack affects the reduction of strength. A sharp pointed crack is much more of a stress riser than a blunt crack tip.<sup>3</sup>

Acid etching is used to help compensate for these crack properties. By etching away the surface layer of a glass, the length of the microcracks on the surface is reduced. Additionally, the use of acid etching has been shown to help reduce the sharpness of the crack tips. This process, in turn, reduces the stress riser effect of these microcracks and increases the strength of the glass.<sup>3</sup>

### 1.3 Mechanical Strengthening

As previously noted, microcracks formed across the surface of the glass result in a large decrease in the actual strength. These cracks are randomly distributed on the surface of the glass, with widely varying concentrations and crack lengths. As a result, two pieces of glass that were prepared using the exact same methods can have a large variation in strength.

In order to account for this large deviation in properties, some glasses go through a mechanical surface modification process where the glass is rolled in an abrasive substance, such as alumina. This process, while increasing the prevalence of microcracks on the surface of a glass and decreasing the overall strength of the glass, does result in a more uniform composition of microcracks and limits the variability of the strength, ultimately making it easier to predict at what stress the glass will fail.<sup>4</sup>

#### 1.4 Three-point Bend Testing

Surface flaws in glass cause brittle failure of the parts when under tension. These microcracks have no effect on the glass in compression, since compression forces the cracks closed and allow the glass to behave as though they were not present. Thus, it is most advantageous to test the glass for failure in tension.<sup>5</sup>

However, testing brittle materials in tension via traditional means of pulling in two vice grips often leads to failure at the grips. An alternative method of testing is used where a sample is placed on two supports, with an unsupported span in between. At the halfway point of this span, a force is applied until fracture. From this test, the stress at failure, also known as the modulus of rupture (MOR) in bending, can be determined according to Equation 1:

$$\sigma_{fb} = \frac{PL}{\pi r^3} \quad (1)$$

where P is the load at failure, L is the length of the span between supports, and r is the radius of the test specimen.<sup>5</sup> A sample in the testing set up is shown in Figure 1.

Three-point bend test creates a linear variation of bending moment with the maximum at the center load, shown with Equation 1, while the four-point bend test allows the specimen to fail at its weakest point. The four-point bend test was originally chosen for this project, but due to the size of the rods as well as equipment available to us, the three-point bend test was decided to be the more feasible option. This affects the data by showing failure at the center of the rods and not the overall failure of the rods.

#### 1.5 Surface Analysis

To qualitatively determine how the variation of crack size compared to the control sample, optical microscopy was used to observe the surface of the glass. The shape and size of cracks can be told from micrographs of a thin lengthwise section of the rod. Thus, the effects of a treatment can be compared to the control by visual inspection, which will reinforce the results of the three-point bend testing.

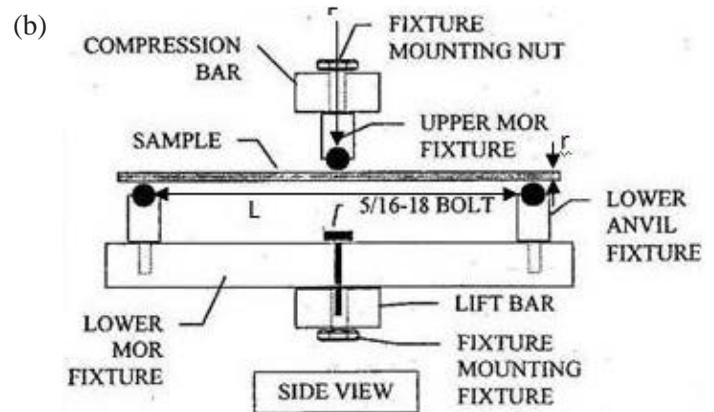


Figure 1: (a) Three-point bend testing set up with sample in supports; (b) diagram of applied loads during testing.<sup>6</sup>

## 2. Procedure

The rod surfaces were altered using three different techniques: mechanical surface modification, molten salt baths, and acid baths. The acid baths and mechanical surface modification were performed for two different lengths of time. Two different compositions of molten salt baths were used for one fixed time. A flowchart of all experimental processing and testing is seen in Figure 2.

### 2.1 Rod Preparation

A low-speed diamond blade saw was used to cut 25 cylindrical glass rods in half. The rods were received from Fisher Scientific and were approximately 150 millimeters long with an approximate 5 millimeter diameter. Cooling fluid/oil was used to decrease the cutting temperature due to friction.

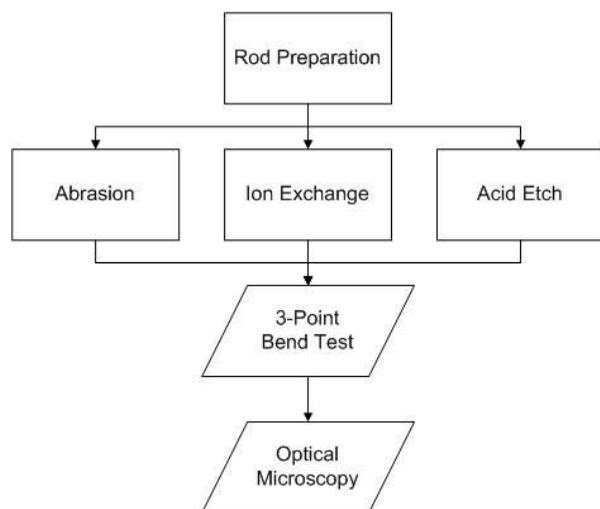


Figure 2: Flowchart of experimental processing and testing

After the cutting was completed, the rods were cleaned using soap and water to remove oil residue that could have skewed experimental results.

### 2.2 Mechanical Surface Modification

Alumina was measured to completely cover 6 glass rods for 3- and 24-hour mechanical surface modification tests. Approximately 212 grams were used for each test to fully cover the samples. Glass rods and alumina were placed in a screw cap plastic bottle taped on the outside to ensure enough friction against the rollers. The bottles were placed on a US Stoneware Roller at a moderate rate of rotation along with a weight for optimal rolling.

### 2.3 Nitric Acid Surface Modification

Two sets of rods were completely submerged in full strength (15.6 M) nitric acid ( $\text{HNO}_3$ ) at room temperature for time lengths of 1 and 2 hours, respectively. Rods were washed off with water once withdrawn from the bath.

### 2.4 Molten Salt Surface Modification

Rods were submerged in molten salt baths at  $375^\circ\text{C}$  for 24 hours. Two baths were used, one of 250g of lithium nitrate ( $\text{LiNO}_3$ ) and one of potassium nitrate ( $\text{KNO}_3$ ), with 6 rods per bath. Rods were covered in salt and the entire contents of the bath were slowly warmed in a ThermoLyne furnace until  $375^\circ\text{C}$ . Upon removal from the furnace after 24 hours, the glass was taken out of the bath, left to cool on a refractory block, and then rinsed with water to remove excess salt.

### 2.5 Three-point Bend Testing

A Com-Ten Series 95 VC three-point bend tester was used to determine the MOR as a result of the different treatments. Rods were placed on supports with a 50 mm unsupported span. A force was applied at the midpoint of the span, and the rate of loading was set at five mm/minute. The load was increased until fracture, at which point the force and MOR were recorded. This test was performed for ten control

samples and five samples for each treatment. Following the testing, the mean was calculated for both the force at fracture and the MOR.

### 2.6 Surface Analysis

A section no more than 2 millimeters lengthwise in thickness was cut off from the inner part of a rod. This operation was performed on each treatment and a control sample. The section was then examined using an Olympus BH2-UMA optical microscope. The amount and shape of surface cracks were noted. Digital images were taken and other observations recorded about the overall appearance of each sample.

## 3. Results and Discussion

### 3.1 Surface Analysis

Optical microscopy was used to observe the resultant microcracks stemming from the different glass treatments. For the 3-hour mechanically abraded sample, the cracks appeared similar to the control, but higher in concentration. The highest crack concentration was found in the 24-hour sample, which showed very wide cracks, seen in Figure 3. Greater crack prevalence was a result of the Vickers hardness of alumina being two orders of magnitude higher than that of soda-lime-silicate glass.<sup>7</sup> Therefore, the alumina powder chipped into the glass during rolling and created more cracks. This increase in crack concentration results in a more predictable MOR.

The 1-hour acid-etched sample showed smoother cracks in comparison to the control sample seen in Figure 4 (a). This effect was more pronounced in the 2-hour sample due to the presence of jagged cracks with large surface areas that were easily etched by the nitric acid. The smoother cracks had a lower stress riser effect, allowing the glass to withstand higher stresses before failure.

The ion-exchange samples showed the most profound departure from the control. The lithium nitrate sample showed cracks that were much larger both in length and width

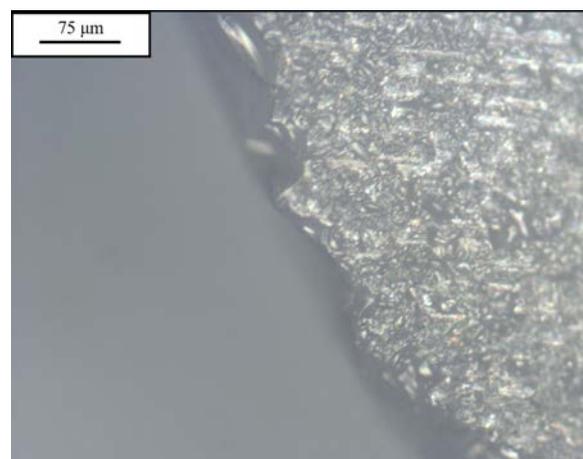


Figure 3: Edge of 24-hour mechanically abraded glass.

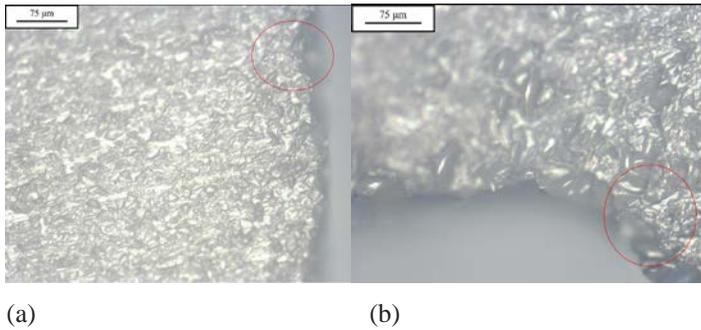


Figure 4: (a) Edge of control, and (b) 2-hour acid-etched glass samples.

Table 1: Results of three-point bend testing.

Group	Force at Fracture (N)	Modulus of Rupture (MPa)	Standard Deviation in MOR
Control Group	104.98	106.93	12.87
Mechanical - 3 Hour	82.74	84.28	5.16
Mechanical - 24 Hour	87.19	88.81	8.23
HNO <sub>3</sub> - 1 Hour	109.43	111.46	17.86
HNO <sub>3</sub> - 2 Hour	126.33	129.40	16.50
LiNO <sub>3</sub> Bath	35.72	36.25	2.03
KNO <sub>3</sub> Bath	429.70	437.69	155.96

than the control section, one of which is circled in Figure 5(a). The potassium nitrate showed cracks that had been forced shut, such as the one circled in Figure 5(b). These results were due to an ion-exchange in which the sodium ions in the glass were exchanged with the alkali metal ions in each salt. The smaller lithium ions caused a shrinkage effect in the surface, spreading out the cracks and resulting in a residual tensile stress. The larger potassium ions created an expansion effect in the crystal lattice that closed cracks and introduced a compressive stress.

### 3.2 Three-point Bend Testing

The experimental values found from completing three-point bend testing for the force at fracture and the calculated MOR are given in Table 1 above. Figure 6 shows the relative differences in the MOR for all the treatments. The top of the blue column for each treatment corresponds to the average MOR. The black bar represents the range of measurements per treatment.

The force at fracture was measured directly from the testing apparatus, and the MOR was calculated using Equation 1.

Mechanical rolling of the glass rods resulted in a decrease in the strength of the glass, due to the increase in surface cracks seen in the micrographs. However, this also resulted in more predictable fracture strengths. The standard deviation in the fracture strengths for the 3-hour samples was lower than the standard deviation for the 24-hour samples, suggesting that the 24-hour samples were rolled for too long.

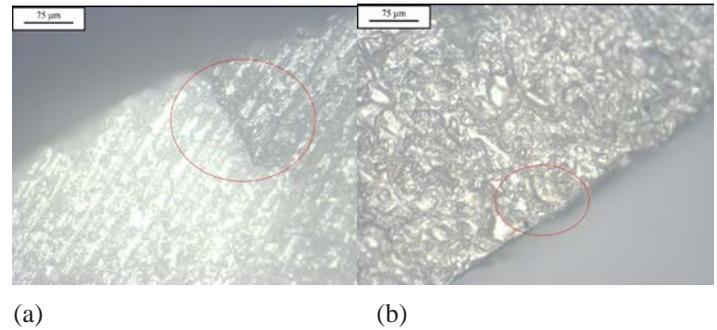


Figure 5: (a) Edge of glass treated with lithium nitrate molten salt bath; (b) edge of glass treated with potassium nitrate molten salt bath.

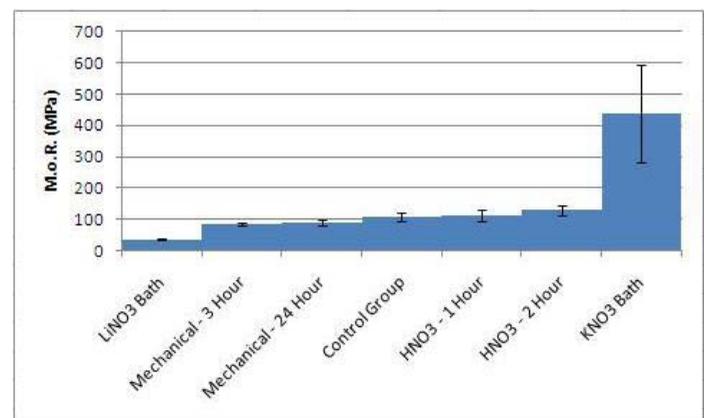


Figure 6: Modulus of rupture averages and ranges for each treatment.

The acid-etched samples both showed increased strength, with the 2-hour acid samples experiencing a larger increase than the 1-hour. This outcome was a result of the smoothing effects of the acid seen in the micrographs, which blunted the crack tips.

Finally, the LiNO<sub>3</sub> samples lost a considerable amount of strength, due to the residual tension opening the cracks and increasing significantly the stress riser effects. Conversely, the KNO<sub>3</sub> samples were much stronger than the controls because of the residual compression effects closing the cracks.

## 4. Conclusions

This experiment attempted to determine the relationship between surface modification of glass with respect to the surface cracks and resultant change in the strength measured by the MOR. The lithium nitrate-treated glass had the lowest MOR and exhibited wide cracks. Glass that was mechanically abraded showed a slight decrease in strength and a lower standard deviation in its MOR, as well as a larger amount of surface cracks. The acid treatments produced a moderate increase in strength with smoother cracks. Finally, rods placed in the potassium nitrate bath displayed a drastic increase in strength, with cracks being forced shut by the expanded lattice. For the strongest glass

possible, a potassium nitrate molten salt bath should be used to treat the rods.

Further work is recommended to discover the optimal processing specifications, such as time and temperature, to maximize the increase in MOR. Also, it may be beneficial to attempt to combine the potassium nitrate salt bath with mechanical abrasion in order to create a stronger glass that fails at a more predictable energy.

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