APS 110 Final Report:

(Topic: Why is Gorilla Glass used successfully in Phone Screens rather than Thermally Tempered Glass?)

Introduction:

In today's digital world, smartphones have become part of every person's needs. New technologies are constantly developed and introduced into new smartphones to improve upon the previous feature or to fill the existing gap. One aspect of a smartphone that has been posing problems to many users is the issue of smartphone screen fracture. According to research conducted by SquareTrade, it has shown that approximately 5,761 smartphone screens break in America every hour [1]. Not only does the smartphone screen fracture easily, but the cost to replace a new screen is expensive. This led to the creation of a special type of glass to resolve this issue: the Gorilla Glass. Gorilla glass is manufactured by corning and has been widely implemented onto many smartphone screens today due to its properties to resist screen fracture and scratch.

Tempered Glass:

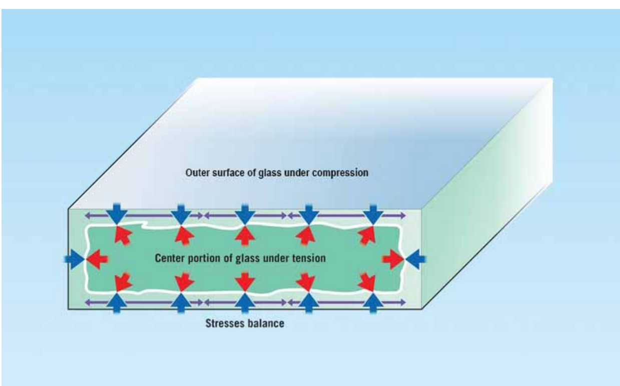


Figure 1: Compressive and Tensile Region in Tempered Glass [14]

= Tempered glass is an annealed glass that undergoes the "Thermal Tempering" process. This process involves heating the glass above the glass transition temperature or the temperature at which the glass transitions from a stiff glass into a viscous fluid or rubbery material [2]. Then, the quenching takes place, where high pressure air is exposed to the glass sheet [3]. In this process, the glass surface undergoes fast cooling, causing the silicon oxide(SiO2) molecules in the surface to not have enough time to organize themselves into an ordered crystals structure. On the other hand, the glass interior undergoes slow cooling, causing the SiO2 molecules to have enough time to rearrange themselves into ordered crystal structures. This results in lower density in the surface and higher density in the interior. Since density$\propto$1/volume, this allows the SiO2 molecules on the surface to achieve a larger volume than the SiO2 molecules in the interior. Since volume$\propto$length, this is equivalent to the glass surface having longer strain and the glass interior to have shorter strain. When the two strains meet, the shorter strain exerts an inward "Residue Compressive" force on the longer strain at the glass surface. Whereas, the longer strain exerts an outward "Tension" force to the shorter strain in the glass's interior. The compressive and tensile region is illustrated in Figure 1. When load is applied to the glass and cracks start to originate on one area of the glass, the compressive stress on the glass surface acts to close the cracks, preventing them from growing to a point of fracture [4].

The Gorilla Glass:

A Gorilla Glass is a special type of glass made from alkali-aluminosilicate composition. Alkali-aluminosilicate glass is a thin and non-fragile toughened glass. This feature results in mechanical properties such as high surface compressive strength and hardness [5].

Composition of Gorilla Glass:

Aluminosilicate occurs naturally as a compound called Zeolite [6]. Zeolite consists of 2 main constituent parts: $[SiO4]^{4-}$ and $[AlO4]^{5-}$, which share all corners to create a three-dimensional framework structure carrying a negative charge [7]. The existence of the cations such as sodium ions contained in interstitial sites within the framework balances the framework charge [7]. The backbone of the silicate glass glass is silica(SiO_2). Structurally, silicate glass is considered as a non-crystalline solid--it does not have long range crystal structure. It is composed of silicon oxide where each silicon(Si) is bonded to 4 Oxygen(O) atoms, but each oxygen atom is shared with 2 silicon atoms [3]. These bonds together form a network of SiO2 tetrahedral structures. This material has a high temperature transformation range of viscosity, which means that it requires significantly high temperature to perform operations such as melting, forming bending, etc [3]. To reduce the transformation temperature of viscosity, alkali metal elements are incorporated into the glass composition in the form of oxides such as Na2O [3]. These so called network modifiers break up the glass network and reduce the network connectivity through interfering with the bonding network between silicon and oxygen [8]. They create non-bridging-oxygens where oxygen is not directly bonded to the silicon but ionically bonded to Na^+ ion.

The introduction of alumina(Al2O3) modifies the structure. Aluminum(Al) acts as a glass former, forming the interconnected backbone of the glass network. This increases the mobility of the alkali metal ion and maintains the network connectivity [3]. The negative [AlO4]- network forming units of aluminosilicate glass results in a weaker bond with alkali ions [7]. The presence of alumina is beneficial because it tends to reduce the number of non-bridging oxygen atoms in the silicate network, which means that the sodium ion will not be indirectly bonded to the Aluminum atom [8]. This causes the alkali diffusion coefficients to be larger as it is easier for the potassium ion in the ion source to diffuse into the aluminosilicate glass and exchanges with the sodium ion [3]. These alkali metal ions with low ionic charge are mobile ions since they are indirectly bonded to the structure through the non-bridging-oxygen.

Fusion Draw Process:

Once the silicon dioxide (SiO2) is combined with compositions such as aluminum and alkali metal oxides(Ex: Na+), it melts the mixture at working temperature into a glass melt [9]. The molten glass is then transported into a V-shape isopipe where it joins and fuses together at the bottom [9]. This results in an especially thin aluminosilicate glass measured in micron [9].

Secondary Process: Ion Exchange Process

Ion Exchange Process(IX) is a type of chemical strengthening. It is a non-equilibrium thermodynamic process driven by electrochemical potential gradients of mobile network modifiers [3]. Unlike thermal tempering where the glass strength comes from the build up of a residual compression up to a certain depth below the surface that is balanced by the tensile stress in the internal layers, the ion exchange strengthens the glass through the "stuffing effect" [8].

For IX to occur, a glass matrix(GM) with mobile modifier ion such as sodium ion and an ion source with mobile ion, such as the KNO3 solution are required [3]. The aluminosilicate glass from the fusion draw process contains sodium ions in the glass matrix. The company Corning dips the aluminosilicate glass matrix into the solution KNO3 (ion source). Both sodium and potassium atoms belong to group 1 or the Alkali group according to the periodic table [10]. Alkali metals are very reactive and unstable due to the presence of 1 valence electron. Therefore, they can become stable by achieving full octet through losing the 1 valence electron. In order for the sodium ion in the glass matrix to be exchanged with the potassium ion in the ion source, the ionic bond between the sodium and the aluminosilicate (SiO2) must be broken. Since the mobility of the alkali metal ions or the Sodium ion largely depends on the temperature [3]. Enhanced by the weak bonds between the sodium ion and Aluminum glass former due to the negative $[AlO4]^{-}$ network forming units of aluminosilicate glass, the bonds can be broken through heat. The potassium salt bath that the aluminosilicate glass is dipped into has a temperature of 400 degree Celsisus. This ties into the concept of Boltzmann Distribution curve as illustrated in Figure 2.

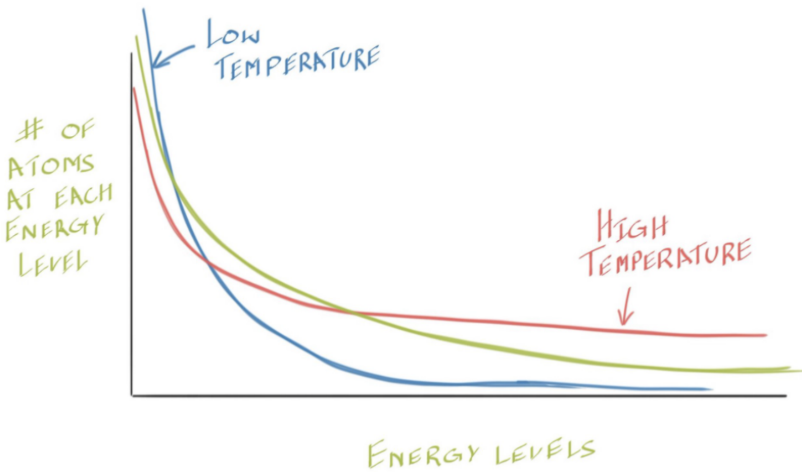


Figure 2: Boltzmann Distribution Curve [13]

The Boltzmann distribution represents the probability of the number of atoms with different internal energies under different temperatures [11]. From Figure 2, we see that at higher temperature, atoms are more distributed across every energy state. This means that there are a greater number of atoms with high energy. Connecting back to the ionic bond between sodium and the aluminosilicate, this means that when the aluminosilicate glass is dipped into the high temperature potassium salt bath(SB), the high temperature causes the large number of sodium atom ion to obtain greater internal energy to ultimately overcome the ionic bond energy between itself and aluminosilicate(SiO2) [10]. With this process, the Ion exchange reaction takes place. The modifier sodium ion in the aluminosilicate glass is exchanged with the invading potassium ions in the KNO3 ion source. This can be expressed as $A_{SB} + B_{GM} \Leftrightarrow B_{SB} + A_{GM}$, where A = K^{+} and B = Na^{+} [3]. Microscopically, the ion exchange can be depicted as in Figure 3.

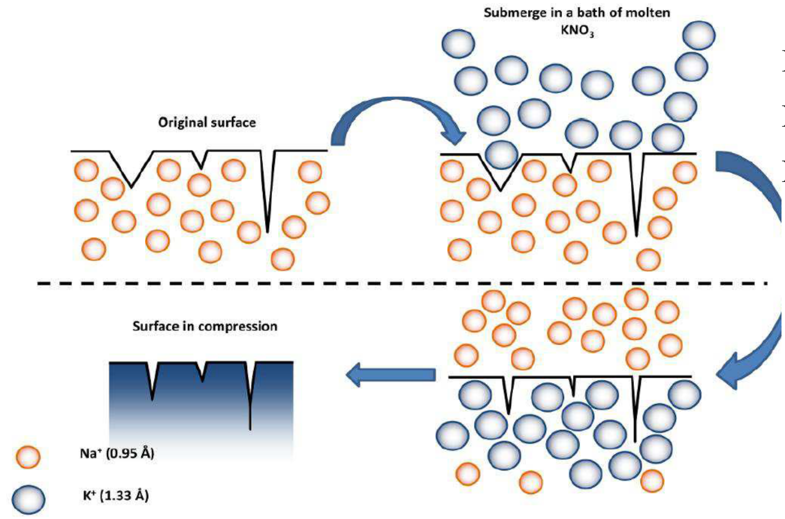
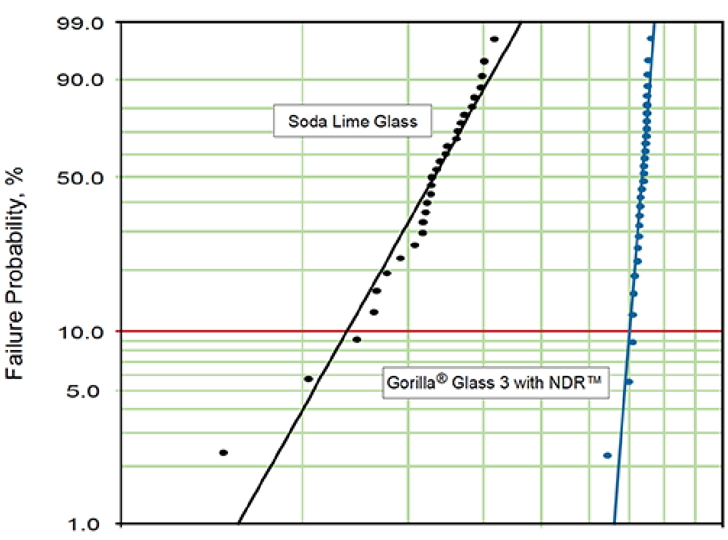


Figure 3: Microscopic Representation of the Ion Exchange Process [3]

The "Stuffing Effect" and Properties:

According to the periodic table, both potassium and sodium belong to the Alkali metal group. By general trend, the atomic radius of the atom increases down the group since elements down the group have more energy level as a result of greater number of electrons. Therefore, potassium ion is larger than sodium ion. For this reason, replacing sodium with potassium ion during the IX process results in a near volume expansion on the glass surface [3]. Due to the unexpanded interior of the glass, the expansion creates a high compressive stress on the surface that is balanced by the tension in the interior of the glass [3]. This stuffing effect plays a vital role in Gorilla Glass high glass strength, allowing Gorilla Glass 3 to require greater applied stress before exhibiting failure probability when compared to the soda lime glass which exhibits failure probability at lower stress as shown in Figure 4 [12]. Likewise, it requires a significantly greater load to initiate radial cracks in the glass as shown in Figure 5 [12].



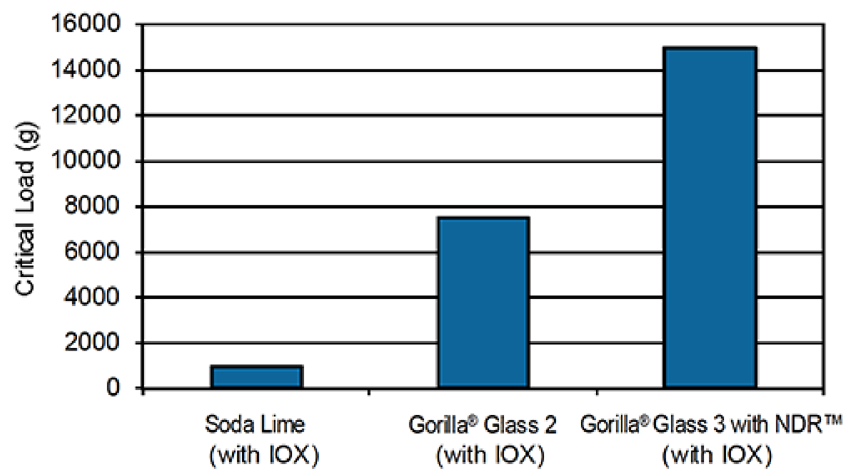


Figure 4: Strength v.s. Failure Probability of Gorilla Glass 3 [12]

Figure 5: Damage Resistance to Critical Load [12]

The innumerable potassium ions that exist within the glass reinforces the residual compression built up on the glass surface. This allows the surface to have high resistance to uniform plastic deformation, which correlates to the glass's resistance to scratch. This is reflected by Gorilla Glass 3 high Young's modulus of 69.3 GPa and Vicker hardness of 534 kgf/mm2 when strengthened and up to 649 kgf/mm2 when strengthened [12]. Likewise, it can be seen that the scratch of Gorilla glass 3 is much lower than its competitor glass under the Knoop scratch test even when greater load is applied to it as shown in Figure 6 [12].

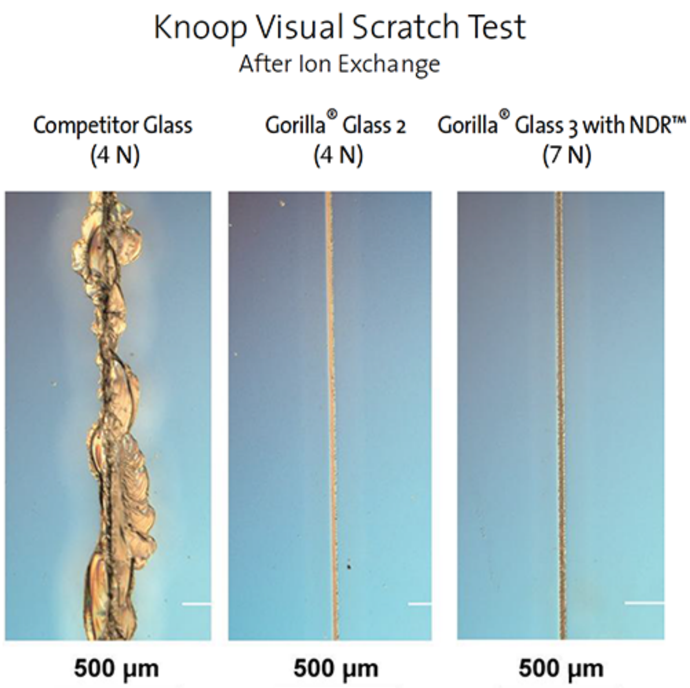


Figure 6: Knoop Visual Scratch Test of Gorilla Glass 3 [12]

Unlike tempered glass, where thermal tempering of thin pieces of glass are not feasible due to the significantly high heat exchange coefficient that requires a large enough difference in core surface temperature upon cooling, thin pieces of glass can be chemically strengthened glass [8]. The surface compression from the IX process does not depend on the glass thickness. This property allows Gorilla glass 3 to have higher load to failure than other glass such as the soda lime glass as shown in Figure 7. It is this thinness along with high strength of Gorilla Glass that differentiates itself from tempered glass and allows for a wide range of applications.

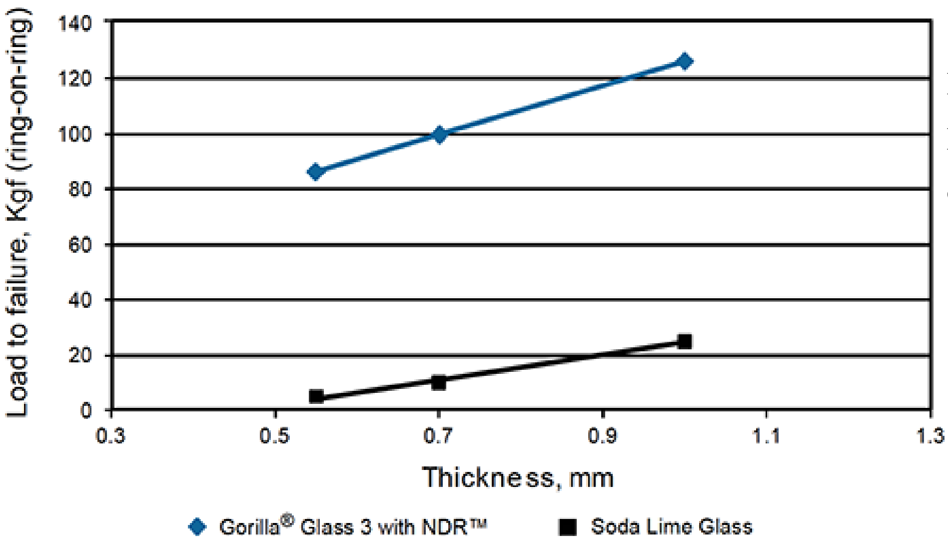


Figure 7: Thickness v.s. Load to Failure of Gorilla Glass 3

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