CHEMICAL STRENGTHENING OF GLASS

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By some estimates, the theoretical strength of a flawless glass is as much as 35 GPa applied in a tensile mode. On the other hand, ordinary glass products break in a brittle mode at as little as 7-100 MPa (~ 1000 – 15,000 psi) primarily because of the interaction of the tensile stress with surface flaws; of the order of a few microns (often termed “Griffith flaws”). Flaws are produced during handling by the manufacturer as well as the user. The atomically-dimensioned tip of a flaw (sharp radius of curvature) assisted by surrounding environment, usually relative humidity, grows through a stress-assisted corrosion mechanism to the point of spontaneous fracture. Almost any material contact abrades a pristine surface of glass to produce what could be a fatal flaw. In contrast, ductile metals are easily able to withstand as much as 150-350 MPa, and plastic products do not break because of their high energy absorption capability (toughness). Indeed, had it not been for the poor usable strength characteristics, glass would have been the material of choice by virtue of its transparency, its inertness to most fluid media, and its perceived aesthetics.

Of the various glass strengthening techniques, chemical strengthening (also called “ion exchange strengthening”) is a relatively newer technology (discovered in 1962) that is attracting much attention lately. The early prime use has been the aircraft cockpit windshield which must be designed to withstand impact of birds flying at 400 knots. In the more recent years, the emphasis on product safety and environmental concerns on the use of fossil fuel products have renewed interest in the process. For a comprehensive review, the reader is directed to Reference [1].

In chemical strengthening, an alkali-containing glass is immersed in an electrically heated bath (tank) containing molten alkali salt having ions larger than the host ions at temperatures below the glass annealing point. An exchange between the host alkali ions of glass and larger invading ions from the salt occurs (see Figure). The resultant stuffing in a near-rigid atomic network of glass leads to the development of high surface compression which rapidly decreases to a small balancing tension in the interior depending upon the ion exchange depth and product wall thickness. Because an applied tension must overcome the compression before crack growth can occur, the introduction of surface compression effectively strengthens the glass product. Strengths can be measured by the usual 3-point or 4-point ball-on-ring, or ring-on-ring flexure methods for a test group of, say, 30 samples. Instead of strength-tests, optical birefringence techniques can also be used to measure the magnitude of surface compression (“CS”) and its depth up to the point of inversion to tensile stress (“DOL”). The advantages of this process are: (i) introduction of relatively high surface compression, (ii) no measurable optical distortion, (iii) thin plates, even 50 μm thin, can be strengthened, and (iv) irregular geometry products can be readily strengthened so long as the surface can be contacted by the molten salt. Disadvantages are (a) limited to alkali-containing glass, (b) low case depth for soda-lime glass which makes the common glass products susceptible to weakness from handling flaws, and (c) high cost due to extended bath immersion and Govt regulations associated with storage and handling of hazardous materials.

The key concept of the science of stress development in the chemical strengthening process was advanced by Cooper and Krohn [2] in 1969, essentially by analogy to thermal stress generation. It soon become clear that practically achieved surface compression was usually a factor of 3-7 lower than what the Cooper analogy predicted. The argument of concurrent viscous relaxation, advanced by Sane and Cooper in 1987 [3], still did not close that gap sufficiently. A fuller understanding was achieved only in 2015 by the author's group [4] using molecular dynamics to suggest the overall loss of compression buildup wasn't just due to the viscosity-driven α-relaxations (usually slow) but also to extremely fast (pico-, nano-second) β-relaxations of the network. Further refinement of this concept was put forward by Macrelli *et. al.* [5] to indicate that free energy-driven non-isochoric relaxations also played a role, mostly in the surface region. It is recognized that the science of stress development is now fairly well understood.

In soda-lime glass products, immersion in KNO_3 salt bath at ~475°C for 16 *h* can develop as much as ~450 MPa surface compression, but a case depth of only about 25 to 30 μm. The interior tension can be < 4 MPa for a 5 mm plate, which means that the glass can be cut afterwards (the exposed edges, however, are no longer strengthened and, hence, must be protected). Chemical strengthening technology works best for lithium and/or sodium aluminosilicate glasses. It is of marginal use for low expansion borosilicate, and "lead crystal" glass compositions, and of no use for fused silica glass. However, "Type I neutral" FDA-approved medium expansion borosilicate glass used in pharmaceutical cartridges, syringes, ampoules, and vials can be strengthened reasonably well with care. The best one can achieve currently in a single-step strengthening process is demonstrated by the author [6] for a high T_g lithium aluminosilicate glass immersed in mixed $NaNO_3/KNO_3$ baths. Surface compression as high as ~ 1 GPa (145,000 psi) decreasing to zero at ~ 1mm depth has been developed.

In autoinjectors sold under the brand name EpiPen®, a Type I borosilicate glass cartridge chemically strengthened by Saxon Glass Technologies, Inc. is the enabling technology that has made the difference between market-acceptability and otherwise a risky product as a first line antidote to avoid anaphylaxis shock from severe allergens such as peanuts, bee-stings, shell foods. Over the 0,4 billion or so glass cartridges supplied over the past 25 years, the chemical strengthening has enabled the glass cartridge failure rate down from nearly 10% to virtually nothing during the auto-administration. *Glass chemical* *strengthening has helped save thousands of human lives each year.* Examples of other commercially successful glass products that use chemical strengthening are display glass covers in mobile personal electronic devices (e.g., cell phone and MP3 players), and compact discs for portable hard drives.

A large variety of glass products could, however, be strengthened and brought to market at acceptable premium. Use of glass for hurricane-resist architectural windows, solar energy conversion tubular and flat-plate collectors, panels for large displays, transparent armor, and needle-free drug delivery cartridges are perhaps around the corner. Pressurized beverage containers could be lightweighted and strengthened to make recycling a cost-effective option. Relative to steel, highly strengthened glass has a higher strength-to-weight ratio, hence, could also be used in support structures for architecture and wide-spread use of thinner, yet stronger, glass windows.

There is reason to celebrate glass as the most transformative material which has done so much for the comforts of human living.

References:

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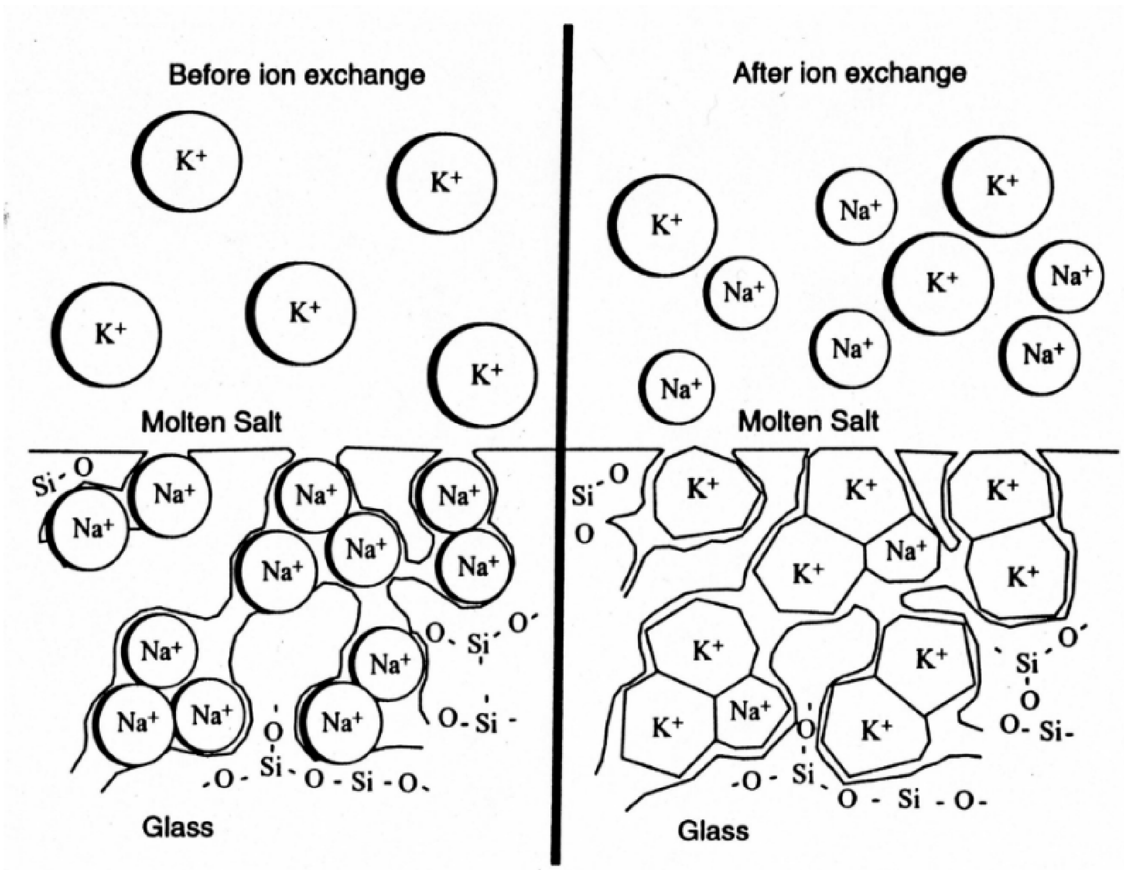
Before ion exchange
After ion exchange
K+
Na+
Molten Salt
Molten Salt
Si - O
O - Si - O
O - Si -
-O - Si - O - Si - O-
Glass
Glass
O - Si - O - Si - O-
Si-