IF 101 (131)

"DECARBONISATION"

Increasing the strength of glass

Bulent E. Yoldas, John T. Brown, Thomas C. Sauer* and Sabine Schweizer, Lalitha Subramanian, and Ian Flynn** discuss a collaboration including Ardagh and Diageo to lightweight glass bottles.

During COP26, a collaboration between Ardagh, Dassault Systèmes, Diageo and Exxergy was announced to develop lightweighting solutions for container glass.

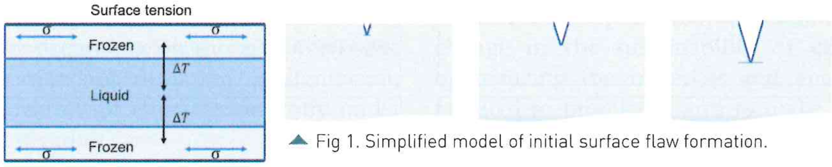
The collaboration was initiated through the Diageo Sustainable Solutions programme with the purpose to demonstrate the potential of this proof of concept.

This article outlines results particularly from the theoretical and physical testing.

The virtual twin part of the project has been sponsored by Ardagh Group and performed by Dassault Systèmes based on one of Exxergy's recipes, with Diageo supporting Exxergy's laboratory work.

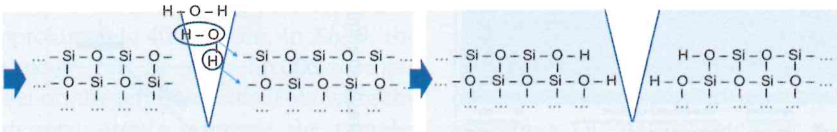
While there is still further work on-going, a paper was presented at the International Congress on Glass (IGC) in Berlin in July.

Expanding and furthering the results presented at IGC, this article deals with preliminary results from both, the virtual twin as well as initial lab test results.



▲ Fig 1. Simplified model of initial surface flaw formation.

▼ Fig 2. Simplified model of crack propagation by creation of terminating OH-groups.



Context

The glass industry is under pressure to decarbonise due to its high energy demand in the production process. This is particularly true as energy prices soar, and in addition, the cost of CO_2 certificates is on the rise as well.

Glass strength drops drastically after glass is exposed to atmospheric moisture and to high forming temperatures. At high temperatures, above 900°C, water is highly chemically reactive. During forming, the newly formed glass surface is rapidly attacked by water hydrolying the Si-O-Si network forming terminating Si-OH groups (***Fig 2***). When it is freezing outside there are an order of 1g/m³ water vapour in the air, and when it is humid in the heat of the summer approximately 40 – 50 g/m³ water vapour. Water is everywhere on this planet, and it is corrosive at high temperatures. A discovery by Dr Yoldas within the past four decades changed our historical definition of glass as a material that must be formed at high temperatures.

Every crack ever studied in glass has hydroxyls concentrated at the crack tip. These OH groups continuously drive the crack tip deeper into the bulk glass. The deeper, the weaker the glass is to stress and breakage. If glass has a strength of about 3.4 GPa (500,000 psi), it has flaws at a depth of only 10 – 50 nm. There is a relationship between flaw depth and measured strength. Now if that reaction was catalysed by water for a chemistry like the glass with the crack, the crack could be healed and the depth of the crack could be reduced increasing the mechanical strength.

The limitations of glass strength and brittleness have been concerns for centuries. As an example, besides being a world famous artist in the 16th century, Michelangelo was also intrigued with glass. He found back in the time that if he redrew rods of glass to smaller and smaller diameters – strength would increase after each redrawing. He reasoned that the cause of failure was surface flaws and by redrawing he was diluting the flaws.

Nearly 100 years ago, Griffith explained why glass failed to achieve its full theoretical strength. It can be reasoned that the above mechanism describes at least one if not the prevalent mechanism why at least conventional mass produced glass such as typical container and sheet glass achieves only less than 1% of the theoretical strength of the Si-O-Si bond.

Be it as it may, one possible approach to reduce carbon footprint might be given by increasing the mechanical strength of glass, which would allow reducing the wall thickness of glass substrates while still achieving the design strength.

Today, the glass industry uses various methods to improve glass strength, mostly imposing compressive stresses to bury the surface defects, including ion exchange (chemical toughening), thermal toughening, or lamination of low expansion glass over high expansion glass. All of these methods have various shortcomings and limitations. For example, the widely used methods of ion exchange and thermal toughening do not work below certain glass thicknesses and have compositional limitations. In the past, no one has ever produced a process to heal the surface flaws described above.

A new glass surface treatment approach is currently under development approaching the stage gate of technology readiness level (TRL 4).

This contribution will discuss intermediate results from lab tests.

The approach

Several recipes have been designed creating a combination of (1) chemical

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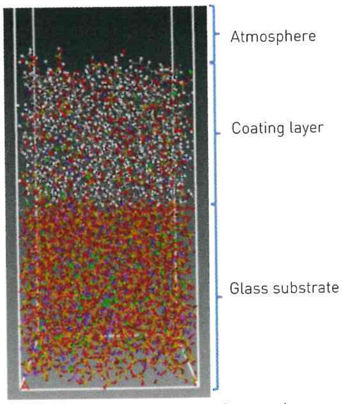


▲ Fig 3. Virtual twin model of the coating on glass.

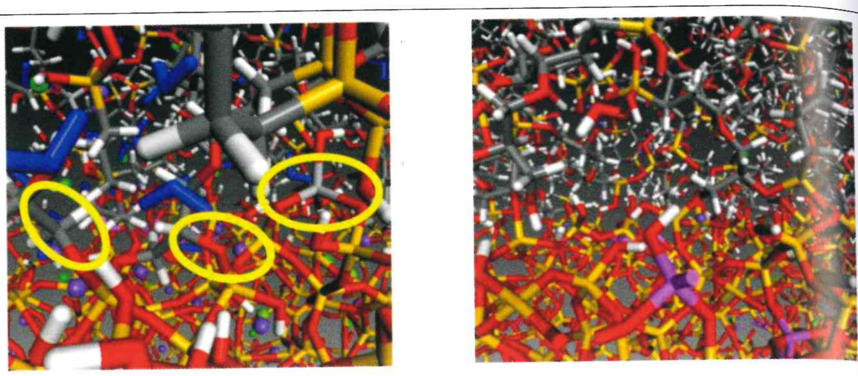
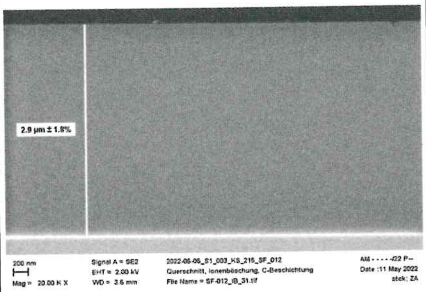
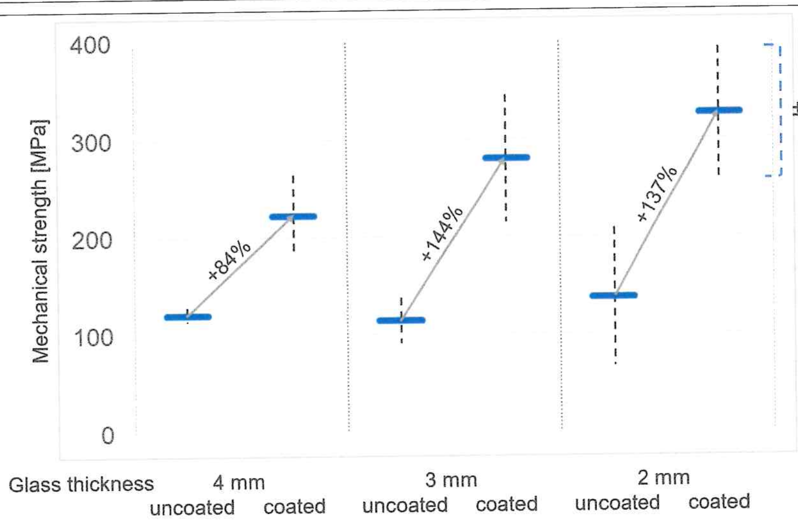


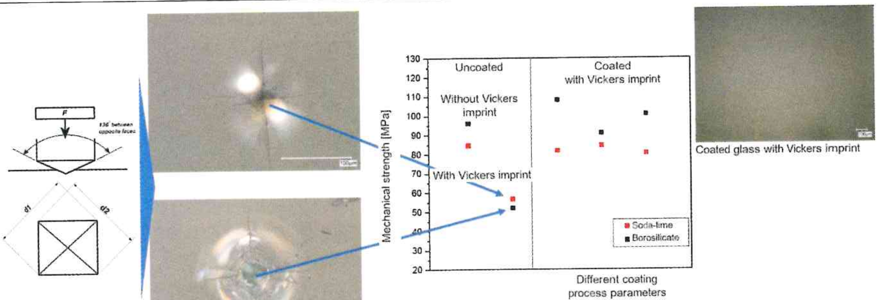
Fig 4 (left) and Fig 5 (right): Zoomed-in-views of the coating-glass interface.



▲ Fig 6. Coating layer on the glass substrate.



▲ Fig 7. Exemplary breakage test results.



▲ Fig 8. Exemplary results from intentionally pre-damaged glass.

compounds and (2) process settings that result in a chemical reaction of the reactive groups of these chemical compounds with the terminating OH-groups of the glass surface. The resulting reaction creates covalent bonds bridging into the Si-O matrix by repairing the covalent bonds cracking the terminating OH-bonds and recreating new covalent bonds. With this approach, the previously cracked Si-OH/HO-Si terminal groups are bridged by creating a new Si-O-X-O-Si covalent bond, X being the reaction product after the chemical compound has reacted with the H- or OH-groups on either end of the terminal OH-groups.

The primary goals of this approach are to heal the surface defects at least partially and to reduce surface brittleness by increasing ductility. As a result of achieving these goals, as the stress capacity and the ductility increase the wall thickness can be reduced and as a result, raw material and energy savings may be achieved. The main task currently is to provide proof of concept in theory and in practice.

Initial results from simulations

To provide critical insights from chemical point of view, a virtual twin of the coated glass surface was modeled at molecular level using Materials Studio and Pipeline Pilot. The coated glass surface was modeled by subjecting the reactants to a proprietary stepwise procedure. The condensation reactions between the reactants of the coating formulation among themselves and with the surface exposed hydroxyl groups of the glass surface have been simulated. The finally obtained model (see ***Figs 3-5***) shows indeed (1) a polymerised and cross-linked coating layer, which is (2) covalently bound to the glass surface ***Fig 3.*** shows a 3D simulation box of the glass substrate with the coating on top. Zoom-in-views of the interface are shown in ***Fig 4 and 5***. Covalent bonds between coating and glass are highlighted in ***Fig 4***. Water from the condensation reaction is shown in blue. ***Fig 5*** illustrates a zoomed-in-view after NPT molecular dynamics simulations and after removal of the by-products. Not all –OH groups have reacted. These –OH groups can, in turn, react in a self-healing process. To explore the impact of surface

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defects and the self-healing properties of the coating, additional simulations were carried out. Models with defects were created and subjected to the simulation protocol. The analysis of the simulations showed that the coating can fill scratches and form covalent bonds, even if the coating has been applied prior to the damage.

Fig 3 shows the modeled structure of the glass substrate near the surface and the topping layer of the coating that has created the covalent bonds to the glass matrix as can be seen in ***Fig 4***.

Preliminary results from the lab

After mixing, the chemical compound is applied to the glass substrate surface as a coating to the surface and then cured at a set temperature and time. Several recipes (composition of the chemical compound, times, temperatures) have been tested to find the best suiting combination. One crucial aspect is naturally economics, and therefore, an optimised coating thickness. As can be seen in ***Fig 3***, a few layers are sufficient. In the current lab setup, the coating thickness is significantly larger, depending on the application to a thickness of ~1.4 to 3.0 µm, see ***Fig 6***.

Following the analysis of the physical properties of the coating, it was applied to flat glass samples, and after the curing procedure exposed to different mechanical stress testing procedures. The results from the breakage tests can be seen in ***Fig 7***. Three different glass thicknesses have been tested, 4 mm, 3 mm, and 2 mm, soda-lime glass as well as borosilicate glass. The test results for the 4 mm glass have been stressed using a 4-point probe, the other glasses with a ring-on-ring method. As can be seen in the figure, the average increase ranges from 84% to 144% depending on the glass thickness. The standard deviation is significant, the reason for which is currently under investigation.

In a further test, mechanical damage has been imposed onto the glass surface by using a Vickers imprint test using 10 and 20 N force resulting in diagonals of approximately 40 – 50 µm. In ***Fig 8,*** the breakage can be seen on microscopic level on the left hand side. Following the intended surface damage, the samples were coated again. On the top right, an image of the sample after coating illustrates that the previously applied damage can hardly be seen anymore.

The breakage test results using a standard 4-point probe method proofs that the original strength can be recuperated, in some cases even exceeded.

Conclusions

In conclusion, given the results of the virtual twin as well as the laboratory tests provide the evidence that the chemistry works. That said, further studies are currently in progress advancing the coating technology to pilot scale and to industrial scale.

There is an opportunity to make a step change in the sustainability of glass, by reducing the materials and energy required to produce it and to make the glass itself more robust lending it to refill and reuse models of consumption. The technology opens a suite of new applications; an opportunity to win terrain back that has been lost to PET containers by means of establishing lightweight bottles; and new repair options. Further results may become available at Glasstec in September. ■

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