Hot Glass, Cold Water: Experiments in the History of Glass Fracture

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Abstract

Prince Rupert’s drops and Bologna flasks are predecessors of modern thermally toughened glass. As in societies of learned men some 300 years ago, demonstrations of their surprising behaviour encourages a closer look. The same is true for the formation of a superficial crack network during quenching of hot glass with water. These experiments may inspire the study of glass craquelure to uncover information hidden in them. Therefore, short instructions for such demonstrations are given.

Introduction

What amazement, even bafflement, must have come over all those natural philosophers when tear drops were demonstrated to the Royal Society in 1661 or shattering bottles to the Bolognese Academy in 1745! Both glasses withstand a sharp blow with a hammer, but noisily explode into tiny pieces when struck at the wrong spot. Curiosity led to systematic experimentation by scholars which resulted in a better understanding of these apparently contradictory phenomena.

This lecture builds on the seventeenth and eighteenth century tradition of scientific education through demonstration experiments in learned societies and private salons. It derived from the study of fracture patterns in historic glasses (Eggert 2006) in order to understand the hidden information in them.

An archaeologist described a Roman glass bottle as ‘fractured like Sekuritglas’, a trade mark for thermally toughened glass. Rottländer (1990) connected such finds from the Rhineland with the ancient story of unbreakable glass and postulated a Roman quenching technique for the production of glass with higher fracture strength. This hypothesis has long been refuted in detail (Eggert 1991), the ‘on a second view’ different crack pattern being just one argument. Nevertheless, these works pointed to glass crack patterns as a source of information and led to a study of the history of thermal glass toughening.

Modern thermal toughening (‘tempering’) of glass to increase fracture strength was invented in 1874 by Alfred Royer de la Bastie, who quenched very hot glasses in hot oil. At the moment when the glass ‘solidifies’ (i.e. when the stresses can no longer relax by viscous flow) the outer zones are colder than the interior (Figure 1a). If the outer and inner layers consisted of
separate sheets, the inner ones would contract more as a result of cooling from a higher starting temperature (Figure 1b). Because they are connected, the more contracted interior puts the outer layer under compression, which is balanced by tensile stress in the interior (Figure 1c). The outer compressive stress acts against the opening of cracks on the surface and, therefore, increases the fracture strength. When the equilibrium of forces is disturbed by a crack moving into the layer of tensile stress, this built-in force shatters the whole glass in a characteristic way, known as ‘dicing’.

**Figure 1.** Schematic diagram of the formation of compressive stress in the surface zone of a quenched glass induced to improve fracture strength.

1a: During quenching of a red hot glass, the outer layers are relatively colder when the glass solidifies. 1b: If the glass zones were separate, the inner zone would contract more as a result of cooling from a higher starting temperature. 1c: The interior’s urge to shrink more puts the exterior layer under compressive stress, while the outer layers’ tendency to contract less puts the interior under tensile stress.

**Prince Rupert’s Drops**

That quenched glass can have an amazing fracture strength was already known 200 years earlier. Glass tears made by simply dropping a gather of glass melt into water had long been produced in glassworks. Their origin is unclear, the earliest reported occurrence points to the early seventeenth century in Mecklenburg where Prince Rupert might have seen them during his
service in the Imperial army against Swedish troops 1659-60. According to Christopher Merrett, Rupert, Count Palatine of the Rhine and Duke of Bavaria, brought them to King Charles II of England and was later credited with their invention. Charles sent samples to his Royal Society for investigation. The 1661 report by the president, Sir Robert Moray, was first published by Merrett (1662) as an appendix to his translation of Neri’s *Art of Glass*. The Latin terms lacrymae batavicae or borussicae (and their translation ‘Dutch’ or ‘Prussian tears’) used since the seventeenth century, point to other possible sources of origin. Brodsley et al. (1986) give a detailed account of how glass tears were discussed by scholars in Europe in the seventeenth century.

**EXPERIMENT 1**

A Prince Rupert’s drop can be struck with a hammer without rupture. If, however, the thin tail is broken, the entire object disintegrates into fine particles.

**Bologna Flasks**

Bologna flasks (or bottles) are blown with the glass pipe like an ordinary small thick walled flask. The only difference is that instead of putting the red hot flask into the lehr to anneal it free from strains, it is left out in the cold air. This works in a similar way as intentional quenching on the outside, but much less so in the interior. Therefore, the flask is toughened only on the outside, while even a tiny scratch with a hard tip on the interior walls leads to explosion. German encyclopaedias (Meyer 1885) ascribe the invention to a Mr. Asmadei in 1716. It must have been discussed all over Europe in the 1740s, as the list of early literature in Krünitz (1780) shows. It was presented to the Bolognese Academy of Sciences and Art by Balbi in 1745. ‘Bologneser Flaschen’ are also known in German as ‘Springkolben’ (literally ‘shatter flasks’).

**EXPERIMENT 2**

A Bologna flask withstands blows with a hammer on the outside and can even be used as a hammer itself to drive a nail (with broad head) into a (not so hard) wood. When a small piece of flintstone or a pointed tool falls into it from a low height it shatters into tiny pieces.

**Modern Thermally Toughened Glass**

De la Bastie’s invention was of no great practical use because the glasses could not be quenched evenly. The resulting stresses often lead to failure after months without apparent external cause. Even the modern technique of working with a stream of cold air can only toughen open forms like sheets (e.g. car side windows), plates, or cups. The French glass company Arcoroc (2007) produces such a ‘verre trempé’ which can be used to demonstrate the increased fracture strength.
EXPERIMENT 3

A plate of ‘verre trempé’ resists blows with a hammer. The tip of a normal nail gets flattened on trying to hammer it into the plate. Even hardened nails often do not suffice to crack the glass. It needs special pointed hammers (no nails) such as those provided to create emergency exits through windows in cars or buses to shatter such a plate.

Fire Extinguishing Craquelure (Eggert 2006)

Some Roman glass fragments from the archaeological context of a cremation (bustum) from the Roman vicus of Bonn (RLMB E77/89, Fundnr. 71/10) were found to have a network of superficial cracks, appearing only on the exterior of the vessels (Figure 2). Only a few of these fragments had been deformed by heat. Cracks of the narrow ‘honey-comb’-like pattern do not extend through the entire thickness of the glass. Weathering, which produces other crack patterns in glass, cannot be the cause, as it would have acted similarly on both surfaces of the totally sedimented glasses.

Experiments showed that such a superficial network with no total fractures appears when glass heated above the transformation temperature is quenched with cold water. Because in the interior the glass still flows like a liquid, no large stresses can build up and, therefore, the cracks occur only in the surface region. Only at places with a lower temperature (e.g. around the spot directly heated with a flame, Figure 3), where the glass was not plastic enough, did the normal thermally-induced fractures, which run through the whole thickness and are known from everyday life, occur. The unusual craquelure pattern is known today from fire-extinguishing damage on glass windows. It is also used in one method to produce ‘ice glass’ (Figure 4). In the case of the cremation, it was the first material proof for the Roman burial rite of extinguishing the still glowing relics of the pyre with water or wine.

Figure 2. Superficial craquelure on three Roman glass fragments compared to the results of a reconstruction experiment, scale in cm. (Photo: H. Lilienthal/RLMB).
EXPERIMENT 4

A normal glass bottle (0.7-1.0 l litre) is held at the bottom in one hand and a spot near the neck is heated with the flame of a plumber’s blowtorch (gently moved) for at least two minutes to red heat. Then the bottle is plunged into a bucket full with water while still holding it in the hand. After about fifteen seconds (when the sizzling sound stops), the bottle is withdrawn. The spot which has been heated shows a superficial hexagonal crack network. Somewhere around the spot (at the colder parts) cracks through the whole thickness can occur. Sometimes this leads to disintegration of the bottle into a few fragments.

Outlook

A closer look at craquelure patterns has also been fruitful for the study of ceramic glaze (Eggert 2006). As is known from Chinese crack glazes they can be quite diverse (e.g. compare the ‘cicadian wing’ or ‘iron wire and golden thread’ types, see Wood 1999) and may contain information on the production or weathering of the glazes. Currently, a student group from the University of Koblenz, supervised by D. Paulus from the Institute for Computational Visualistics, is developing software to automatically analyse such patterns from photographs. Hopefully, new patterns can be identified and interpreted.
Through car accidents, people in the twenty-first century are familiar with the fracture behaviour of thermally toughened glass. But even today these experiments might inspire our sense of awe and wonder. May it lead us to a better understanding of craquelure!

Editor's Note

1 This paper provides scientific and historical background for demonstrations carried out by the author at the meeting.

References


Source of Samples

Every glassworks knows how to produce Prince Rupert’s drops by dropping a gather of molten glass into water.

A glassblower should also be able to produce Bologna flasks. They are also commercially available from Phywe Systeme, Göttingen (www.phywe.de, article no. 03609-00).

Plates of ‘verre trempé’ are found in department stores.
Disclaimer

If you want to repeat these experiments please ask your local safety expert for the necessary precautions and safety regulations. For experiments 1-3 the whole glass was packed in plastic zip lock bags to collect the fragments. For all experiments eye protection was worn. Although the author has done the experiments many times without any misfortune occurring, he cannot give a warranty of any kind.