

Discovering the Science and Technology of Glass Formation from Candy Making

H. Jain and I. H. Jain

Department of Materials Science and Engineering
Lehigh University, Bethlehem, PA 18015

Abstract

Glass is a material that has been used for centuries in numerous common, consumer applications. In recent decades, it has become one of the key high-tech materials for applications in thermal insulation, optical communication and microelectronics. Notwithstanding its importance, the average student's understanding of glass science and technology remains very primitive, partly because of its ill-defined structure and complex behavior. Therefore, to illustrate the underlying principles of this class of materials, we have proposed a set of laboratory demonstrations involving sucrose, water and corn starch (the major ingredients of common candy). These low cost simple experiments provide a convenient paradigm for the numerous features of a prototypic glass. The students' feedback has been very positive as they find the unusual experiments exciting, and can relate to the results from previous experiences.

Introduction

Glass is a common material that has been known to man for several thousand years. Early applications of glass such as in windows, containers, lenses, tableware, jewelry depended on their transparency, luster and durability. Many recent high-tech applications such as optical fiber for high-speed communication or dielectrics in microelectronics also exploit some such qualities, but these are neither necessary nor sufficient attributes for a material to be called as glass. A general definition of glass is that it is 'a solid with liquid like structure', 'a noncrystalline solid' or simply 'an amorphous solid'.¹ None of these definitions is very helpful to typical engineering students, even the ones majoring in Materials Science and Engineering, so that they can appreciate the characteristics of this important class of material. Clearly, an experimental demonstration of the essential features of glass will go long way in a student's learning of this subject. The candy experiments described here not only illustrate well the science and technology of glass, but also serve as excellent paradigm due to the students' pre-existing familiarity and interest in the topic.²

Interestingly, both the glass making and the candy making share same underlying principles, although the two technologies developed independently as empirical art in ancient times. Common glasses such as the ones used in windows, tableware, bottles, etc. are based on silicon dioxide (SiO_2) (a.k.a. silica or common sand) as the main constituent. Silica is one of the best *glass-formers*, which can be made as glass readily by cooling from the molten state. Among glass forming oxides it has one of the highest glass transition temperature (T_g)³, strength,

chemical durability, etc. In spite of its superior properties, however, pure silica (or quartz) glass is not used much due to its very high melting temperature (T_m). The high cost of its melting and difficulty of processing at high temperatures make it uneconomical for most applications. Commercial solution to this problem is to lower the melting temperature by adding alkali or alkaline earth oxides as flux (typically 13-18 wt% of Na_2O and 8-13 wt% ($\text{CaO}+\text{MgO}$)). These additives, which on their own do not form glass easily, decrease the melting temperature by forming eutectics. They break the network connectivity of silica glass, and therefore, are known as network *modifiers*. In general, the addition of a modifier also deteriorates chemical durability, lowers T_g and decreases glass-forming ability of the glass. Therefore, a glass engineer must optimize the glass composition depending on the use and acceptable cost of the final product.

Common candy has close analogy to the above mentioned commercial glass, where sugar (i.e. sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ with $T_m=186^\circ\text{C}$) is a good glass former and water (H_2O with $T_m=0^\circ\text{C}$) is a good modifier, just like SiO_2 ($T_m=1723^\circ\text{C}$) and Na_2O ($T_m=1275^\circ\text{C}$), respectively, are in a common glass. Major advantages of candy demonstration are that the observations of interest are accessible at much lower temperatures, and the experiments can be performed with simple, inexpensive tools and ingredients. In the following sections, we describe the experiments briefly, followed by a discussion of how they demonstrate various aspects of glass formation. Details of experimental procedure and examples of typical results can be found elsewhere.⁴ We have also determined the effect of composition on the properties (chemical durability, strength, density, etc.) of the so-formed samples, which will be communicated in a separate paper.

Experiments

National Confectioners Association has given a recipe for making rock candy using sugar, corn syrup and water as the key ingredients.⁵ Since our interest is in learning the role of each component, we suggest making sugar candies by splitting the suggested procedure in four experiments.

- (a) Grow crystal candy from slow evaporation of saturated solution.
- (b) Make candy by rapidly cooling the molten sugar.
- (c) Make candy by rapidly cooling the hot liquid phase of sugar and water.
- (d) Make candy by rapidly cooling the hot liquid phase of sugar, water and corn syrup.

Experiment (a): Growth of sugar crystals from solution.

For this experiment, commercial kits of prepared saturated solution of sugar in water are available from popular science stores. Each kit also contains small crystallites of sugar on a stick, which act as seeds for the growth of larger crystals. The important points to note from this experiment are: (i) the sugar solution is about as fluid as water, and (ii) the growth of crystals, even a few mm in size, takes several days.

For the remaining three experiments, we need the following readily available Equipment and Supplies:

- 1 one-quart stainless steel pan
- 1 hotplate
- 12 metal tablespoon
- 1 laboratory balance (or fluid measuring cup at home)
- 1 metal tray to hold hot candies (up to $\sim 175^\circ\text{C}$ / 350°F)
- 1 laboratory or good quality candy thermometer that reads up to $\sim 205^\circ\text{C}$ or 400°F .
- 5 pounds of granulated cane sugar

16 oz.-bottle of corn syrup (e.g. Karo syrup available in supermarkets)
Tap water
20 molds for casting the candies e.g. the metal containers of *Tea Light* candles (small cookie cutters will also work well).
Four 8-oz. glasses.

Experiment (b): Formation of candy from pure sugar.

Take 410 g sugar in the pan and start heating it gradually on a hotplate, while stirring with a spoon and monitoring the temperature (T) by thermometer. The stirring speed should be such that solid and molten parts mix together, until all the sugar has melted. Take a tablespoon of melt and cast the candy in one of the molds. (During this stage the temperature should not be allowed to increase any further, as it would cause formation of bubbles from the decomposition of sugar.) Make a note of the physical appearance of the samples as they cool to room temperature (RT), especially about the transparency, presence of small white crystals and/or bubbles, and whether solid or liquid. Turn the hotplate off. Attempt drawing fiber by taking the spoon slowly away from the syrup. Repeat this process as the temperature of syrup decreases to solidification when fiber drawing becomes impossible. Make a note of fiber drawing ability as a function of decreasing temperature. When cooled to room temperature, compare the appearance of cast candy with that of crystal candy obtained from Experiment (a).

Experiment (c): Effect of water addition on the formation of candies from hot syrup.

Take 410 g sugar and 100 g water in the pan, and begin heating the mixture as in (b). Observe the dissolution of sugar due to the rapid increase in its solubility with increasing temperature. Continue heating and stirring until the syrup begins to boil, say at temperature T_b . Cast candy from this syrup, and let the remaining syrup continue to boil until $T = T_b + 5^\circ\text{C}$. Cast another candy in a different mold. Repeat this step for each 5°C increment, until the temperature reaches $\sim 170^\circ\text{C}$. Every time use clean spoon to cast a new sample. Note the physical appearance of the samples as they cool to room temperature, especially about the transparency, presence of small white crystals, whether solid or liquid, and relative viscosity at RT if the sample remains fluid.

Experiment (d): Effect of addition of corn syrup to the hot syrup (sugar + water) in (c) on the formation of candies.

This experiment is essentially a repetition of Experiment (c), with the exception that now the ingredients also include 240 g corn syrup, in addition to 410 g sugar and 100 g water. To begin, place all the three ingredients in clean pan, follow all the steps of (c), and note corresponding observations.

Major Observations and What They Teach

The most significant observations from the above experiments are summarized next. Their implications are discussed briefly, which may be expanded and supplemented by other observations by the instructor/student. The summary statements, drawn from these experiments and written in italics, apply to prototypic sodium silicate glass just as well.

1. In all the experiments, solid candies are formed from a liquid state in which sugar molecules are in random Brownian motion. In experiment (a) one obtains single crystals of sugar, which

are easily identified as such due to their symmetric, faceted appearance. The crystal growth is very slow, taking several days to reach just a few mm. The low viscosity of the solution implies high mobility of the molecules. By contrast, in experiment (b) the casting of relatively viscous, molten sugar gives glass-like candy. It is light to dark brown, and translucent to opaque depending on the size and volume fraction of the bubbles formed from the decomposition of sugar. The casting takes the shape of the mold - a characteristic of the liquid state. The candy is formed from the liquid state in a very short time as the melt solidifies to form the sugar glass.

So we learn: if sufficiently long time is available, on solidification the molecules (initially in the liquid state) will organize to form crystals. Low viscosity promotes crystal formation. High viscosity of the liquid state is conducive to glass formation.

2. In Experiment (c), initially the (sucrose + water) mixture consisted of both liquid syrup and undissolved solid sugar. However, on heating all the sugar dissolved to form a clear liquid.

So we learn: the solubility of sugar in water must be increasing with temperature - an observation that is generally valid for the dissolution of a solid in a liquid.

3. In Experiment (c), on further heating, the single-phase syrup begins to boil (at $T_{bp}105\text{ }^{\circ}\text{C}$), and continues to boil as the temperature increases. This can happen only if boiling causes a change in the syrup composition. Since water has a much lower boiling temperature than sucrose, we infer that boiling causes preferential loss of water from the syrup. In turn, the syrup becomes increasingly viscous and concentrated with sucrose - ultimately approaching the 100% sugar composition. In a way, the boiling temperature becomes an indicator of the sugar content of the syrup. The concentration of water in the syrup decreases as the successive candies are cast. Thus, a comparison of the samples cast with increasing boiling time (or temperature) will indicate the effect of decreasing water content. The syrup in Experiment (d) behaves likewise, hence a similar variation of the water content of the samples must be occurring in these samples.

As shown in Figure 1, soon after casting, the initial samples of Experiment (c) did not fully solidify but remained as a transparent, colorless, viscous liquid. Next samples (i.e. with a lower water content) appeared as a mixture of viscous liquid and an aggregate of white sugar. On further decrease of water content, the fraction of polycrystalline aggregate increased at the expense of viscous liquid. Ultimately, the samples from a much later stage of casting i.e. with much less water content were solid, transparent glass.

In Experiment (d), the increase of RT viscosity with decreasing modifier content can be characterized as chewy to hard candy. If a candy is chewy and clear, it means that its glass transition temperature is below RT. The less chewy is the candy; much lower is its T_g than the room temperature. In popular literature, the hardness of a candy is said to depend on the temperature at which the syrup was boiled before casting. Now we know that a more accurate cause of a candy's softness is the amount of water (the modifier) it contains.

We learn two consequences of the water content on the ability of the syrup to form glass: First, the glass transition temperature at which the supercooled liquid can be transformed into the glassy state is increasingly suppressed by the addition of modifier oxide (water). Second, for the later compositions that have T_g above RT, polycrystalline solid is formed if the water content is high, or a glass is formed if the water content is low. *Thus, on the one hand addition of water*

reduces the T_g of the sucrose- H_2O system. On the other hand, it decreases the ability to form glass. This behavior exactly parallels the behavior of the SiO_2 - Na_2O system.



Figure 1. Appearance of samples from Experiment (c) after casting at room temperature. From left to right, the boiling temperature of the melt is increasing i.e. the modifier content decreasing. Note that the first sample is a liquid, the second is a mixture of crystalline aggregates and liquid syrup, the third is mostly crystalline aggregate with some glassy/liquid phase, the fourth is mostly a glass with small, white crystalline regions and the last sample is completely glassy.

4. In comparison to the samples of Experiment (c), none of the samples of Experiment (d) showed formation of white crystalline powder. They all remained transparent, suggesting that the tendency of water-sugar glass to devitrify (i.e. revert back to the crystalline form) is strongly suppressed by the addition of corn syrup, making it possible to obtain clear, glassy candy at high modifier concentrations. Without the addition of corn syrup it will be too difficult to obtain chewy clear candies from water-sugar mixture alone. In addition, we note that the viscosity of the liquid is increased by the addition of corn syrup. The three components are soluble in each other. The intimate mixing of sugar and corn syrup makes it difficult for sugar molecules to organize as crystals.

Thus we learn the so-called principle of confusion: *The addition of a third glass-forming component can significantly stabilize the glassy state. The molecules of the added component disorganize the structure further and confuse the crystallization process.*

5. In Experiment (d) (also in Experiment (c) but less clearly), the viscosity of the molten syrup (just before casting) increases as water boils off gradually. This occurs even as the temperature of observation i.e. the boiling temperature increases.⁶ Also at RT the viscosity of liquid samples increases with decreasing H_2O content, ultimately only solid state is obtained. So we learn: *The addition of a modifier oxide (i.e. water in the present case) decreases the viscosity of glass forming sucrose strongly. The same statement is true for the SiO_2 - Na_2O glass system.*

6. In Experiment (c), the observation of various samples over a period of time shows gradual conversion of the glassy parts of the sample to polycrystalline white powder (see Fig. 2). A comparison of Figures 2(a) and 2(b) shows that the rate of this transformation is faster, the higher is the water content.

Thus we learn: *a glass would ultimately transform into a more stable crystalline state. The rate of this conversion is strongly dependent on composition, which can be infinite for many practical purposes.*

7. In Experiment (b) or (d), as the syrup cooled, the ability to draw fibers (essentially making of cotton candy) passes through a narrow maximum. At high temperature, the syrup is too fluid and so the surface tension prevents it from being drawn into long fibers. At low temperature, the syrup does not have enough plasticity to be drawn into long fibers without breaking into pieces.

Thus we learn: *There is, but a narrow viscosity (hence the temperature) range, over which long fibers can be drawn from a glass-forming melt.*



Figure 2 [(a) Upper row. (b) Lower row]. Crystallization of two cast candies (made from sugar and water in Experiment (c)) with increasing time from left to right at room temperature. The sample in the upper row has much larger modifier (water) content than the one in the lower row.

8. Finally, in Experiment (c) the formation of white crystalline powder was significantly enhanced if the melt was stirred before casting. Also, if some of the sugar collected on the pan walls dropped in the syrup, it did not dissolve back easily, but instead helped in subsequent crystallization.

So we learn: *mechanical agitation or pre-existing sugar particles help nucleate the crystalline phase. Once, the crystallites are formed they do not revert back to the glassy state.*

Student Response

The present demonstration has been performed in front of three student settings: (a) In the 'Mat 342 Inorganic Glasses' course which is offered as an elective to the Materials Science and Engineering Seniors at Lehigh University. The demonstration was shown once in the first week of the semester, but its observations were referred to several times throughout the semester in the context of different topics. (b) At a graduate seminar entitled, 'Rules of glass formation - how well do they work?' at the Materials Science and Engineering Department of another University. (c) In the Science class of the sixth grade at a local Middle School. Although we do not have a rigorous evaluation of the demonstration's impact, the written comments by the students of MAT 342, and intense questioning / curiosity by students under all settings suggest that the candy experiment introduces the concepts of glass science and technology at all levels very successfully.

Conclusions

For teaching the principles of glass formation, we have proposed a set of experiments based on traditional candy making. It is shown that the two main ingredients of common candies (sugar and water) serve the same function as do silica and sodium oxide in common glasses. The two components behave as classical former and modifier of the glass network. Furthermore, the benefit of adding corn syrup to candy making parallels the addition of alumina in common glasses. Thus a very close connection is demonstrated between the two technologies. Since candy making is inherently interesting to students, the proposed demonstrations provide a memorable experience to the students for learning several principles of glass formation.

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References:

- ¹ A. K. Varshneya, Fundamentals of Inorganic Glasses, Academic Press, New York, 1994.
- ² The experiments discussed in this paper are a result of an Elementary School science project. Often College teachers outreach pre-college students by introducing advanced scientific concepts. In this respect, the present work is just the converse; it is an 'inreach' effort where the interest of the College students is inherently assured.
- ³ Roughly defined as the temperature below which the supercooled liquid behaves as a solid.
- ⁴ H. Jain and I. H. Jain, 'Learning the Principles of Glass Science and Technology from Candy Making', Standard Experiments in Engineering Materials, Science and Technology, NEW: Update 2000. NASA/CP-2001-211029. pp. 169-182 (2001).
- ⁵ Chocolate Manufacturers Association / National Confectioners Association. <http://www.candyusa.org>
- ⁶ Contrary to this observation, generally the viscosity of liquids decreases with increasing temperature.

HIMANSHU JAIN is the Diamond Chair Professor of Materials Science & Engineering, specializing in glasses and ceramics. A Fellow of the American Ceramic Society, he received Zachariasen international award for outstanding contribution to glass research, Doan teaching award by the Senior class, a Fulbright Fellowship for lecturing and research at Cambridge and Aberdeen in UK, and a Humboldt Fellowship for research in Germany.

ISHA H. JAIN is a sixth grade student at East Hills Middle School in Bethlehem, PA. A great enthusiast of math and science, she initiated the present work as her Science Fair project two years ago, and has continued developing it further since then.