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Learning the Principles of Glass Science and Technology from Candy Making

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Key Words:
Glass formation, glass transition, nucleation, crystal growth, crystallization, viscosity, fiber drawing, glass-former, network-modifier, chemical durability, candy, hardness.

Prerequisite Knowledge:

The steps of candy making can demonstrate numerous principles of physical chemistry and materials science & engineering, which are typically taught from Middle School through College level. Notwithstanding, we discuss the experiment assuming that the student has completed High School level chemistry. Additional knowledge of the principles of binary phase diagram is desirable. The experiment is well suited for an Introductory course in Materials Science and Engineering, typically taken by most engineering majors. It will be also an excellent paradigm for a course on glass science or technology.

Objectives:

To observe and understand the following principles of glass science and technology:

1. When a homogeneous melt is cooled sufficiently slowly, one obtains a single crystal. Fast cooling yields polycrystalline solid. Glass is formed on increasing the cooling rate further, when crystal formation is fully suppressed.
2. Surfaces, insoluble impurities, mechanical agitation, bubbles, etc. in the melt can act as nucleating agents for crystal formation. These should be avoided if the goal is to obtain glass.
3. The addition of a modifier oxide to a glass-former oxide decreases the ability of the melt to form glass.
4. The glass-forming ability of a melt may be enhanced by increasing the number of components.
5. The addition of a modifier oxide generally deteriorates the chemical durability and mechanical properties of glass.
6. It is possible to draw glass fibers from melt but within a narrow range of viscosity, which in turn can be controlled by varying the temperature.

Equipment and Supplies:

1 one-quart stainless steel pan.
12 metal tablespoon
1 laboratory balance (or fluid measuring cup at home)
1 metal tray to hold hot candies (up to ~175 °C/ 350 °F)
1 laboratory or good quality candy thermometer that reads up to ~ 205 °C or 400 °F.
5 pounds of granulated cane sugar
16 oz.-bottle of corn syrup (e.g. Karo syrup available in supermarkets)
Drinking water

20 molds for casting the candies. The metal containers of *Tea Light* candles (small cookie cutters will also work well).
Four 8-oz. glasses.
Crystal candy, readily available as an aggregate of large clear, colorless crystals

Background:

Both the glass making and the candy making developed independently as empirical art in ancient times. Interestingly, the two technologies share same underlying principles, which can be learnt conveniently using kitchen tools. 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.[1] Silica is one of the best *glass-formers*. It forms glass readily when cooled from the molten state. Among glass forming oxides it has one of the highest glass transition temperature (Tg)[2], 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), which makes cost of its manufacture prohibitively high. 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% (CaO+MgO)). These additives, which alone 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 Tg 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.

The candy making process serves as an excellent illustration of these principles of glass science and technology. Here sugar (i.e. sucrose, $C_{12}H_{22}O_{11}$ with T_m=186 °C) is a good glass former and water (H_2O with T_m=0 °C) a good modifier in a candy, just like SiO_2 (T_m=1723 °C) and Na_2O (T_m=1275 °C), respectively, are in a common glass.

Experimental Procedure:

Caution: The present experiments require working with high temperatures and hot liquids, which should be handled with appropriate insulation to avoid burning.

Note: The following recipe is suggested by the National Confectioners Association for making rock candy using sugar, corn syrup and water as the key ingredients. We break it down in three experiments by working with (a) sugar alone, (b) mixture of sugar and water, and finally (c) the mixture of all three ingredients.

Main steps of the suggested recipe:

- *Put 3.75 cups of granulated sugar (~820 g), 1.5 cups of Karo corn syrup (~480 g) and 1 cup of water (~200 g) into the saucepan, and heat gently until the sugar has dissolved, constantly stirring with the tablespoon.*
- *Bring to a boil and cook, without stirring, until the temperature reaches 310 F/154 °C.*
- *Remove from heat (and add candy flavoring and food coloring - not important for our experiment).*
- *Pour mixture onto a foil lined baking pan.*
- *Immediately remove foil from baking pan by sliding the pan out from under it.*
- *As mixture cools, cut with scissors*

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[1] The broad scientific definition of glass is: It is a non-crystalline or amorphous solid. Common glass is but one sub-class of this wide range of solids that may include metals, polymers as well as ceramics.

[2] Roughly defined as the temperature below that the supercooled liquid behaves as a solid.

Experiment A. Formation of candy from pure sugar.

a. Take 410 g sugar in the pan and start heating gradually on hotplate or electric cook-top at Low-Medium temperature setting. Insert thermometer and monitor the temperature of sugar. Use the spoon to stir sugar, thus maintaining uniformity of temperature. Note: the thermometer bulb should be in the middle of sugar, and away from the bottom of the pan.
b. Continue heating and stirring until all the sugar has melted. The stirring speed should be such that solid and molten parts mix together. Note the temperature (T_m) when all the sugar has just melted, giving its melting point.
c. Stop stirring the melt. The temperature during this time should not be allowed to increase to avoid excessive browning of the melt and bubble formation, which occur from the decomposition of sugar.
d. Cast two candy samples (#A1 and #A2) by taking one and three, respectively, tablespoons of the molten sugar and pouring into two separate molds that were placed on the metal tray. 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.
e. Turn the hotplate off. Attempt drawing fiber by slowly taking the spoon away from the syrup. Continue 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. Estimate the temperature (T_d) at which fiber drawing ability is maximum.
f. Compare the appearance of samples #A1 and #A2 with that of crystal candy that is also made of pure sugar.

Experiment B. Determine the effect of addition of water to sugar on the processing of candies.

a. Put 410 g sugar and 100 g water in the pan (these ingredients are in the same ratio as in the original recipe), and begin heating while stirring the melt. Monitor the increase of temperature as sugar dissolves. Note the temperature (T_s) at which all the sugar dissolves in solution.
b. Continue heating and stirring. Note the temperature (T_b) at which the syrup begins to boil. Cast candy from the syrup (sample #B1). Make a note of the physical appearance of the candy as it cools to room temperature, especially about the transparency, presence of small white crystals, whether solid or liquid, and relative viscosity at RT if it remains fluid.
c. Boil the remaining syrup, while also stirring, until the temperature increases by 5 °C i.e. it reaches $T_2=T_b+5$ °C. (A temperature increase of 10 °F may be used if working with a Fahrenheit thermometer, typically used in kitchen.) If solid sugar is deposited at the edges of the syrup, scrape and stir it into the liquid. Cast candy from this more concentrated syrup (sample #B2). Make a note of the physical appearance as before.
d. Continue repeating the previous step, casting a new candy for each 5 °C (or 10 °F) increment in temperature (sample #B3, #B4, … etc.), until the temperature reaches ~170 °C (338 °F). Every time use a clean spoon to cast a new sample.

Experiment B(a). Determine the effect of stirring on the processing of candies made from sugar and water.

According to Objective #2, mechanical disturbances, the interface between the melt and surface of the pan, etc. can help nucleate the crystal formation. To verify this statement, repeat all the steps of Experiment B except that this time do not stir the solution after the sugar has settled at the bottom of the pan (at ~ 200 F). Try to cast the samples (#B1(a), #B2(a), #B3(a),… etc.) when the melt is at the same temperature as in Experiment B.

Record the changes in samples as they cool to room temperature, making special note of any differences compared to the corresponding B samples.

Experiment C. Determine the effect of addition of corn syrup to (sugar + water) mixture on the processing of candies.

This experiment is essentially a repetition of Experiment B(a), 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 Experiment B(a), and note corresponding observations.

Experiment D. Effect of processing conditions on the properties of candies.

The experiments described below are designed so that little specialized equipment is needed. If appropriate equipment is available, such as for measuring hardness or viscosity, the students are encouraged to obtain quantitative data.

Hardness or Chewy character. The samples would have a wide range of hardness from brittle solid to a watery liquid. To make a comparison of this property, use a paper clip. Open the clip up from one end, providing one sharp end, and one bent end of the wire. Use the sharp end for testing solid samples by inserting the pin under approximately the same force. Compare the size of the dent thus created on different samples. For liquid samples, use the bent end of the pin. Dip it into the liquid and take it out, noting the relative force needed to do so.

Durability in water. Select one each of the A, B, B(a) and C samples (say the one cast from the melt at ~150 °C or 302 °F). Determine their weight (still in mold), using laboratory balance, and place them in separate 8-oz. glasses with 200 g tap water. (Note: all the water should be at the same temperature). Drain the water out after 1 h. Take the samples out, dry and weigh them again. This is a static experiment, so the sample and water should not be disturbed. Calculate the respective weight loss from dissolution in water. The loss of a sample's weight occurs from dissolution at the top surface that is exposed to water. Since the mold cross-section area is the same for all samples, the weight loss is inversely proportional to the durability. Therefore greater is a sample's weight loss, lower is its durability.

Some of the glassy or partly glassy samples may devitrify rather slowly. In that case, make a note of slow changes in the physical appearance of such samples over the next several days.

Record the qualitative information in the Table below by assigning relative grades 1 through 5, when possible. For example, in the Transparency column write 1 for an opaque and 5 for a completely transparent sample.

Example of Results:

Melting Temperature of sugar, T_m	= 344 °F
Temperature of maximum fiber drawing, T_d	= 190 °F
Temperature where the solubility of sugar in water is 410 g / 100 g, T_s	= 210 °F
Boiling temperature of the initial (sugar + water) syrup, T_b	= 220 °F

Temperature at which 410 g sugar dissolves in 100 g water + 120 g corn syrup, T_s'	= 228 °F
Boiling temp. of the initial (sugar + water + corn syrup) solution, T_b'	= 220 °F
Weight of as cast sample #A1	= 10.1 g
Weight of sample #A1 after dissolution in water	= 9.1 g
Weight loss	= 1.0 g
Weight of as cast sample #B5	= 22.7 g
Weight of as prepared sample #B5 after dissolution in water	= 17.9 g
Weight loss	= 4.8 g
Weight of as cast sample #B10(a)	= 16.5 g
Weight of as prepared sample #B10(a) after dissolution in water	= 15.1 g
Weight loss	= 1.3 g
Weight of as cast sample #C10	= 19.8 g
Weight of as prepared sample #C10 after dissolution in water	= 18.7 g
Weight loss	= 1.1 g

<u>Table of Observations</u>

Sample # and time since casting	Casting Temp.	Transparency	Crystallinity	Relative Hardness (H) or Viscosity (V)	Comments
#A1		3.5	1.1	H: 5	Red-brown solid. Many bubbles. Sample used in durability test. (Fig. 1)
#A2		2	1.5 (?)	H: 5	Dark brown solid. Very large number of bubbles. (Fig. 1)
#B1	228	5→ 4→2.5	1→1.5	Cryst.+Liq.	
#B2	236	5→ 3→2.5	1→2	Cryst.+Liq.	Prior to casting, the hot syrup contained small white crystals (Fig. 2)
#B3	242	5→ 2	2→3	H:3 Cryst+Liq.	
#B4	256	5→ 1	2→4→4.5	H:4 Cryst+Liq.	
#B5		3→1	4→4.5	H:4.5 Polycrystal	
#B6		2→1	5→5	H:5.0 polycrystal	
#B1(a)	228	5→4.5→2.5	1→1→1.2→ 1.5	Cryst.+Liq.	Liquid fraction decreases as #B1(a)→ #B3(a)
#B2(a)	238	5→4.5→2.5	1→1.5→1.5	Cryst.+Liq.	
#B3(a)	248	5→2.0	1→2→2.5	V:4 Cryst.+Liq.	
#B4(a)	258	5→4→2.0	1→2.5	H:2	Bubbles form on pouring in mold.

Sample # and time since casting	Casting Temp.	Transparency	Crystallinity	Relative Hardness (H) or Viscosity (V)	Comments
				Non-sticky	Colorless liquid.
#B5(a)	268	5→2.0	1→3→3.5	H:3 Non-sticky	Many bubbles form on pouring in mold. Colorless liquid.
#B6(a)	274	5→2.0	1→2.5→3.5	H:2.5 Non-sticky	Many bubbles form on pouring in mold.
#B7(a)	288	5→2.0	1.5→2→3	H:3 Non-sticky	Light yellow liquid. Bubbles form on casting.
#B8(a)	298	5→1.0	1→2→3	H:3 Less sticky	Light yellow liquid. Bubbles form on casting.
#B9(a)	300	5→3.0→1.5	1→1.5→2.5 →2.5	H:3.5 More sticky	Yellow liquid. Shows crystal growth easily.
#B10(a)	310	4.5→4.5	1.5→1.5→2 →2	H:3.5 Sticky	Light brown liquid. Shows crystal growth easily.
#B11(a)	317	5→5.0	1→1.1→1.2	H:4	Brown liquid. Less bubble formation on casting.
#B12(a)	338	5→5.0	1→1	H:4.5	Dark brown liquid. Some bubbling.
#C1	228	5	1	V:2 Thick syrup	Can draw fiber at RT
#C2	238	5	1	V:3	
#C3	248	5	1	V:4	Wrinkling of surface later
#C4	258	5	1	H:1.5 V:4.5 Chewy	Crinkling of surface.
#C5	268	5	1	H:2.5 Sticky	Colorless. Surface crinkles after casting
#C6	278	5	1	H:3	Hue of yellow. Wrinkled next day.
#C7	288	5	1	H:3.5	
#C8	298	5	1	H:4	Pale yellow glass
#C9	300	5	1	H:4.5	Light yellow glass
#C10	310	5	1	H:4.5	Yellow glass.
#C11	320	5	1	H:4.5	Yellow glass
#C12	330	5	1	H:~5	Light brown glass
#C13	340	5	1	H:5	Brown glass

Brief Discussion:

Note: The following information is primarily for instructors. It is provided as an illustration of anticipated results and discussion of students' observations.

1. The melting temperature of pure sugar is observed to be 344 °F, which is lower than the value reported in literature, possibly because the present value was measured in a somewhat supercooled state.
2. The casting of pure molten sugar in a mold at RT gives a glass-like candy (A samples). It is light to dark brown, and translucent to opaque depending on the bubbles produced presumably from the decomposition of sugar (Fig. 1). The cast candy takes the shape of the

mold, which contrasts with the faceted crystals of rock candy. Therefore, we infer that the cast candy is a non-crystalline or glassy solid.

When crushed by a hammer, the cast glassy candy behaves as hard and brittle as the crystalline rock candy, suggesting that most likely there is no major difference between their mechanical properties.

(In a separate experiment, we grew sugar crystals from slow evaporation of saturated solution of sugar in water over a couple of weeks. (Note: Kits for this experiment are available from popular science stores). Many orders of magnitude longer time was available for sugar molecules in solution to organize in large crystals than the time of solidification of the cast. Therefore, we infer that shorter time for solid formation from disorganized liquid state promotes non-crystalline structure.)

3. From Experiment B, we observed that at room temperature the (sucrose + water) mixture consisted of both liquid syrup and undissolved solid sugar. On slow heating and stirring the solid phase disappeared at T_s=210 °F. Therefore, the solubility of sugar in water must be increasing with temperature. Furthermore, at 210 °F its value should be about 410 g per 100 g H_2O.
4. On heating the solution after all the sugar has dissolved, the single-phase syrup begins to boil at T_b=220 °F. On further heating, the syrup continues to boil and at the same time the temperature also 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 (at 220 °F) causes preferential loss of water from the syrup. In turn, the syrup becomes increasingly viscous and concentrated with sucrose - ultimately it would approach the 100% sugar composition. In a way, the boiling temperature becomes an indicator of the sugar content of the syrup. Therefore, the concentration of modifier oxide decreases in the sample order, #B1(a) > #B2(a)> #B3(a)> #B4(a) … etc. Similar variation occurs among the C samples.
5. The stirring of syrup induces crystal formation, thereby suppressing glass formation. Once formed, the crystals are difficult to dissolve back. The crystalline solid preferentially formed at the thermometer and pan-syrup boundary. A comparison of B and B(a) samples clearly shows that the samples cast from stirred syrup crystallize much more easily than the ones cast from unstirred solution (Fig. 3). We were not able to obtain solid glass in B samples at RT - either we obtained a mixture of crystal and liquid phases (#B1 – #B4) or a chunk of polycrystalline sugar solid (#B5 and #B6).
6. Within the B or B(a) series the appearance of most samples changed with time. If the modifier content was high, the formation of polycrystalline chunks ensued after casting. Figure 4 shows the crystal formation in B2 sample with increasing time. With decreasing modifier content, the crystal formation decreased gradually, if the sample was not stirred. Contrast Fig. 5 vs. Fig. 4.
7. At room temperature, the glass forming ability increased with decreasing H_2O modifier content, as shown by Fig. 6 recorded about 12 hours after casting. Here the samples B1(a) through B3(a) were a mixture of liquid syrup and polycrystalline solid sugar. They did not form glass. With decreasing water content the transparency of the samples decreased as the fraction of polycrystalline sugar increased. However, on further decrease of H_2O content the samples became increasingly more transparent. Thus, sample #B11(a) and #B12(a) remained completely transparent and glassy. These observations confirm similar behavior of the SiO_2-Na_2O system.

8. The viscosity of the molten syrup (just before casting) increased as water boiled off gradually. This occurred even as the temperature of observation i.e. the boiling temperature increased.[3] Also at RT the viscosity of liquid samples increased with decreasing H2O content. These observations are best exemplified by the experiment C for which glass formation was not a problem. In this series the viscosity increased in the order #C1 < #C2 < .. < #C13. (see Table). Clearly, the addition of modifier oxide decreases the viscosity of glass forming sucrose strongly. The same statement is true for the SiO_2-Na_2O glass system.
9. 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 Tg than the room temperature. Thus, the Tg of sucrose-water glass decreases with increasing modifier content. The same is also true for the SiO_2-Na_2O glass system. 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!
10. For the glassy candy below Tg, such as #C7 - #C13, hardness increased with decreasing water content. In other words, the break up of network structure by a modifier decreases the hardness of a glass, as is also true when Na_2O is added to SiO_2.
11. As the melt temperature decreases, the melt viscosity increases and the ability to draw sugar fibers (essentially making of cotton candy) increases (see Fig. 7). However, after a while the ability to draw fibers becomes increasingly difficult. These observations show that viscosity of melt increases with decreasing temperature, and only in a narrow range of viscosity (i.e. the temperature) it is possible to draw long fibers.
12. Since the duration and surface area exposed to water were about the same for the samples of Experiment D, the weight loss values indicate their susceptibility to attack by water. The results show that pure sugar glass is most durable among the four samples. Addition of H_2O modifier renders the glass more susceptible to the attack by water. Some of this loss of chemical durability of the sugar glass is recovered when corn syrup is added. Very much parallel technology is adopted for making common oxide glasses where the loss of durability of silica by the addition of Na_2O is regained by the addition of other oxides such as Al_2O_3.
13. The polycrystalline sample #B5 showed much larger weight loss for two reasons: (a) The sample was inherently less durable than the glassy form, especially at the grain boundaries. (b) The sample was not a monolithic solid and was cracked. Thus the surface area exposed to water was larger than for the other samples.
14. Overall the observations of Experiment C confirm the various conclusions that are derived from Experiment B and B(a). 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. The tendency of sugar-water glass to devitrify 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 sugar-water mixture alone.

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[3] Contrary to this observation, generally the viscosity of liquids decreases with increasing temperature.

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For color photographs in this paper, please refer to the web page at:
http://www.lehigh.edu/~inmatsci/jain.html

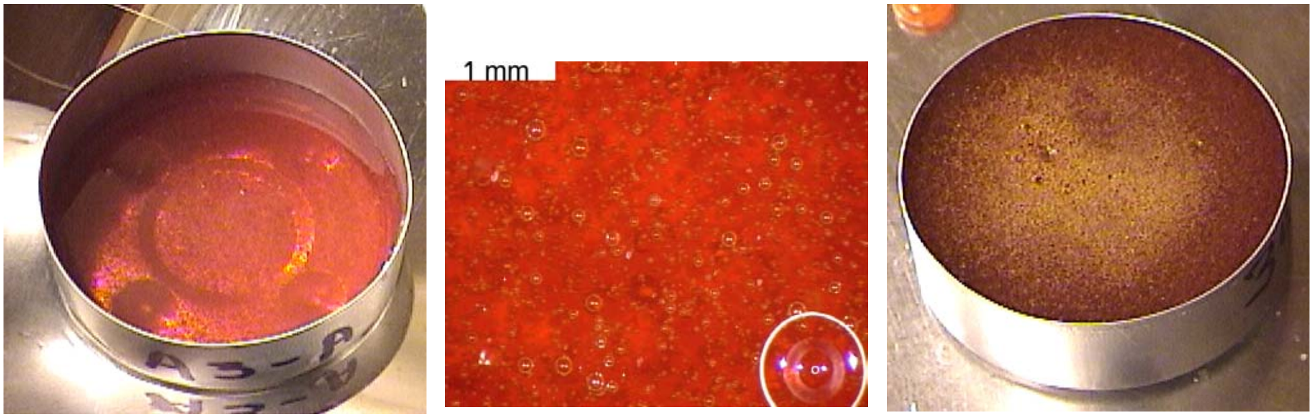

Figure 1. Candies cast from pure molten sugar, showing different bubble density that determines transparency. The figure in the middle is a magnified part of the one on the left. The right sample is thicker and opaque. It has a much higher bubble density.

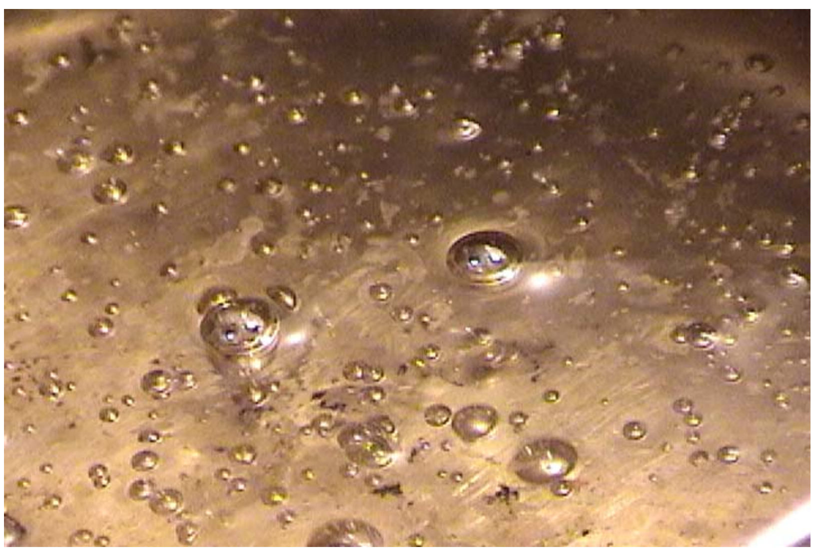

Fig.2. Small white crystals in the boiling liquid syrup, resulted from stirring action. These did not exist in the unstirred syrup. Scale: Figure diagonal = 14 cm.

Fig. 3. The figure shows the effect of melt-stirring on glass formation. The samples in top row were stirred before casting, whereas the ones on bottom row were not stirred.

Fig. 4. Growth of sugar crystals in high modifier content mixture. The figure shows B2 sample with increasing time from left to right.

Fig. 5. Growth of sugar crystals in low modifier content mixture. The figure shows B10(a) sample with increasing time from left to right.

Fig. 6. Demonstration of increasing glass-forming ability with decreasing modifier content from left to right. Unstirred sugar+H_2O samples from Experiment B(a). Sample #B1(a) is mostly liquid with a few crystals floating. The fraction of crystals increases in #B4(a) and #B8(a), the latter being mostly solid. #10(a) is mostly solid glass with a few crystalline regions. Finally, the last sample (#B12(a)) is just solid glass.

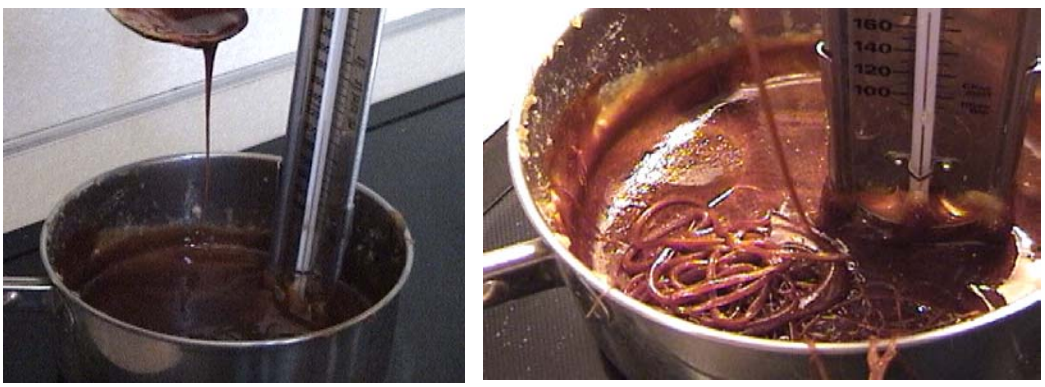

Fig. 7 Large changes in fiber drawing ability with a change in temperature just by a few F.