

Code and Title of the Paper: F01FS Food Science

Code and Title of the Module: F01FS38 Factors affecting crystallization, crystallized & on crystallized
candies

Name of the Content Writer: Dr. Munira Husain

FACTORS AFFECTING CRYSTALLIZATION, CRYSTALLISED AND NON – CRYSTALLISED CANDIES

Crystallization is a process of formation of solid crystals precipitating from a solution through a natural or an artificial method. It is also a chemical solid-liquid separation technique, through mass transfer of a solute from the liquid solution to crystalline phase in the form of a solid matter. Crystallization is therefore is a precipitation process, obtained through a change of the solubility of the solute in the solvent. The crystallization process proceeds into two major steps, Nuclei formation and *Crystal growth*

Nuclei formation or Nucleation is the step where the solute molecules which are dispersed in the solvent become gather and forms clusters in nano sizes. However, if the clusters are not stable, they dissolve. Therefore, the clusters need to reach an optimum size in order to become stable nuclei. Moreover the formation of stable cluster depends upon the temperature at which the solution has been boiled and kept and the Level of Supersaturation of the solution. The *crystal growth* is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists.

Supersaturation is the driving force of the crystallization; hence the rate of nuclei formation and growth is determined by the existing supersaturation in the solution. Depending upon the conditions, either nucleation or growth may be predominant over each other, and as a result, crystals with different sizes and shapes are obtained so

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control of crystal size and shape constitutes one of the main challenges in industrial manufacturing of crystallized products Sugar crystals grow by having sugar molecules deposited on their outer faces If we cool the syrup down to just a little above room temperature, the crystals will have less time to grow before they reach room temperature and stop growing . This is important because in candy (and frozen desserts) crystal size = texture

- Large crystals = coarse, crunchy texture = No good
- Small crystals = smooth, velvety texture= This is desirable

The concentration of sugar in the solution is increasing due to the evaporation of water The boiling point is increasing due to the colligative property of boiling point elevation, which says that as the concentration increases, the boiling point increases. There is no change in the sugar concentration but there is a decrease in temperature at some point (a unique combination of concentration and temperature) the solution will become saturated (has all the sugar it can dissolve at that temperature)

When making a caramel or candies we want a smooth texture and not a grainy one. Large sugar crystals will cause a grainy texture in confectionary products. It is imperative to know that How prevention of the over-crystallization of the sugar can be done and smooth imperceptible sugar crystals can be made in confectionary products.

Dissolving sugar in liquid makes sugar syrup. The dissolution of sugar is promoted by heating the mixture most of the time. When the solution starts to boil, water evaporates and the solution becomes

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more concentrated. Crystals start to form only when the sugar solution reaches a certain concentration. This state is called a supersaturated solution. The term 'supersaturated' refers to the situation where more sugar than theoretically possible from the solubility data is in solution. The supersaturated solution has been achieved either by lowering the temperature or by increasing the sucrose concentration, or both. A metastable region exists where the solution is in fact supersaturated but in practice no crystallization is likely to occur.

Now the solution is in a state where not all of the sugar can be solubilised. So the sugar goes out of solution and forms crystals. The saturation point (the maximum concentration of sugar in water without crystal formation) is influenced by the temperature of the solution. It is possible to cool an unsaturated solution to a state of supersaturation. And vice versa, it is possible to heat a supersaturated mixture to an unsaturated solution. When boiling the solution, water will evaporate and the sugars will get more concentrated. It is possible to supersaturate the boiling solution; this can be observed when crystals form in the solution while boiling. In most cases this is unwanted. Better results will be obtained when the boiling solution is kept unsaturated and subsequently cooled down to a supersaturated state. In crystallized candy, like fudge, a creamy texture is desirable. This creamy texture comes from the formation of tiny sugar crystals. So preparation of fudge needs to steer the crystallisation towards the formation of tiny crystals and avoid the growth of these crystals, because big crystals result in a grainy texture.

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FACTORS AFFECTING CRYSTALLIZATION OF SUGARS

In making icings, frostings, or candy like fondant and fudge, it is necessary to crystallize the sugar solution. For crystallization to occur, nuclei must form in the solution. To these nuclei the material of the solution is added to form crystals. Both the rate of formation of nuclei and the rate of crystallization are affected by the nature of the crystallizing substance, the concentration, the temperature, agitation, and the impurities present in the solution.

Nature of the crystallizing substance: Some substances like salt crystallize readily from water solution. It requires only a very slight super-saturation to start nuclear formation, and all excess salt in the solution beyond the saturation point is precipitated as crystals. Some substances do not form nuclei or crystallize so readily as salt. With sucrose it is often necessary to have a considerable degree of supersaturation before crystallization commences. Sucrose crystallizes more readily than levulose.

Formation of nuclei: Nuclei cannot form and crystallization cannot occur except from a supersaturated solution. The formation of nuclei, that is the uniting of atoms to form nuclei, is influenced by several factors. If a solution is left to stand, a few nuclei may form spontaneously in various places, and from these nuclei crystallization proceeds. When only a few nuclei develop spontaneously in the

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solution, the crystals grow to large size. Usually nuclei formation and crystallization do not begin immediately after supersaturation occurs. The rate of nuclear formation may be favored by specks of dust in the solution. Agitation or stirring of a solution increases the rate of nuclear formation. A drop in temperature at first favors, and then retards, the formation of nuclei. Instead of spontaneous formation of nuclei, seeding a solution may be used to start crystallization.

Seeding: When crystals of the same material are added to start crystallization the process is called seeding. These crystals serve as nuclei for crystal growth. If the quantity of crystals added is large and the size of the crystals small, it serves as many nuclei in the solution and the resulting crystals are small. If the quantity of material added is very small, the nuclei formed are few in number and the crystals formed are large. One may think of all crystals as being large enough to be visible, whereas many of them may be very small, so small in fact that they may float in the air. If crystals are floating in the air there is the possibility that they may serve to seed solutions, and thus start crystallization.

Rate of crystallization: To the nuclei formed in the solution new molecules from the solution are deposited, in a regular order or manner, so that each crystal has a typical shape. One side or face of a crystal may grow more rapidly than another. The rate at which the nuclei grow to larger size is called the rate of crystallization. This rate

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may be favored by the concentration of the solution and its temperature; it may be hindered by foreign substances.

Concentration of the solution: A more concentrated solution favors the formation of nuclei. Fondant syrup cooked to 114°C. Contains less water and is more concentrated than one cooked to 111°C. Thus nuclei form more readily in the one cooked to 114°C. Large, well-shaped crystals form more readily if the degree of supersaturation is not too great. The most favorable supersaturation for crystal growth, of a sucrose solution boiled to 112°C, is that between 70° and 90°C. Although crystallization occurs in a very short time when the syrup is stirred at these temperatures, the crystals formed are larger than when the syrup is cooled to a lower temperature. Supersaturation and a low temperature are desirable for the development of small crystals.

Temperature at which crystallization occurs: It is a well-known fact that, in general, chemical precipitates come down more coarsely crystalline if crystallized at high temperatures. The sugars follow this general rule. Other things being equal, i.e., concentration, etc., the higher the temperature at which crystal formation occurs, the coarser the crystals formed.

A drop in temperature at first favors the formation of nuclei, and then hinders it. Crystallization is favored in sugar syrups by cooling to a certain temperature, but is hindered when cooled to a lower temperature. Since the viscosity of a saturated sugar solution

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becomes increasingly greater as the temperature falls below 70°C, crystal formation is also slower as the temperature falls. Time and temperature of boiling

Agitation: Stirring a solution favors the formation of nuclei and hinders the depositing of the material of the solution on the nuclei already formed. Hence, crystals in solutions that are stirred do not develop to the size that they do in spontaneous crystallization. If small crystals are desired, then the conditions should be such that many nuclei are formed. Small crystals are obtained in syrups of definite concentration and temperature, if the syrup is stirred until the mass is kneadable. However, if the syrup is stirred for only a short time, some nuclei are formed, but after agitation is stopped, the formation of new nuclei is not favored and crystal growth is favored. This emphasizes the importance of stirring candy and icing syrups until practically all the material is crystallized, if small crystals are desired.

Impurities in the sugar syrup may also result in the formation large sugar crystals. Impurities promote premature crystal formation, which will grow to big unwanted crystals.

Interfering substances: Some products can be added prevent the formation and growth of crystals. These products such as cream, butter, egg white etc., are called interfering agents. The agents coat the crystals and prevent the growth of large crystals. Boiling the sugar syrup to the exact temperature is also very important, complete solution of the sugar is very important.

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Degree of inversion: Sweets containing high concentrations of sugar (sucrose) may crystallize either during manufacture or on storage (commonly referred to as graining). Although this may be desirable for certain products (such as fondant and fudge), in most other cases it is seen as a quality defect.

When a sugar solution is heated a certain percentage of sucrose breaks down into 'invert sugar'. This invert sugar inhibits sucrose crystallization and increases the overall concentration of sugars in the mixture. This natural process of inversion, however, makes it difficult to accurately assess the degree of invert sugar that will be produced. As a way of controlling the amount of inversion, certain ingredients, such as cream of tartar or citric acid, may be used. Such ingredients accelerate the breakdown of sucrose into invert sugar, and thereby increase the overall percentage of invert sugar in the solution. A more accurate method of ensuring the correct balance of invert sugar is to add glucose syrup, as this will directly increase the proportion of invert sugar in the mixture.

The amount of invert sugar in the sweet must be controlled, as too much may make the sweet prone to take up water from the air and become sticky. Too little invert sugar will be insufficient to prevent crystallization of the sucrose. About 10-15 per cent of invert sugar is the amount required to give a non-crystalline product.

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Added ingredients: The addition of certain ingredients can affect the temperature of boiling. For example, if liquid milk is used in the production of toffees, the moisture content of the mixture immediately increases, and will therefore require a longer boiling time in order to reach the desired moisture content.

Added ingredients also have an effect on the shelf-life of the sweet. Toffees, caramels, and fudges, which contain milk-solids and fat, have a higher viscosity, which controls crystallization. On the other hand, the use of fats may make the sweet prone to rancidity, and consequently the shelf-life will be shortened.

CRYSTALLIZED AND NON CRYSTALLIZED CANDIES

Chemically, sugar candies are broadly divided into two groups: crystalline candies and amorphous or non crystallized candies. *Crystalline candies* are not as hard as crystals of the mineral variety, but derive their name and their texture from their microscopically organized sugar structure, formed through a process of crystallization, which makes them easy to bite or cut into. Fudge, creams, and fondant are examples of crystalline candies. *Amorphous candies* have a disorganized crystalline structure. They usually have higher sugar concentrations, and the texture may be chewy, hard, or brittle. Hard candies, such as lollipops, caramels, nut brittles and toffees are all examples of amorphous candies, even though some of them are as hard as rocks and resemble crystals in their overall appearance.

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Crystalline candies are chemically described as having two phases, because the tiny, solid sugar crystals are suspended in a thick liquid solution. These are also called *grained* candies, because they can have a grainy texture. Amorphous candies are have only one phase, which is either solid or liquid, and do not have a grainy texture, so they may be called *ungrained*.

Commercially, candies are often divided into three groups, according to the amount of sugar they contain:

- 100% sugar (or nearly so), such as hard candies or creams
- 95% sugar or more, with up to 5% other ingredients, such as marshmallows or nougats, and
- 75 to 95% sugar, with 5 to 25% other ingredients, such as fudge or caramels.

Each of these three groups contains both crystalline (grained) and amorphous (ungrained) candies.

Preparation of Crystalline and Non Crystalline Candies:

Candy making is an exact science and an art, its success largely dependant on the knowledge of the science of sugar crystallization and timing. The goal in preparing soft, creamy and smooth textured crystalline candy is to develop numerous very fine nuclei in the sugar syrup solution. They are formed by: 1) controlling the form and content of the sugar; 2) controlling the temperature; and, 3) stirring

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correctly. As the solution cools, the sugar crystallizes into the proper size. If the nuclei appear slowly in the syrup solution, there is more time for the sugar molecules to aggregate around the nuclei and form large crystals.

STEP 1: Prepare the sugar solution

This step is basically the same for crystalline and noncrystalline candy. There are different ingredient (formulas) used depending upon the candy recipe. All sugar based candies, whether creamy or chewy or brittle, typically start out with crystalline sugar (sucrose), sometimes along with its close relative such as glucose or corn syrup (invert sugars), as its main ingredient. What determines the type of candy being made is done through the type and proportion of ingredients that make up the initial sugar solution.

Weighing ingredients is the most accurate way to measure solids, such as sugar, but it can also be measured in a dry measuring cup. Measuring liquids in a liquid measuring cup or weigh, preparing all equipment and tools in advance; keeping all pots and utensils spotless and dry and work surface is must. If using a buttered pan or mold at the end, always have it ready. Keep a container of ice water handy. Dissolve the sugar (a solute) in liquid, typically water (a solvent): and optionally mixed with other ingredients to create a sugar solution.

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The sugar and water ingredients are put into pot large enough so boiled sugar does not overflow and placed over medium heat. Stir the mixture constantly until the sugar is dissolved. If one tiny speck of a sugar crystal that hasn't been dissolved falls into the mixture during cooking, the whole batch will return to a solid state, ruining it.

Place the sugar in the pot by pouring it in the center. Mix the sugar and water together by drawing an "X" across the sugar, but avoid touching the sides with the sugar. Never stir solution after the sugar crystals are completely dissolved in the water and when it has started boiling - this will incite the formation of big crystals that will make a candy grainy when it cools. Ensuring all crystals are off the side of the pan could be done either oiling the sides or brushing sides of the pan with a heatproof brush dipped in water. Covering the pan during first few minute causes steam forms, condenses and then washes off the side of the pan.

STEP 2: Cook (boil) the sugar solution into a concentrated sugar syrup

Sucrose tolerates the high heat of boiling; after a sugar solution is formed, it can be heated and boiled to certain temperatures concentrating the solution as sugar syrup, whereby chemical changes or reactions in the sugar crystals take place. Depending on the candy being made, the syrup is boiled to a codified temperature, measured with a Candy Thermometer, and/or to

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the syrup's specific concentration indicated on the. Keep the temperature constant; never try to rush a candy mixture by cooking it at a higher temperature than the recipe directs, or slow it down by reducing the heat.

STEPS 3 AND 4: Cooling and beating (optional)

When done, the candy mixture is cooled by pouring its contents onto a marble slab, silpat mat or into a glass bowl or into a pan or mold to harden. (Do not scrape the bottom of the pan while removing its contents, unless specified.) Whether cooling and/or stirring the sugar syrup during cooking or afterwards is determined by the type of candy being made. Many of the non-crystalline candies are poured out of pan immediately after cooking. They harden quickly because they are made from highly dehydrated sugar syrups and any agitation or stirring will cause unwanted crystallization. For example, in the case of caramels and hard candy, such as lollipops, their finished cooked recipes are poured directly into their molds or pans, and left to cool.

Beat (Knead): When boiling stops and the cooling process starts, if everything is done right, the syrup continues to cool as a supersaturated solution and is able to get recrystallized, the size of which is also influenced by stirring, kneading or beating. Fudge is kneaded to break crystals into smaller pieces, making its texture smooth and creamy. As the syrup has been stirred, the candy will begin to lose its glossy appearance, becoming somewhat opaque and lighter in color. As crystallization proceeds, the candy will become much thicker and cease to flow. At this point, crystallization is complete and candy should be removed from the pan as

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quickly as possible and kneaded to dissolve lumps and the mass become creamy and shinny in appearance.

Shape and final cooling: After kneading, fudge is pressed into a pan and left to set. There are two main ways of forming sweets: cutting into pieces, or setting in molds. Molds may be as simple as greased and lined pans or those which make more complex impressions.

The table below outlines the processing stages for a selected range of confectionery items.

	<i>Mix ingredients</i>	<i>Boil</i>	<i>Cool</i>	<i>Beat</i>	<i>Form/set</i>
Hard-boiled sweets	*	*	*		*
Fondant	*	*	*	*	*
Toffees/caramels	*	*	*		*
Fudge	*	*	*	*	*
Jellies	*	*	*		*
Marshmallows	*	*	*	*	*

TYPES OF CRYSTALLINE AND NON CRYSTALLINE CANDIES

Hard candies and pulled candies: Hard candies (also called *boiled sweets*) are single-phase, amorphous sugar candies that are commonly made from a combination of sucrose and glucose syrups.^[1]

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They are typically about 98% or more solid sugar. They have a glassy, translucent appearance. Pulled candy, like rock or Brach's starlight mints, is a hard candy that has been pulled or stretched to incorporate air. This process makes the candy opaque.

Fondants: Fondant candy is a partly crystallized, two-phased sugar candy. It is about 88% sugar by weight, usually with much more sucrose than glucose. In making fondant, a stiff sugar paste is cooked to a high temperature, then carefully cooled and mechanically beaten to produce the desired texture.

Caramels and toffees: Caramels contain milk and are cooked to a lower temperature than most sugar candies; toffees are similar, but use less milk and are cooked hotter. In both cases, the milk protein causes these emulsified candies to hold their shapes and prevents the sugars from crystallizing. Their brown color is due to a Maillard reaction between the milk protein and the sugars.

Fudges: Fudges, which are made in a wide variety of flavors, are essentially two-phased, crystallized caramels, with a short texture (easily broken).^[1] Sugar crystals are formed either due to agitation or the addition of crystal seeds in the form of powdered sugar or crushed fondant candy. The texture depends on the number and size of sugar crystals, the fat content, and the dispersion of milk solids.

Nougats and marshmallows: Nougats and marshmallows are confectionery foams, full of air. In the final product, there is often as

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much air, or even more, than sugar; for marshmallows, a ratio of 5 parts air to two parts syrup by volume is typical. Chemically, they may be single-phase or two-phased. Marshmallows are stabilized by a colloid like gelatin. Compared to nougats, marshmallows have higher moisture content, are softer and more rubbery, and dry out more easily.

Jellies and gums: Jellies and gums are thick liquid sugar candies.^[1] Gums, such as wine gums, are drier than jellies. They are made from sugar syrup plus a gelling agent. They are cooked to the lowest temperature of all sugar candies and consequently have the highest water content of sugar candies, about 20 to 25% water. Their stiffness depends on the type and amount of gelling agent, the final concentration, the pH of the product, and other factors. The most popular forms of gelling agent are gelatin, agar-agar, starch, and pectin. These produce different effects.

Nut pastes: The most common nut paste candy is marzipan, which is an almond nut paste. Nut pastes are made by mixing crushed nuts with sugar syrup.

Panned candies: Panned candy is a category of candy that includes dragées and comfits.^[1] These candies are formed by coating nuts, preserved fruits, or other candies with either sugar or chocolate in a revolving pan.

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Pralines, truffles, and noisettes: There is significant variation among pralines, truffles, and noisettes. In general, they involve roasting nuts in a high-temperature sugar syrup, and then grinding the cooled result into a paste.

Lozenge pastes and cream pastes: Lozenge paste is a sugar candy made by combining fine sugar with a natural gum like gum arabic. The paste is stamped, cut, and dried until almost no water content remains. A cream paste may include gelatin and is not dried as completely.

