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Title of assignment	:	Mid Term
Title of course	:	Confectionary and Snack Foods
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Submission date	:	07-06-2021

Q1: FACTORS AFFECTING THE DEGREE OF CRYSTALLIZATION:

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.

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 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 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.

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 knead able. 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:

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 whites. 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.

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.

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.

Q2: ENZYMATIC BROWNING:

Enzymatic browning is a natural phenomenon that occurs widely in many fruits and vegetables. When fruits and vegetables are bruised, cut, peeled, diseased, or exposed to any abnormal conditions, they darken rapidly on exposure to air as a result of the formation of brown melanin from the oxidation of phenolic compounds. Polyphenol oxidase (PPO) present in most fruits and vegetables, and some seafood, is responsible for enzymatic browning. In addition to PPO, the presence of peroxidase, a similar oxidative enzyme, may initiate enzymatic browning of fruits and vegetables.

Polyphenols – main components in enzymatic browning:

Polyphenols, also called phenolic compounds, are group of chemical substances present in plants (fruits, vegetables) which play an important role during enzymatic browning, because they are substrates for the browning-enzymes.

Phenolic compounds are responsible for the color of many plants, such as apples, they are part of the taste and flavor of beverages (apple juice, tea), and are important anti-oxidants in plants.

Polyphenols are normally complex organic substances, which contain more than one phenol group (carbolic acid). Polyphenols can be divided into many different sub categories, such as anthocyanins (colors in fruits), flavonoids (Catechins, tannins in tea and wine) and non-flavonoids components (Gallic acid in tea leaves). Flavonoids are formed in plants from the aromatic amino acids phenylalanine and tyrosine. During food processing and storage many polyphenols are unstable due to the fact that they undergo chemical and biochemical reactions. The most important is enzymatic oxidation causing browning of vegetables, fruits. This reaction mostly occurs after cutting or other mechanical treatment of product due to breaking cells.

Polyphenol oxidase (PPO, phenolase):

Polyphenol oxidases are a class of enzymes that were first discovered in mushrooms and are widely distributed in nature. They appear to reside in the plastids and chloroplasts of plants, although freely existing in the cytoplasm of senescing or ripening plants. Polyphenol oxidase is thought to play an important role in the resistance of plants to microbial and viral infections and to adverse climatic conditions. Polyphenol oxidase also occurs in animals and is thought to increase disease resistance in insects and crustaceans. In the presence of oxygen from air, the enzyme catalyzes the first steps in the biochemical conversion of phenolics to produce quinones, which undergo further polymerization to yield dark, insoluble polymers referred to as melanin. These melanin form barriers and have antimicrobial properties which prevent the spread of infection or bruising in plant tissues. Plants, which exhibit comparably high resistance to climatic stress, have been shown to possess relatively higher polyphenol oxidase levels than susceptible varieties. Polyphenol oxidase catalyzes two basic reactions: hydroxylation and oxidation. Both reactions utilize molecular oxygen (air) as a co-substrate. The reaction is not only dependent on the presence of air, but also on the pH (acidity). The reaction does not occur at acid (pH <5) or alkaline (pH >8) conditions. An example of the formation of melanin from a simple polyphenol, tyrosine, is shown in the figure below:

