EFFECT OF ICE CRYSTAL SIZE ON THE TEXTURAL PROPERTIES OF ICE CREAM AND SORBET

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ABSTRACT

Coarsening of ice crystals adversely affects the texture and shelf life of frozen products. The addition of stabilizers offers a potential solution to this problem. The goals of this project were to examine the coarsening behavior and the impact of stabilizers in a variety of frozen products. Various techniques including fluorescence microscopy, differential scanning calorimetry, viscometry and hardness measurements were used to study the kinetics of coarsening. The results indicated that ice crystal size can change significantly during handling and as a result leads to variations in the hardness. The data suggested a mixed control kinetic mechanism for coarsening. The addition of stabilizers was found to generally reduce the coarsening rate.

ACKNOWLEDGEMENTS

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1.0 EXECUTIVE SUMMARY

Ice cream is one of most popular global dairy products. In 2010, the total global ice cream production was 16.3 billion liters. Asia Pacific had the largest ice cream production globally which was about 31% of the total global production in 2010, followed by North America (29%) and Western Europe (20%). In the same year, the revenue from ice cream and sorbet sales was worth US $8.9 billion. In countries like United States and Australia, take-home ice cream product occupies over 60% of the overall ice cream consumption (Goff et Hartel, 2013). Annually there is about US $740 million of loss in revenue in the ice cream industry mainly due to quality deterioration. And one of the major causes is recrystallization, which takes place because of temperature fluctuation during and between shipping, handling and storage in stores and at home. Hence, it is crucial for manufacturers to control recrystallization rate in ice cream. Otherwise, low quality and coarsened ice cream products would drive customers away and result in a decrease of revenue.

The goal of the project is to study coarsening of ice cream due to recrystallization. Additionally, since stabilizers have a significant impact on retarding recrystallization, the use of stabilizers in ice cream were also examined. Last but not least, the coarsening effects were studied in ice cream with and without stabilizers.

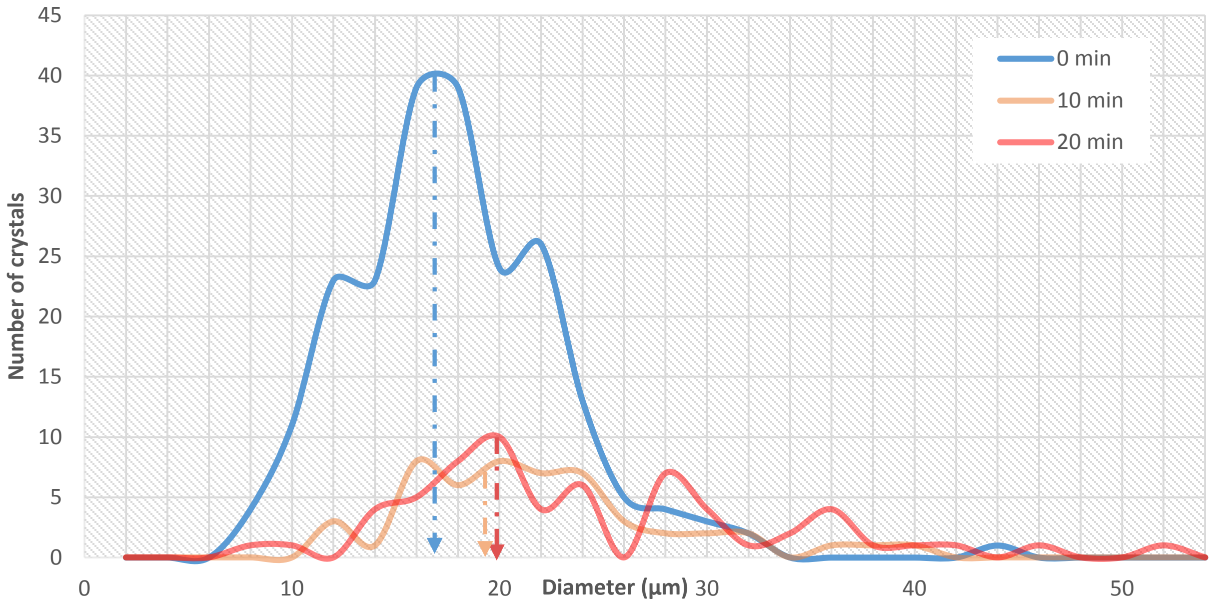

Figure 1. Ice crystal size distribution in ice cream for various recrystallization times. An initial sample (0 min) was obtained and left in the freezer. Subsequently, the sample was placed outside for the times indicated (hereon referred to as recrystallization time) and immediately placed in the freezer. It was taken out after 12 hr and tested immediately. The arrows indicate the mean in the distribution.

In this project Haagen-Dazs mango sorbet and a typical ice cream formulation as in numerous literature reviews were used for all the experiments. Coarsening of sorbet and ice cream crystals were observed through crystal size and distribution graphs. Figure 1 above shows that the crystal distribution shifts to the right and becomes more widespread for longer time intervals, which indicates a larger weighted average crystal size and a higher number of large crystals over time. Besides, coarsening increases hardness of sorbet and ice cream, since hardness is proportional to the number of large crystals as shown in Figure 2. The peak force for sorbet over time intervals 0, 10, and 20 minutes are 5.1 N, 8.6 N, and 14.9 N respectively, which demonstrates that hardness increases over longer time intervals.

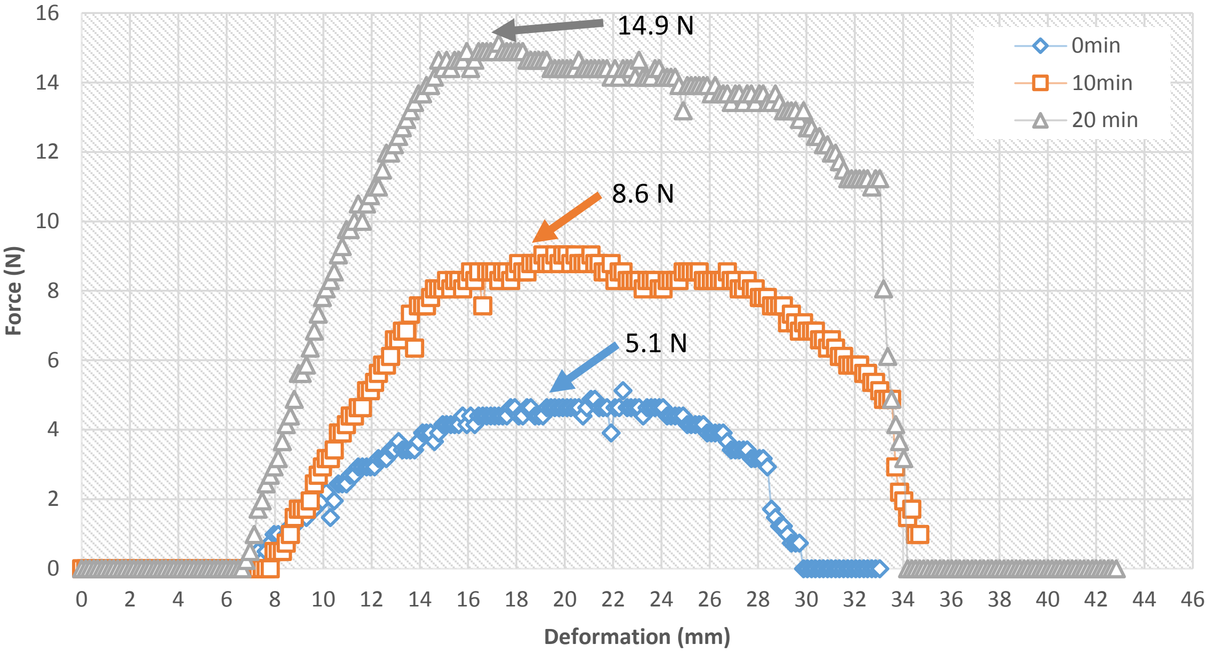

Figure 2. Hardness of sorbet for various recrystallization times. The arrows indicate the peak force or the hardness of sorbet.

Coarsening of ice cream was studied with the kinetic equation below.

$$\bar{R}^n - \bar{R}_o^n = k * t \tag{1}$$

The crystal size data fit both n values of 2 and 3 (Figure 3). However, the data has large standard deviations, due to the unhomogenized nature of the ice cream mix, the impure stabilizers, as well as the temperature and humidity fluctuations during the experiments. Therefore, further experiments should be conducted to confirm the dominant kinetic mechanism for this particular ice cream.

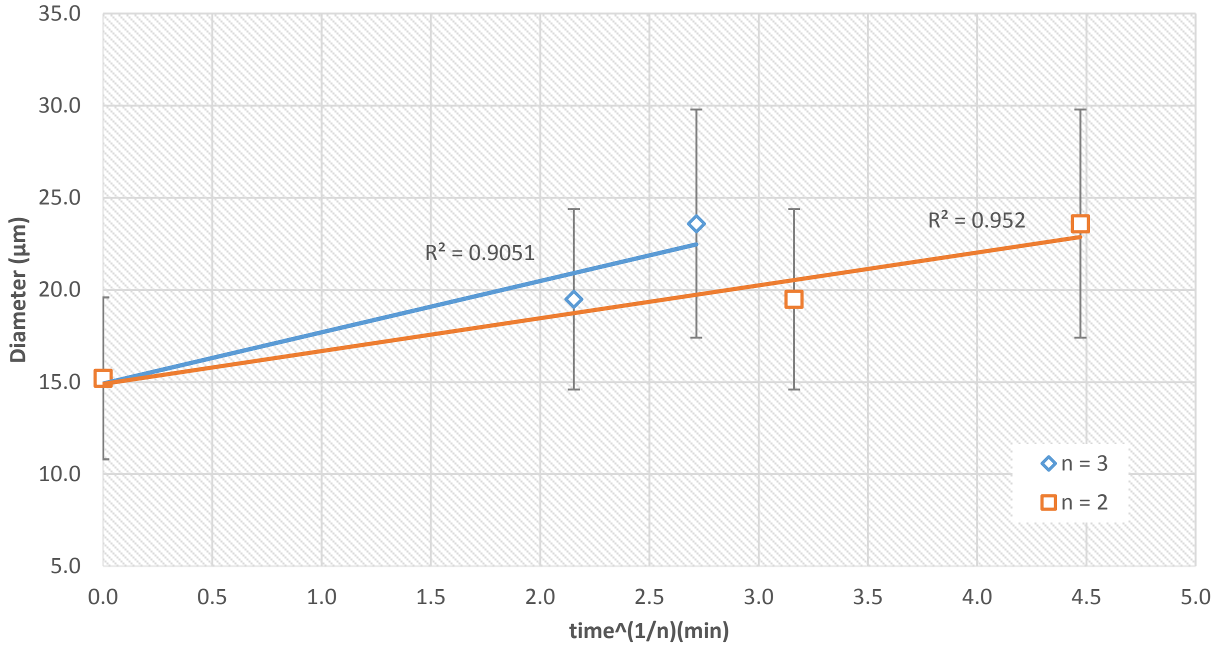

Figure 3. Kinetic models for ice cream, where n = 2 represents interface surface energy kinetics and n = 3 represents diffusion kinetics.

In order to reduce the coarsening effects in sorbet and especially in ice cream, a combination of locust bean gum and guar gum stabilizers was added into the ice cream formulation. Stabilizers reduce the growth rate of ice crystals over time by increasing the viscosity of the ice cream mixture. Viscometry experiments yield that the higher the stabilizers concentration, the higher the ice cream viscosity (Table 1).

Table 1. Viscosity measurements of ice cream with and without stabilizers at a constant shear rate of 50 RPM.

	Viscosity (mPa·s)
0.00% stabilized ice cream	22.0 ± 5.0
0.05% stabilized ice cream	52.2 ± 13.3
0.10% stabilized ice cream	68.9 ± 10.0
0.15% stabilized ice cream	108.3 ± 6.0

However, due to the low quality of stabilizers as well as the lack of controls in conducted experiments, stabilizers increase the initial crystal size. Addition of stabilizers also result in a higher weighted averaged crystal size over time compared to unstabilized ice cream. Hardness of stabilized ice cream was found to be higher than that of unstabilized ice cream, indicating that there are a larger number of large crystals in ice cream with stabilizers. Differential scanning calorimetry experiment also shows that at higher concentrations of stabilizers, the crystallinity increases (Table 2).

Table 2. Heat of fusion and crystallinity of unstabilized and stabilized ice cream.

	Heat of fusion (J/g)	Crystallinity (%)
0.00% stabilized ice cream	80.11	27
0.05% stabilized ice cream	91.43	31
0.10% stabilized ice cream	101.7	35
0.15% stabilized ice cream	139.8	48

Overall, coarsening of sorbet and ice cream increases over time due to a larger weighted average crystal size. As a result, hardness also increases for longer time intervals. In order to reduce the coarsening effects of ice cream, a combination of locust bean gum and guar gum stabilizers was added to the ice cream. However, the addition of stabilizers increases the initial crystal size mainly due to the unhomogenized ice cream mix, impure stabilizers and lack of controls in the conducted experiments. Besides, hardness of stabilized ice cream is higher than that of unstabilized ice cream, indicating that there are a larger number of large crystals. The higher crystallinity of stabilized ice cream further confirms the indicated trend. Therefore, future experiments should be conducted in a more controlled environment and with better-equipped instruments. Specifically the fluorescence microscopy should be equipped with a cold stage for more accurate data. An industrial blender is required to obtain a homogenized ice cream mix. In addition, the quality of ice cream ingredients, especially stabilizers, should be ensured.

2.0 OBJECTIVES

Since coarsening is currently a significant problem in ice cream industry leading to a big loss on sales and customer satisfaction, the project focused on three objectives: develop methodologies to study coarsening of ice cream, examine coarsening in a variety of frozen food products including sorbet and ice cream, and study the effects of coarsening on hardness and texture of ice cream.

3.0 BACKGROUND REVIEW

3.1. OVERVIEW OF ICE CREAM INDUSTRY

Ice cream is one of the most popular global dairy products. In 2010, the total global ice cream production was 16.3 billion liters. Asia Pacific had the largest ice cream production globally which was about 31% of the total global production in 2010, followed by North America (29%) and Western Europe (20%). In the same year, the revenue from ice cream and sorbet sales was worth US $8.9. Moreover, Italy had the highest expenditure for ice cream of US $113 per capita, while US had an ice cream expenditure of US $50 per capita in 2010. The data from Euromonitor International in 2011 demonstrated that the world ice cream production has been increasing slightly every year; the average growth of product from 2006 to 2010 was about 1.56% per year. Furthermore, the take-home ice cream consumption in the global market has been shrinking since 2006. In countries like United States and Australia, take-home ice cream product occupies over 60% over the overall ice cream consumption (Goff et Hartel, 2013). Since take-home market takes up a significant portion of the American, European and Australian market, it is critical for ice cream companies to manufacture products that retain their maximum quality when the customers bring home their products. The main reason of ice cream quality deterioration is recrystallization. The outcome of recrystallization is the coarsening of ice cream, which makes ice cream icy and undesirable. Further information about the mechanism of recrystallization is presented in later sections of the paper. As a result, it is important to investigate recrystallization and find a way to slow down the process so that customers can get the best quality products possible. This can help ice cream companies to maintain their customer with the declining clientele that they are facing. But first of all, it is necessary to introduce what ice cream is made of and it will lay out a platform to understand how recrystallization affects ice cream quality.

3.2 ICE CREAM STRUCTURE

Ice cream consists of water, air, sugar, milk fat, milk-solid-non-fat, sugar/sweeteners, stabilizer, emulsifier and flavoring agents (Goff & Hartel, 2013). A typical composition of ice cream consists of about 30% ice, 5% fat, 15% matrix and 50% air by volume; the concentrations of ingredients above vary for different ice cream brands and countries. Below is a table showing the weight component of different ingredients in a typical ice cream. The ingredients in ice cream exist in three states: fat and ice crystals as solid, matrix as liquid and air as gas. The ice crystals, fat droplets and air bubbles are dispersed in the continuous matrix phase that is made of stabilizer, sugar and protein suspensions (Clark, 2013).

Table 3. Formulation of a typical ice cream

Ingredient	Amount (% weight)
Milk Protein	4 – 5 %
Fat	7 – 15 %
Sugars	17 – 23 %
Water	60 – 72 %
Emulsifier & Stabilizer	0.5 %

3.2.1 MILK PROTEIN

The two major functions of milk protein are the stabilization of water-continuous emulsion and foams, as well as the contribution to the unique flavor of ice cream. The sources of milk protein are milk, skimmed milk powder, whey powders and buttermilk. Casein and whey protein are two kinds of milk protein and they respectively make up 80% and 20% of the whole protein structure. Caseins are surface-active colloidal proteins that contain both hydrophilic and hydrophobic ends, allowing them to form micelles. Whey proteins are globular and also surface-active. They are around 3-6 nm while caseins are approximately 100 nm. They have a critical function in stabilizing and forming air pockets in ice cream (Clark, 2013).

3.2.2 FATS

Fats have a critical role in stabilizing air bubbles in ice cream, contributing to the creamy texture and flavor, as well as slowing down the melting rate of ice cream. Typical commercial ice cream has a fat content of about 8-10% and the fat content of some premium ice cream can reach as high as 15-20%. The main sources of fat for ice cream manufacturing are cream and vegetable fat. Milk fat is the most common fat that is present in ice cream. They are about 0.1 – 10 µm in size and mostly in solid phase between -5°C and 5°C.

3.2.3 SUGARS

The purposes of sugar are to sweeten and control the hardness of ice cream (i.e. the higher the sugar content, the lower ice content, and the softer the ice cream). Sugar depresses the freezing point of the ice cream mix and hence lowers the amount of ice crystals in ice cream production. Sugar also increases the viscosity of the ice cream matrix; the higher the degree of polymerization of sugar is, the more viscous the matrix is. The sensation of creaminess is correlated with higher viscosity of ice cream; however, higher viscosity causes stickiness and difficulty in scooping ice cream. The common examples of sugars used in ice cream are dextrose, sucrose, fructose, lactose, corn syrup and sugar alcohol (Clark, 2013).

3.2.4 ICE CRYSTAL AND WATER

Ice cream has water content of about 60-72 weight %. During ice cream production, the majority of water is converted to ice crystals (Clark, 2013). The average size range of ice crystal is 20 -55 µm and the size range varies with different formulations of ice cream (Hagiwara & Hartel, 1995).

3.2.5 EMULSIFIER

Emulsifier is another surface-active component found in ice cream. Its function is to de-emulsify a portion of fat to help the stabilization of air pockets during ice cream production. The most common emulsifier in the industry is mono-/diglycerides. Another source of emulsifier is egg yolk. The surface active properties of mono-/diglycerides come from the hydrophilic head and hydrophobic end of the molecule. The sources of mono-/diglycerides are from the hydrogenation of vegetable fats such as palm oils and soybean oils (Clark, 2013).

3.2.6 STABILIZERS

The advantages of using stabilizers are to enhance smoothness of ice cream, slow down melting rate, prevent shrinkage of ice cream due to loss of moisture, disguise the detection of ice crystal in ice cream and stabilize the foam structure of ice cream. Stabilizers are water-soluble polymers that contain hydroxyl functional groups. They usually have a degree of polymerization of about 1000 and molecular weight of approximately $10^5 - 10^6$ g/mol. They are able to produce high viscosity even at a small concentration (typically around 0.2%). Furthermore, stabilizers have a synergistic property where their effectiveness in ice crystal growth retardation can be enhanced by combining two different stabilizers. Some common stabilizers are locust bean gum, guar gum, xanthan and carrageenan (Clark, 2013).Figure 1 below shows the appearance of different components in ice cream under a microscope. The air bubbles are the largest particles within ice cream and they are round in shape. On the other hand, the outlines of the ice crystals are definite, which is a characteristic of crystalline matters. Fat globule have relatively smaller size compared to the size of air pockets and ice crystals. The space between all the solids are the continuous phase, which is the matrix of ice cream.

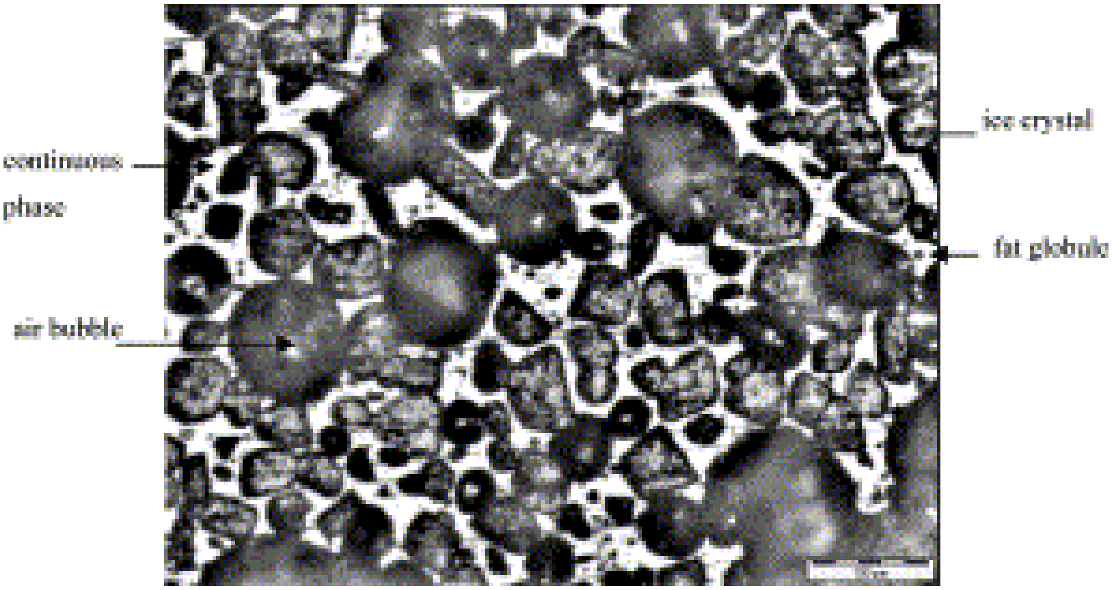

Figure 4. Ice cream composition (Caillet et. al, 2003).

3.3 ICE CREAM MECHANISM

3.3.1 CRYSTALLIZATION KINETICS

In order to produce the smoothness texture in ice cream, it is important to control the amount and size of ice crystals in ice cream during initial freezing as well as storage and distribution process. Crystallization is the process at which ice crystals form on the wall of a scraped-surface freezer. During ice crystallization, proper preparation and control of ice cream solution can maximize the shelf life of ice cream. In the ice cream industry, a scraped-surface freezer with ammonia vaporizing on the outside of the freezer barrel is often used, providing the means for small crystals to form. The scraper blades need to remain sharp every time a new batch of ice cream is produced, and they must touch the inner surface of the freezer evenly in order to produce consistently small crystals. The newly-formed crystals at the wall are believed to disperse into the center of the barrel thanks to the rotation of the blades, as shown in Figure 1. At a higher temperature than the freezer wall, the center of the barrel is where ice crystals start to grow and ripen. The formation or nucleation of ice crystals at the freezer wall is due to the large temperature driving force there. Based on the temperature difference between the ammonia blanket and the thickness of the ice layer on the inner surface, there is an approximate temperature gradient of 20 to 25°C at the wall (Hartel, 1996). Since ice cream is such a complex material, and changing one factor during the freezing step affects several properties of the mix, the exact nucleation mechanism has not been confirmed. However, there have been many speculated hypotheses regarding this process.

According to Schwartzberg (1990) research, ice nucleation favors formation at the wall due to its heterogeneous mechanism. The crystals formed then grow towards the center of the freezer in the shape of dendrites. Due to the large temperature difference between the newly formed crystals and the center solution, the dendrites cool the mix and ripen into crystals. Another theory on the formation of initial crystals is based on heterogeneous nucleation on foreign particles such as dust or suspended solids in the mix. In other words, the formation of the nuclei is due to such foreign particles and not the large temperature driving force, as described above. Lastly, secondary nucleation is also suggested as a potential mechanism inside the freezer barrel, even though no detailed experiment or study has been conducted to prove the contribution of such mechanism. According to secondary nucleation theory, the initially-formed crystals collide with nearby crystals or the agitator, which leads to the generation of new nuclei through contact.

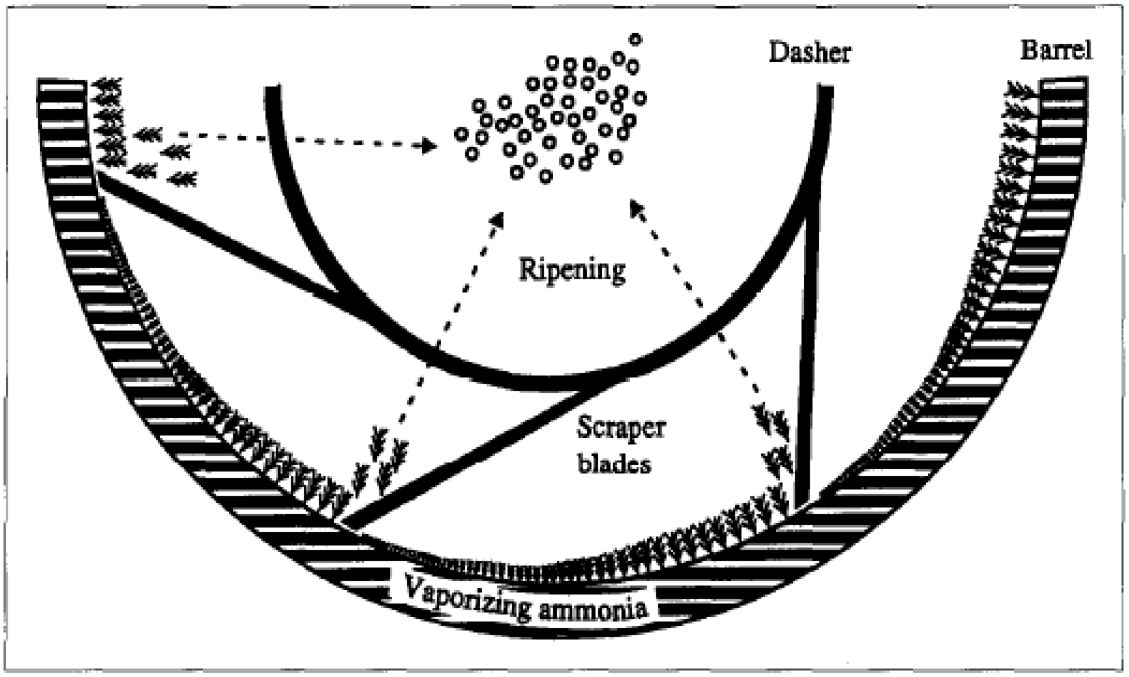

Figure 5. Schematic of a scrap-surface freezer (Hartel, 1996).

After the initial freezing step, when the ice cream mix leaves the freezer at approximately -5°C to -6°C for packaging, about half of the water in the solution is frozen (Berger, 1990; Arbuckle, 1986). During the next step, hardening, there is no new crystal formed but only the growth of the existing ice crystals. Often the hardening temperature remains low, about -18°C, in order to lower the crystal growth rate. The mean crystal size at this step is reported to be approximately 45 to 50 µm, increasing slightly from the mean crystal size during initial freezing, 30 – 35 µm (Berger, 1990; Donhowe, Hartel, & Bradley, 1991). Even though the hardening temperature remains low, the glass transition temperature of ice cream is generally lower. Therefore, the amount of frozen water at this stage is still only 75 to 80%. Further development of ice crystals in the ice cream solution in the next stage, storage and distribution, is discussed below in the recrystallization section. Because of the complicated mechanism of crystallization and its strong effect on the final texture of ice cream, it is essential to control the nucleation and growth rate of ice crystals that are depicted in Figure 3 from Hartel (1996) research.

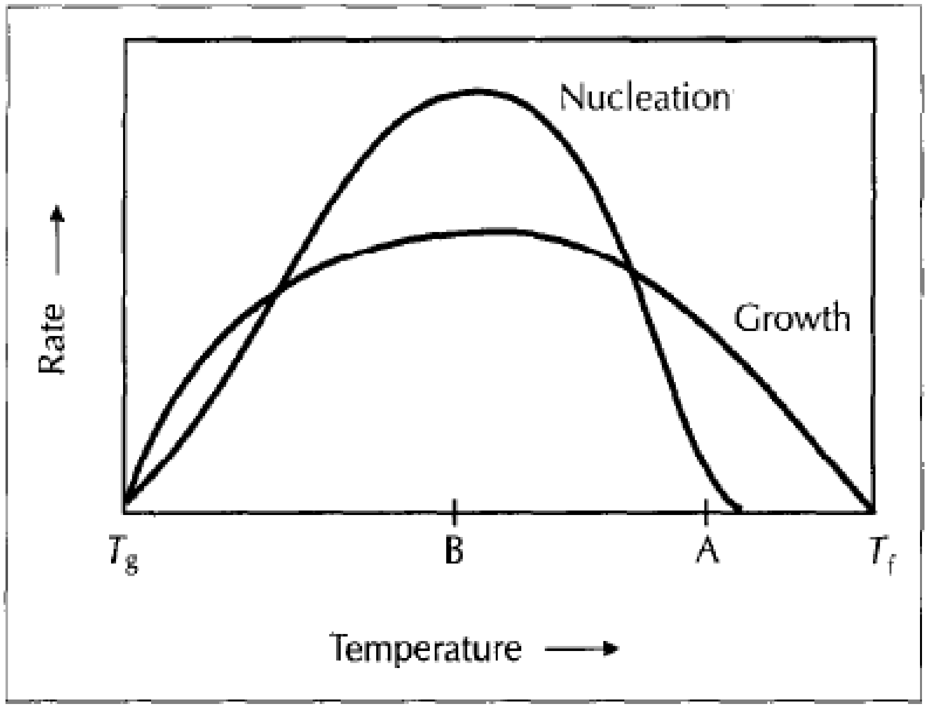

Figure 6. Relationship between nucleation and growth rate over a range of temperature (Hartel, 1996).

At temperature nearby the freezing point (T_f), the rates increase. However, the increasing viscosity of the ice cream mix decrease both rates as temperature approaches glass transition temperature T_g. From the kinetic curves, there are two potential processes at which ice crystallization could occur, nucleation and growth. If the ice cream mix temperature is lowered rapidly to that at point B on the graph, there should be more crystals formed inside the barrel. In comparison, if the mix temperature is lowered slowly to that at point A, fewer crystals would form. Once hardened, the ice phase volume is expected to be the same between two processes. However, the former process would result in more crystals, and therefore they would have smaller size, leading to a better texture for ice cream. Due to the inadequacy of equipment and process controls, homemade ice cream would most likely follow the latter path to point A, whereas the industrial process should lead to point B.

Formulation and process conditions are the two most significant factors that affect ice crystallization. As mentioned in the earlier section of ice cream structure, water content or total solids in the ice cream plays a significant role in the final ice crystal size. The lower the amount of water in the mix, the smaller the ice crystal size would be. Sweetener concentration has the opposite relationship with ice crystal size: a higher concentration of sweetener is preferred, since it alters the freezing point depression and the glass transition temperature of the ice cream (Hartel, 1996). Similar with sweetener, a higher amount of MSNF would result in a decrease in averaged ice crystal size. Emulsifiers have little effect on ice crystals, whereas stabilizers play a major role in the retardation of ice crystal growth rates. As stabilizers increase the viscosity of the ice cream mix, the diffusion rate of ice crystals in the solution is lowered. Among all the potential process conditions that affect ice crystallization process, the draw temperature of the ice cream freezer is the most important. As a measure of the amount of heat removal, the draw temperature is different for each freezer type. It is also dependent on various factors including ammonia temperature, overall heat transfer coefficient between ice cream and ammonia, and the throughput rate (Hartel, 1996). Therefore, it is essential for the industry to have proper control of the ice cream initial freezing step, since it has tremendous effects on the quality of the final product.

3.3.2 RECRYSTALLIZATION KINETICS

During storage and distribution, ice crystal size increases due to recrystallization phenomenon and thus gives ice cream a coarsening texture. Therefore, it is important to minimize the ice crystal size in order to increase ice cream shelf life. There are many factors that would result in a larger crystal size including low solids, low freezing point, high draw temperature, slow hardening, inadequate stabilizer, etc., among which the group has chosen to focus on the use of stabilizers to minimize the rate of recrystallization (Goff & Hartel, 2013).

The average threshold size of ice crystals has been reported to be from 20 to 55 µm depending on the ice cream formulation and storage conditions, above which the sensory gland can pick up the coarse and grainy texture of ice cream. More important than the average crystal size is the uniform distribution of many small crystals, since it helps minimize the influence of thermal shock from fluctuating storage temperature and enhance shelf-life (Hagiwara & Hartel, 1995).

Recrystallization is defined as "any change in number, size, shape, orientation or perfection of crystals (grains) following completion of initial solidification" (Fennema, 1973). The thermal driving force for recrystallization includes the completion of phase equilibration and the slight difference in melting points of very small and large crystals: "the fine dispersion of small ice crystals in freshly made ice cream moves towards a lower energy state where surface energy is minimized through melting of small crystals and growth of large ones" (Goff & Hartel, 2013). Even though temperature fluctuations promote recrystallization, the rate of recrystallization is still affected at constant storage temperature. As stated by Goff and Hartel (2013), the fundamental driving force for ice crystal ripening is expressed by Kelvin or Gibbs-Thomson equation, which defines the effect of curvature on equilibrium temperature.

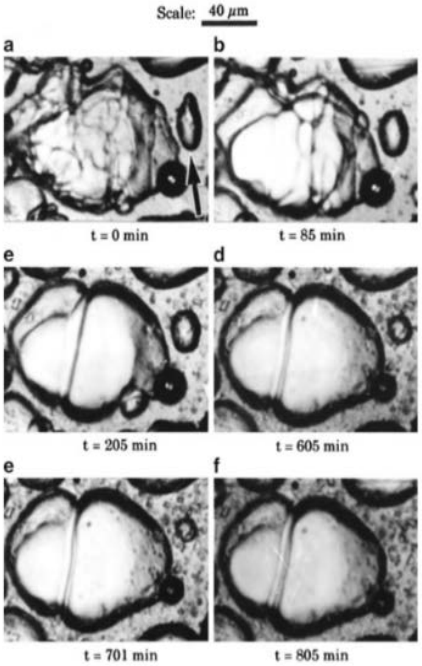

Figure 7. Ostwald ripening of a small crystal during hold at -10 ± 0.01°C on a microscope stage (Donhowe, 1993; Hartel, 1998).

$$\Delta T = T_\infty - T(r) = \frac{2\sigma T_\infty}{\rho(\Delta H_r)r} \qquad (2)$$

In the above equation, ΔT represents the difference in melting temperature for a crystal of infinite size with a flat surface and crystal of size r, T(r), σ is the interfacial tension at the crystal surface, ρ is the crystal density, and ΔH_r is the latent heat of fusion. Radius of curvature is defined as the radius of a circle that fits within the surface curvature. Small crystals have a sharply curved surface and thus a lower radius of curvature compared to larger crystals that have flat surfaces. Therefore, small crystals melt while large crystals grow with rates that are dependent on the radius of curvature and storage temperature. In other words, an increase in the size of large crystals is favored thermodynamically at the expense of smaller crystals.

Ostwald ripening is the most important among all mechanisms of recrystallization. Ostwald ripening, also known as migratory recrystallization, is defined as the process at which a small ice crystal melts away as a large neighboring crystal grows, as described in the equation above. The transfer of individual molecules from smaller to larger crystals by diffusion through the continuous phase is augmented by temperature fluctuations. According to the equation, as ice crystal size (r) decreases, the thermodynamic driving force (ΔT) increases. Figure 4 shows the Ostwald ripening process for the small ice crystal in the vicinity of larger crystals. As mentioned before, fluctuating temperatures enhance this process. Another form of recrystallization is isomass rounding, which occurs rapidly at warm storage temperature (Goff & Hartel, 2013). Isomass rounding refers to any change in the surface of an individual crystal as it moves to a lower energy level, as defined by Yoseph and Hartel (1998). Figure 5 below exhibits the change of an ice crystal undergoing the isomass rounding.

Accretion is another mechanism of recrystallization. Accretion refers to the joining of two individual ice crystals, whose driving force is the point of contact. It has a high surface energy that drives material to transfer to that area. Although accretion rate is significantly faster than Ostwald ripening, the latter has an immense impact on the ice crystal distribution over time that would inherently affect the overall texture of the ice cream.

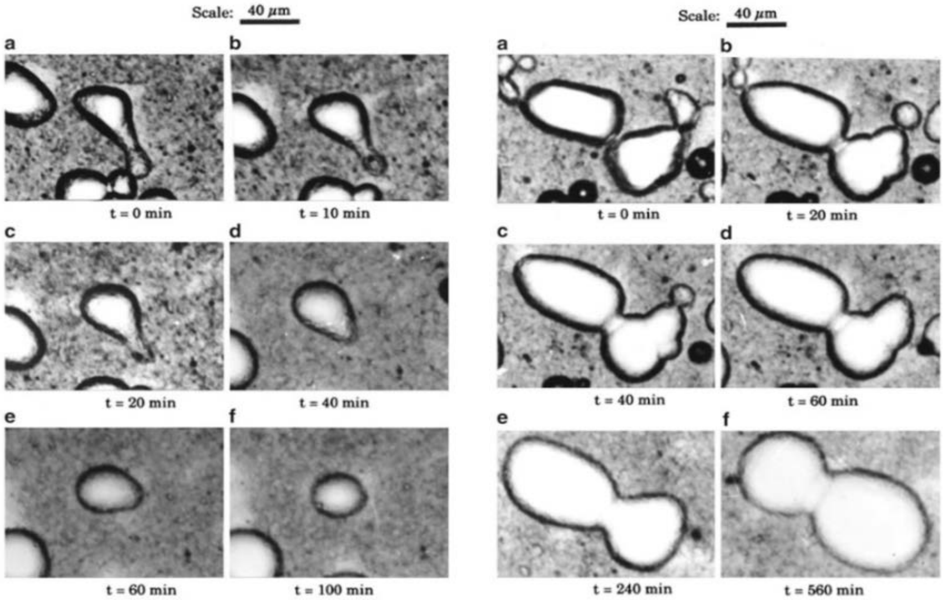

Figure 8. Isomass rounding and accretion phenomenon of crystals during hold at -5 ± 0.01°C on a microstage (Donhowe, 1993; Hartel, 1998).

The increase in average crystal size over time is summarized in the following formula by Lifshitz and Slyozov,

$$\bar{R}^n - \bar{R}_o^n = kt \qquad (1)$$

in which $\bar{R}$ represents the average crystal size at a specific time t, $\overline{R_o}$ the average initial ice crystal size, and k_1 the recrystallization rate. The crystal size is expected to be directly proportional to the nth root of time. If n is equivalent with 3, the coarsening mechanism of ice crystals is largely dependent on the diffusion kinetics of crystals in the ice cream mix. However, if n has a value of 2, the coarsening mechanism then is affected by the interface surface kinetics. In the case where n falls in the region between 2 and 3, the coarsening mechanism follows both diffusion and interface surface kinetics and therefore is mix controlled. Rarely if n value is outside of the region 2 to 3, the kinetics of the ice cream mix would then depend on a different factor that would require further investigation to figure out.

Martino and Zaritzky (1987) offer a mechanism known as melt-refreeze recrystallization. As the temperature increases during the melting process, large crystals start decreasing in size while small crystals may melt completely as in isomass rounding. When the temperature decreases, no new crystals would form since nucleation only occurs during the initial freezing stage of ice cream. While the driving force for recrystallization is slower at this time, the crystals continue growing to larger sizes. Overall, the larger crystals continue to grow and merge as smaller crystals melt and disappear. During ice cream distribution and many melt-refreeze cycles at home refrigerators, the ice cream undergoes temperature changes that result in an overall increase in ice crystal size and a decrease in the total number of crystals.

3.3.3 DIFFUSION KINETICS

Since ice cream is a very "complex systems consisting of air cells, ice crystals, fat globules partially coalesced or aggregated, surrounded by a sugar, protein, salts and water matrix," it is very difficult to [i]understand thoroughly the diffusion mechanism of ice cream solution (Pintor & Totosaus, 2012). Quantitatively the diffusion kinetics is best described by Williams-Landel-Ferry (WLF) equation,

$$log_{10}\left(\frac{\frac{\eta}{\rho T}}{\frac{\eta_g}{\rho_g {T_g}'}}\right) = -\frac{C_1\left(T - {T_g}'\right)}{C_2 + (T - {T_g}')} \tag{3}$$

where η is viscosity, ρ is density, C_1 and C_2 are constants, the subscript g refers to the glass transition, T_g' substitutes the conventional glass transition temperature (T_g) of polymer systems, and T is in K. The universal constants' of C_1 = 17.44 and C_2 = 51.6 were shown to fit the viscosity of concentrated sucrose and fructose solutions (Soesanto & Williams, 1981).

The glass transition refers to a change in state from a glassy solid to a rubbery viscous liquid. At low temperature, ice crystal growth is greatly impaired by low mas transfer rate due to the high viscosity of the unfrozen solution. Therefore, recrystallization rate is the slowest and essentially negligible when the ice cream is ideally stored below the glass transition temperature, T_g', according to Pintor and Totosaus (2012). However, Levin and Slade (1989) determined the glass transition temperature for commercial ice cream to range from -27 to -41°C; storing ice cream at such low temperature would be uneconomical and would produce a substantial amount of greenhouse gases. Since diffusion rate is inversely proportional to the viscosity, it is important to formulate a sufficiently viscous ice cream mix solution with the aid of stabilizers. As seen in the above equation, the rate of diffusion increases rapidly with increases in temperature or concentration of water. Hence, Ostwald ripening mechanism would happen more quickly with lower solids in the ice cream mix and higher storage temperature. Furthermore, the glass transition temperature decreases with the inverse of the weight-average molecular weight of the solution, which means an increase in water content of the ice cream mix would result in a depression effect for T_g'. In other words, there is a greater decrease in viscosity as temperature increases than predicted in WLF equation.

3.4 EFFECTS AND DEFECTS OF STABILIZERS ON ICE CREAM

Stabilizers are one of the most important factors that influence the texture of ice cream despite the low concentration in the formulation. One of its significant effects is to reduce or retard the coarsening rate in ice cream. Stabilizers are also known as colloids, hydrocolloids and gums. These materials are macromolecules, mostly polysaccharides, and they are capable of interacting with water.

Stabilizers used in ice cream must have a clean, neutral flavor that does not impart off ice cream flavors. The type and amount of stabilizer in ice cream depend on its properties, mix composition and ingredients used, as well as processing times, temperature, and pressure. Storage time and temperature are also considered when choosing stabilizer. 0.1-0.5% is usually used in the ice cream mix (Bahramparvar & Tehrani, 2011).

Using stabilizers in ice cream produces smoothness in body and texture, retards or reduces ice and lactose crystal growth during storage, provides uniformity to the product, and increases in viscosity of ice cream mix, slows down moisture migration from the product to the package on the air and prevents shrinkage of the product volume during storage.

3.4.1 RHEOLOGY

Rheology is the study of flow and deformation of materials under applied forces. One of the main rheology measurements in ice cream mix is viscosity, a measure of a fluid's ability to resist gradual deformation by shear or tensile stresses. Viscosity is affected by composition of ice cream mix, especially the stabilizer content and level. Ice cream behaves as a non-Newtonian pseudoplastic fluid, meaning that its apparent viscosity decreases with increasing shear rate. The relationship between shear rate and shear stress is nonlinear, as shown in the power law model below:

$$\tau = K\dot{\gamma}^n \tag{4}$$

where τ the shear stress (Pa), K is is the consistency index (Pa.s^n), $\dot{\gamma}$ is the shear rate (s^{-1}) and n is the flow behavior index. The values of K and n define the flow characteristics of fluid foods such as ice cream. The smaller the n value, the greater ice cream departs from Newtonian behavior, leading to greater pseudoplasticity. As shown in previous studies, the pseudoplasticity increases (n value decreases) as the concentration increases and as the temperature decreases. According to Bahramparvar and Tehrani (2011), the consistency index, a measure of the viscous nature of food, increases with stabilizer concentration. As a results, ice cream with more stabilizer bind the mobility and diffusion rate of ice crystals, leading to a smaller number of large crystals in ice cream.

3.4.2 OVERRUN

Overrun is the percentage increase in volume of ice cream, which is greater than the amount of mix used to produce that ice cream, as shown in formula below:

$$Overrun\ (\%) = \frac{weight\ of\ the\ ice\ cream\ mix - weight\ of\ the\ ice\ cream}{weight\ of\ te\ ice\ cream\ mix} \tag{5}$$

In other words, overrun refers to the amount of air that is whipped into the ice cream mixture. A churning or mixing process during the freezing stage traps air within the liquid and produces the creamy, airy texture. The amount of air incorporated into the mix changes the eating attributes of the ice cream. If a lower amount of air is used, the resulting ice cream is dense, heavy and colder. If a higher amount is used, the texture becomes light, creamy and a bit warmer. Furthermore, the air cell structure influences melting rate, and shape retention during meltdown.

Stabilizers help increase ice cream volume by increasing viscosity and stabilizing air bubbles. Changes in air cell size during storage due to three mechanisms: disproportionation (Ostwald ripening), coalescence and drainage. Addition of stabilizer increases viscosity of serum phase, thus, inhibits disproportion of air cells, air cell coarsening, as well as retard drainage during storage of ice cream (Bahramparvar & Tehrani, 2011). As a result, ice cream containing stabilizer also has smaller air cell size compared to the ice cream mix without stabilizer, improving the texture of ice cream.

3.4.3 THERMODYNAMIC PROPERTIES

Differential scanning calorimeter (DSC) is applied to determine glass transition temperatures and heat involved in thermal transitions. Thermodynamic properties such as glass transition, heat capacity and ice content could be determined from DSC. Stabilizers provide resistance to thermal deformation and affect the thermal conductivity values. Previous articles demonstrated that with the increasing concentration of stabilizer, heat of fusion decreases due to the water binding ability of stabilizer (Bahramparvar & Tehrani, 2011).

3.4.4 CRYOPROTECTION

Even though stabilizers have no effects on the initial ice crystal size distribution in ice cream when it was first taken out from the scraped surface heat exchanger or the initial ice growth during freezing and hardening, they reduce the growth rate of ice crystals during recrystallization through three mechanisms: viscosity and molecular mobility, cryo-gel formation and hydrocolloid phase separation.

Addition of stabilizers in ice cream mix increases viscosity through controlling ice crystals growth. However, the definitive correlation between viscosity and recrystallization of the mix has not been found. Budiaman and Fennema (1987) stated that for any given stabilizer, the linear rate of water crystallization decreases with increasing viscosity. However, each stabilizer has a different rate, so viscosity is not a good predictor of the capacity of a stabilizer in inhibiting crystallization. In other words, mix viscosity does not correlate well with stabilizer effects. At the same level of viscosity, different stabilizers are unequally effective for retarding ice crystal growth. However, at least some aspects of stabilizer functionality with respect to recrystallization protection come from the increased viscoelasticity that results from freeze-concentration of the polysaccharide in the unfrozen phase of ice cream. It is perhaps due to hyper-entanglements and solution structure formation. This concept was related to the rate at which water can diffuse to the surface of a growing crystal during temperature fluctuation or the rate at which solutes and macromolecules can diffuse away from the surface of a growing ice crystal. Thus, studying the relationship between water mobility in freeze-concentrated matrix and recrystallization rate is suggested in order to gain better understanding the mechanism of stabilizer in controlling the ice recrystallization.

The capacity to form cryo-gels of stabilizers as a result of heat shock during storage is the second mechanism of stabilizer action. The cryo-gel structure restricts the diffusion of water and solutes within their network, along with holding free water as water of hydration around the polysaccharide structure. The higher the self-diffusion coefficients of water in the freeze-concentrated matrix of sugar solution, the higher the recrystallization rate. A gel-like network also hinders the water mobility of the system, resulting in preservation of ice crystal size and in a small span of ice crystal size distribution. Nevertheless, this is not the only mechanism of stabilizer action since some stabilizers that do not form a gel-like network are still effective in retarding the ice crystal growth (Bahramparvar & Tehrani, 2011).

Last but not least, the incompatibility of stabilizers with milk proteins in the ice cream mix is also an important factor in reducing the ice cream recrystallization.

3.4.5 MELTING RATE

Desirable qualities of ice cream include a slow melting rate, good shape retention and slower foam collapse. As the ice cream melts, heat from the warm air surrounding the product transfers into the ice cream to melt the ice crystals. Initially the ice at the exterior of the ice cream melts and a local cooling effect occurs. The water from the melting ice must diffuse into the viscous unfrozen serum phase, and this diluted solution then flows downwards (due to gravity) through the structural elements (destabilized fat globules, air cells, and remaining ice crystals) to drip. Fat destabilization, ice crystal size, and consistency coefficient of ice cream mix were found to affect the melting rate of ice cream. One function of stabilizers in ice cream is to increase the melting resistance, as described in numerous studies. Hydrocolloids, due to their water-holding and microviscosity enhancement ability, significantly affect melting quality of ice cream. Moreover, it seems that the influence of stabilizers on thermal properties of ice cream such as thermal conductivity, melting onset, and heat of fusion could affect the melting rate (Muse & Hartel, 2004).

3.4.6 MIXTURE OF STABILIZERS

Various substances have been used as stabilizers. Each of them has its own characteristics and optimal percentage in ice cream mix. Some common commercial stabilizers utilized in ice cream are guar gum (GG), sodium carboxyl methyl cellulose (CMC), locust bean gum (LBG), xanthan and so on. Besides, local hydrocolloids have also been used as ice cream stabilizers. For instance, salep serves as stabilizers in traditional ice cream in Iran and Turkey at 0.78-1% level (Kaya & Tekin, 2001). Water-soluble gums obtained from the seeds of achi, which is commonly found in Nigeria, was also studied and compared with commercial stabilizers (Uzomah & Ahligwo, 1999). Other local gums have also been examined.

Since each stabilizer has its own characteristics and limitations, individual stabilizers are usually mixed to improve the overall effectiveness in ice cream mix. According to Guven and Kacar (2003), using multiple stabilizer ingredients reduced the cost of stabilizer system and led to better results than using solely one stabilizer. Adapa showed that guar gum and locust bean gum are considered to be the most widely used stabilizers to inhibit ice cream recrystallization. Hence in this project, a mixture of GG and LBG was used. Obtained from the seeds of guar- a tropical legume, GG effectively decreases the unwanted effects of heat shock in ice cream. It disperses well and does not cause excessive viscosity in the mix. GG is considered to be a strong stabilizer since it only requires 0.1-0.2% in ice cream mix. LBG is extracted from the beans of the tree *Ceratonia siliqua*. LBG is only partially soluble in cold water, so it must be heated above 85°C in order to be dissolved in the ice cream mix. LBG does not bind to ice cream flavor and forms a cryo-gel, which is effective in cryo protection. LBC creates a uniform medium and reproduces viscosity that is not destroyed by agitation. It also cools uniformly and easily incorporates air into the mix. Additionally, LBG effectively thwarts the effect of heat shock. Therefore, it is also considered a strong stabilizer with only 0.1-0.2% needed in the mix. Furthermore, LBG was proved to be more effective than GG in retarding ice cream recrystallization. Ice cream mix having the highest LBG to GG ratio has the highest thermal conductivities. Ice cream mix with more LBG also freezes faster because the relatively lower amount of bound water makes them less viscous compared to ice creams containing GG. Thus, the ratio of LBG to GG was chosen to be 75:25 for this project. Moreover, none of the previous literatures articles has used various technique such as microscope, rheometer, viscometer and DSC to thorough study the effects of this combination in ice crystal coarsening. Therefore, the combination of LBG and GG was chosen for this project.

3.4.7 DEFECTS CAUSED BY STABILIZERS

Even though stabilizers are effective in retarding ice cream recrystallization, excessive use of stabilizers may lead to undesirable melting characteristics, excessive viscosity of the ice cream mix and contributes to a heavy, soggy texture. Moreover, stabilizers can also impart off the ice cream flavor since they can be oxidized if not kept in a dry and cool environment. The most important defect is excessive stabilizers reduce amount of air incorporated into ice cream mix, leading to lower overrun. Thus, excess of stabilizers in ice cream mix can reduce the quality of the products.

4.0 MATERIALS AND METHODS

4.1 SORBET AND ICE CREAM PREPARATION

In order to do a preliminary study on coarsening effects, Häagen-Dazs mango sorbet was sampled for the experiments. Table 2 below summarizes the ingredients of mango sorbet, with the weight percent of ingredients decreasing down the column.

Table 4. Ingredients of Häagen-Daz mango sorbet used in sorbet experiments.

Ingredients
Water
Sugar
Mango puree
Lemon juice concentrate
Pumpkin juice concentrate (for color)
Carrot juice concentrate (for color)
Natural flavor
Pectin

Besides sorbet, the coarsening effects were studied on ice cream. Since investigating the effects of stabilizers is one of the main objectives, ice cream was made in the lab based on a typical formulation from numerous literature reviews. Then, the percent of stabilizers in the ice cream mix were changed accordingly. Table 3 below summarizes the ingredients that were used to make ice cream for the experiments, whereas table 4 indicates the compositions of fat, protein, sugar, emulsifier, stabilizer and water in the ice cream mix. Heavy cream and milk-solid non-fat were obtained in commercial grocery stores. Dextrose, emulsifier and stabilizer (guar gum and locust bean gum) were purchased from an online supplier, Modernist Pantry (York, ME). The final compositions of ice cream mixes were: 10% fat, 15% sugar, 5.3 % protein, emulsifier 0.15%. The weight composition of stabilizers was the variable of the experiments, and the total composition ranged from 0.00% to 0.15%.

Table 5. Ice cream formulation for the experiments.

Ingredient	Amount (weight %)
Heavy cream	32.8%
Milk-solid non-fat (MSNF)	12 %
Dextrose	6.74 %
Mono/diglyceride	0.15%
Guar gum & locust bean gum	0.0 – 0.2%
Water	64.45 – 64.57% (Depends on stabilizer composition)

Table 6. Compositions of main ingredients in the ice cream mix.

Ingredient	Amount (weight %)	Source of ingredient (Supplier)
Fat	10%	Heavy Cream (Garelick)
Protein	6.11 %	Milk Powder (Price Chopper)
Sugar	15 %	Pure Source (Modernist Pantry)
Emulsifier (Mono/diglyceride)	0.15%	Pure Source (Modernist Pantry)
Stabilizer	0.0 – 0.2%	Pure Source (Modernist Pantry)
Water	45.27 – 45.39% (Depends on stabilizer composition)	Tap Water

4.2 PROCESSING CONDITIONS

The ice cream mix was made in batches that weighed 1000g each with the steps, as shown in Figure 9 below.

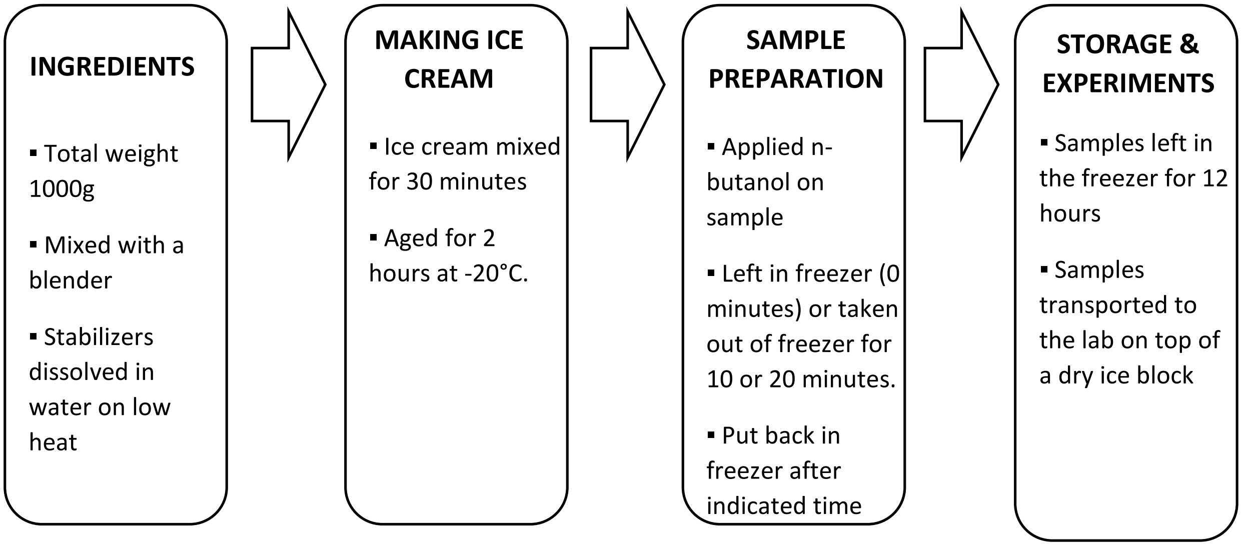

Figure 9. Flow chart of ice cream making and samples preparation processes.

The ice cream machine that was selected is Cuisinart *Pure Indulgence™ 2 Qt. Frozen Yogurt-Sorbet & Ice Cream Maker*, since it closely resembled an industrial scrap-surface freezer. Each batch of ice cream mix was churned for 30 minutes in the ice cream machine. The freezer bowl in the ice cream machine was stored in the freezer (-20 °C) with a piece of dry ice inside for approximately 12 hours before the ice cream production. After the ice cream was made, the batch aged in the freezer (-20 °C) for 2 hours. Then the ice cream samples were prepared for the hardness and the fluorescence microscopy test. They were stored in the freezer for 12 hours before the experiments.

For each mix, samples were drawn from the center of the ice cream batch for experiment. For microscopy test, the sample was placed on a microscopic glass slide that were stored in the freezer (-20 °C). For hardness test, the sample was also extracted from the center of the ice cream after it aged in the freezer for 2 hours. In order to make a two inch by two inch cube, the samples were filled in a soft silicone ice cube tray.

4.3 FLUORESCENCE MICROSCOPY

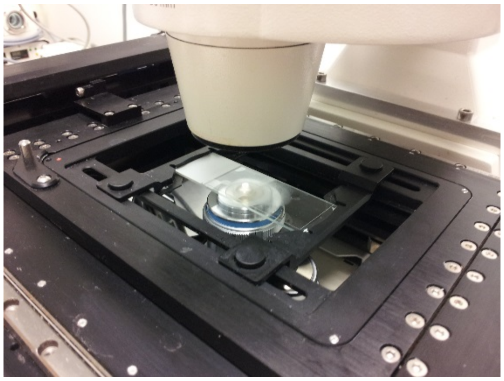

Figure 10. Carl Zeiss fluorescence microscope at Gateway Park.

In a typical experiment, a small amount of ice cream or sorbet was taken from the inner bulk of the hardened ice cream or sorbet at -20^{o}C, thinly spread on a microscope slide using a spatula and was then covered with a drop of n-butanol. A coverslip was then placed on top. The microscope slide, the coverslip as well as the spatula and n-butanol were pre-chilled at -20^{o}C prior to the sample preparation. The whole process was carried out in the freezer. Three glass slides for 0 min were placed inside the freezer right away and held at -20^{o}C for 12 hours. The glass slides for 10 and 20 minutes were placed outside the freezer at room temperature for 10 and 20 minutes respectively, and then put back in the freezer and held at -20^{o}C for 12 hours. Three samples were prepared for each time interval. 10 and 20-minute intervals were chosen for the experiments to represent the typical times that ice cream or sorbet was left out of the fridge. After 12 hours, the glass slides were placed in an insulated box with dry ice and transported to the microscope room. Each glass slide was then placed on the *Carl Zeiss* fluorescence microscope (Figure 10), and the microscopic image of the sample at a magnification of 40X was captured. For each time interval, 100-300 crystals were taken. A decrease in the number and the size of the ice crystals in the presence of additives would indicate the additives' ability to inhibit ice crystal growth.

4.4 IMAGE ANALYSIS AND CRYSTAL SIZE DISTRIBUTION

Using AxioVision LE 4.8 for Windows, each captured microscopic image was analyzed. By using the measurement tool of this software, the ‘length’ or diameter of each crystal was manually traced. The measurements then automatically appeared right by the drawn line. About 100 to 300 crystals were measured by hand, with the number of crystals depended on the clarity of the image as well as the quality of the samples. After measurements from the images were entered into Microsoft Excel sheets per category of the samples, the ice crystal size distribution was determined using the Data Analysis package in Excel. Since most of the experimental runs were conducted for samples at 0 to 20-minute interval, the ice crystal size was assumed to range up to 54 µm in diameter. Hence, choosing the Bin range from 2 to 54, the frequency of the crystal size was generated for the histogram graph.

The weight average mean crystal size ($\overline{D}_w$) was calculated based on the formulas acquired from Indian Academy of Sciences.

$$\overline{D}_w = \frac{\sum_{i=1}^{\infty} N_i {D_i}^2}{\sum_{i=1}^{\infty} N_i D_i} \tag{6}$$

The formula contained N_i, which represented the number of crystals of diameter i (Di). In order to calculate the standard deviation of the weight average crystal size $\overline{D}_w$, the number average crystal size, $\overline{D}_N$, was also determined. The equation for $\overline{D}_N$ was determined as the following equation

$$\overline{D_N} = \frac{1}{\sum_{i=1}^{\infty} \frac{w_i}{D_i}} \tag{7}$$

where w_i represented the crystal size fraction of a crystal size D_i. The crystal size fraction was calculated as the size of crystal i divided by the total crystal size.

$$w_i = \frac{N_i D_i}{\sum_{i=1}^{\infty} N_i D_i} \tag{8}$$

After the determination of the number average crystal size, the standard deviation, which characterized the spread of the crystal size distribution function, was therefore generated with the below equation.

$$\sigma = \overline{D_N} \sqrt{\frac{\overline{D_W}}{\overline{D_N}} - 1} \tag{9}$$

4.5 HARDNESS MEASUREMENT

Hardness, as a physical properties of ice cream or sorbet, measures the resistance of the sample to deformation when an external force is applied. Additionally, hardness is an indirect measure of the ice crystal size in both sorbet and ice cream. Therefore, the hardness measurement was conducted to confirm the coarsening in ice cream and sorbet over time observed in the microscopy experiment.

Figure 11. Hardness test set up in Washburn food engineering laboratory.

Hence, the experiment was designed to compare the change of the hardness of both sorbet and ice cream over time by measuring the applied force to penetrate the sample cube. The samples were left out of the fridge for different time periods: 0 to 20 minutes with a 10-minute increment. At a constant strain rate of 0.00166 meters per second, an aluminum rod with a diameter of 6 mm was used to penetrate the sample cube until a depth of 2.54 cm was reached. The sample cube was 5.08 cm by 5.08 cm. For each time interval, three samples were tested. Then, a graph of force versus time of ice cream was generated per sample per time interval. The deformation of the sample was calculated for each data point following the below equation.

$$Deformation\ (mm) = Time\ elapsed * 0.00166\frac{m}{s} * 1000\frac{mm}{m} \tag{10}$$

After that, the force was graphed as a function of deformation, as shown in the following figure (Figure 12). The peak force here is the hardness, representing the mouth feel or the texture of ice cream or sorbet. Wilbey et al. (1998) found the relationship between the ice content and the hardness: as the amount of large ice crystals increases, similarly hardness of the sample would go up. Furthermore, Muse and Hartel (2004) also found the same trend between the crystal size and hardness. So it was expected that at longer time interval, the hardness would increase.

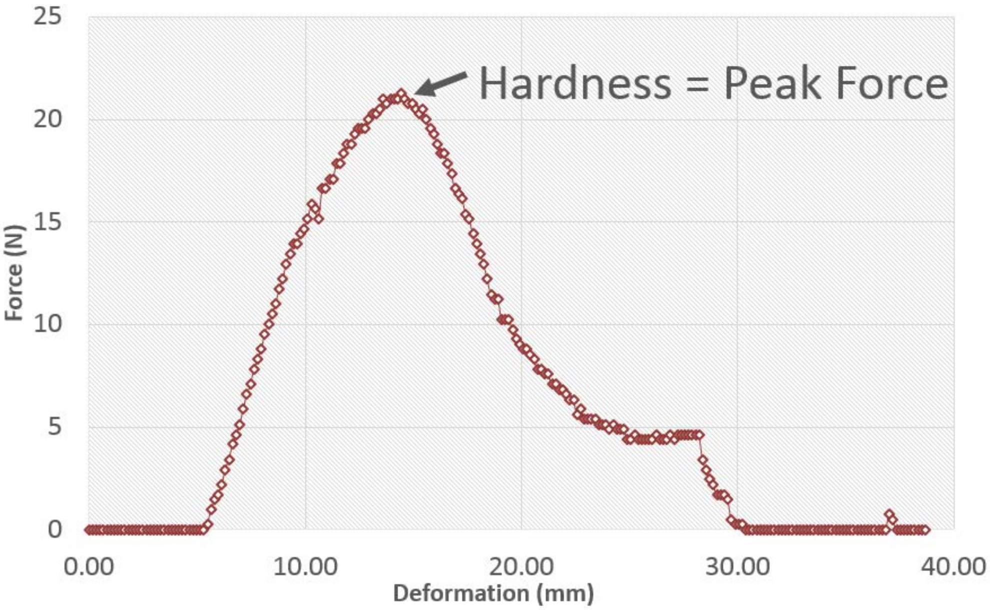

Figure 12. A typical graph of force as a function of deformation. The peak force represents the hardness of the sample.

The experiment was also designed to study the effect of stabilizers on the hardness of ice cream. Therefore, the same procedure was also applied to ice cream samples with different mass of stabilizers. As the weight percent of stabilizers in the mix increased, the viscosity of the solution should increase, which in turn slowed down the thermal diffusion of molecules from small crystals to the surface of growing crystals. In other words, the higher the mass of stabilizers, the higher the applied force should be over time.

4.6 VISCOSITY MEASUREMENT

The rheological properties of ice cream were measured using *Brookfield Model DV-III +* programmable rheometer. After ice cream was aged for 2 hours in the freezer, a part of the center of the ice cream batch was put into a separate container for viscosity measurement. The ice cream container was stored overnight in the freezer at about -20°C. After about 19 hours, the ice cream samples were placed on a dry ice block inside an insulated Styrofoam box and transported to the laboratory. About 15mL of ice cream sample was placed inside the stainless steel chamber of the rheometer. Spindle #40 was used for the shear contact surface for the viscometer. The viscosity test was conducted with three different shear rates: 50 RPM, 100 RPM and 150 RPM. As long as the torque percentage was between 10 and 100% to maintain measurement accuracy, the viscosity and temperature of the sample were recorded after 10 seconds. Three samples per shear rate were used for each ice cream batch. The same procedures were repeated for ice cream mix with different concentrations of stabilizers. After the recorded measurements, Power Law model was applied in order to determine the flow behavior index (n) and the consistency index (K).

$$\tau = K\dot{\gamma}^n$$

$$\eta\dot{\gamma} = K\dot{\gamma}^n$$

$$\eta = K\dot{\gamma}^{n-1}$$

$$\ln(\eta) = (n-1)\ln(K) + (n-1)\ln(\dot{\gamma}) \tag{11}$$

In order to find n and K values, a log-log graph was generated per ice cream batch for shear rate ($\dot{\gamma}$) versus viscosity (η). The slope of the graph was then equivalent to (n-1) and the intercept of the graph was the value of (n-1)*lnK. Consequently, the values for n and K were compared among different ice cream mixes.

4.7 DIFFERENTIAL SCANNING CALORIMETRY MEASUREMENT

Differential scanning calorimetry (DSC) was used to measure thermal properties of ice cream in order to further understand the effects of stabilizers. Nitrogen gas was continuously flushed through the cell to eliminate problems associated with water condensation. Besides, some regular checking runs were also performed with pure water to check the calorimeter calibration. The DSC was calibrated with indium and mercury standards. Melted ice cream samples in the range of 10mg to 30mg was placed in aluminum pans and precisely weighted. The aluminum pans were then placed in the DSC and cooled quickly to -10°C. After that, the samples were heated to 10 °C at a rate of 1 °C/min. An identical empty aluminum pan, used as a reference, was exposed to the same temperature rate increase of 1°C/min for all the experimental runs with frozen samples. All the measurements were carried out by using temperature increase to avoid nucleation and the supercooling problems. Then, these experimental data were analyzed in order to derive the enthalpy values according to the temperature changes. The heat of fusion, which is the amount of energy required to change a gram of a substance from the solid to the liquid state without changing its temperature, was determined by measuring the area of the melting peak. The crystallinity, the percent of crystals in ice cream, was calculated using the following equation.

$$Crystallinity = \frac{\left(\frac{Measured\ heat\ of\ fusion\ of\ ice\ cream}{fraction\ of\ water\ in\ ice\ cream}\right)}{Heat\ of\ fusion\ of\ pure\ water} * 100\% \tag{12}$$

These experiment procedures and calculations were conducted for ice cream with and without stabilizer. Three samples were tested for each ice cream mix with different amount of stabilizers. The data was then analyzed and compared to study the effect of stabilizer on crystal size and coarsening process.

5.0 RESULTS AND DISCUSSION

5.1 SORBET ANALYSIS

5.1.1 ICE CRYSTAL SIZE AND DISTRIBUTION MEASUREMENT

Since sorbet is mostly made of water and sugar, whereas ice cream composition is much more complex, with the addition of fat and additives, a preliminary study on the coarsening effect was conducted on sorbet. Figure 12 indicates the coarsening of sorbet ice crystals over time interval of 0, 10, and 20 minutes.

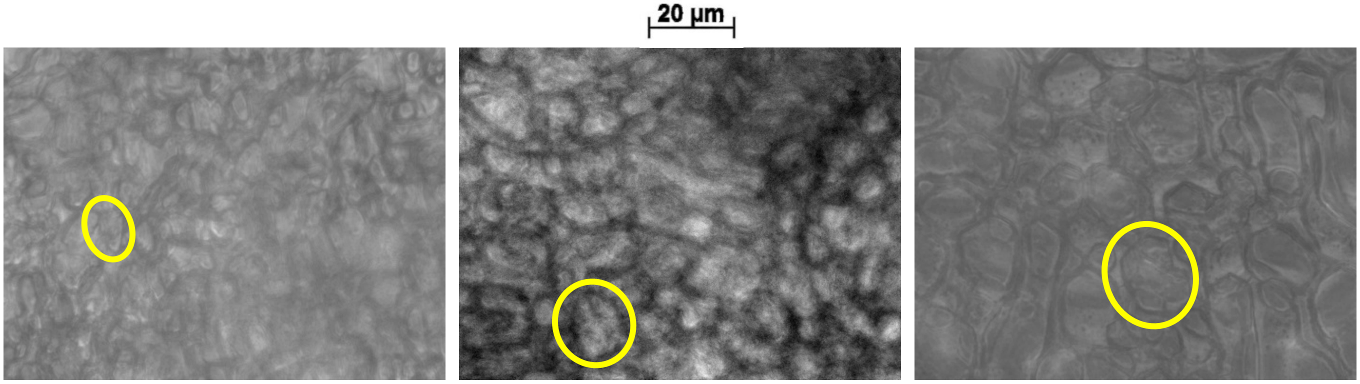

Figure 13. Variation of ice crystal size with recrystallization time. An initial sample (0 min) was obtained and stored in the freezer as soon as the container was opened. Subsequently, the sample was placed outside for the times indicated (hereon referred to as recrystallization time) and immediately placed in the freezer. They were all taken out after 12 hours, transported to the lab on dry ice and tested immediately. The yellow circles represent the typical ice crystals that were analyzed and measured.

As sorbet samples were left out of the refrigerator for a longer period of time, the ice crystal size increased. In order to further confirm the increasing trend, Figure 13 summarized the distribution of sorbet ice crystal over the three indicated time intervals. The peak of the distribution curve shifted to the right as time interval increases; the arrow representing the mean of the distribution also shifted to the right. This indicated that the weighted average crystal size became larger at longer time interval. Also, the crystal size distribution became more widespread at longer time intervals with a decrease in the number of crystals. The trend confirmed the literature study about recrystallization: the longer the time interval, the larger the ice crystal size and the smaller the number of crystals. Because of the three mechanisms of recrystallization, Ostwald ripening, accretion, and isomass rounding, ice crystals merged with one another while small crystals diffuse over time. Therefore, at a longer time interval, small ice crystals diffused to the growing crystals and the solution was left with a small number of merged, larger-sized crystals.

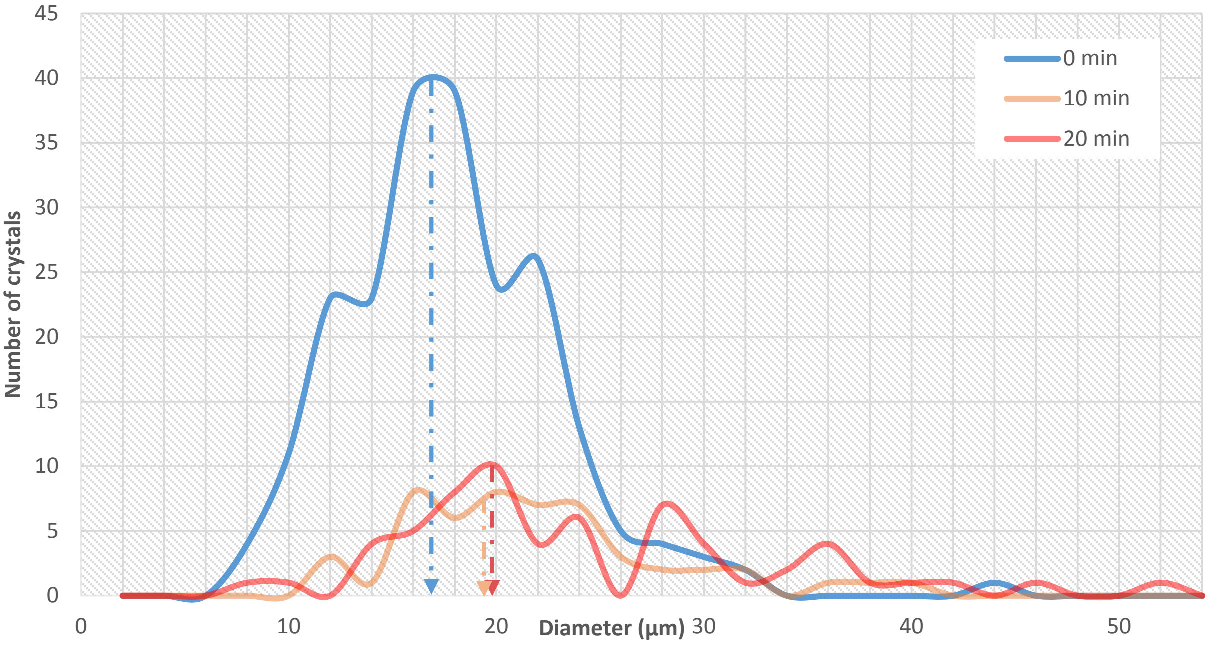

Figure 14. Typical ice crystal distributions in Häagen-Dazs mango sorbet. Data are plotted for various recrystallization times of 0, 10, and 20 minute. The arrows indicate the mean in the distribution.

The weighted average crystal sizes of sorbet also indicated the same trend with the crystal images and the distribution graph, according to Table 7. At longer time interval, the weighted average crystal size increased.

Table 7. Variation of ice crystal size in Häagen-Daz mango sorbet for various recrystallization times.

Time (min)	Weighted average crystal size (μm)
0	27.9 ± 10.7
10	28.8 ± 2.9
20	34.3 ± 4.6

In addition, the rate of recrystallization over different time intervals also increased: from 0-minute to 10-minute interval the change in ice crystal size was 1.1 μm, while from 10-minute to 20-minute interval that was 6.5μm. The increase in size change indicated that recrystallization rate increased over time, since the solution became less viscous. The liquid fraction of the solution increased, leading to a higher diffusion rate. This trend affirmed the Kelvin or Gibbs-Thomson equation that as ice crystal size increases, the driving force of recrystallization increases.

In order to investigate the cause of recrystallization, sorbet crystal size was graphed according to the commonly used kinetic equation by Lifshitz and Slyozov for both common n values of 2 and 3, as shown in Figure 15.

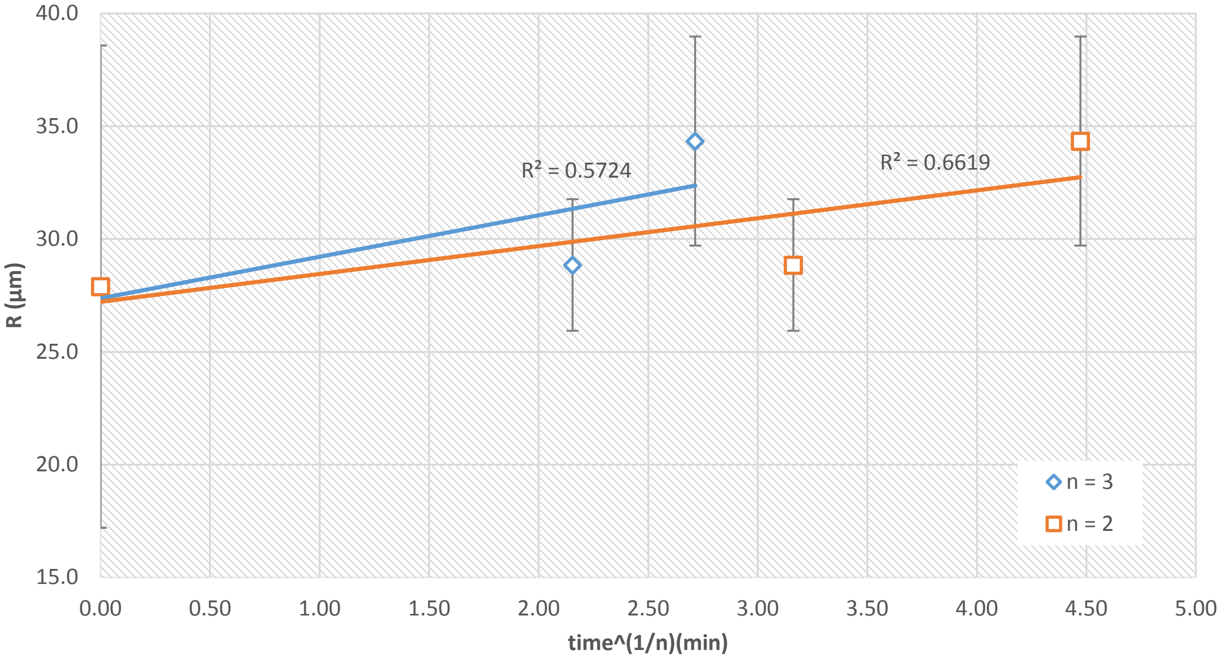

Figure 15. Kinetic models for Häagen-Daz mango sorbet, where n = 2 represents interface surface energy kinetic and n = 3 represents diffusion kinetic.

If the model fits the n value of 2, recrystallization is mostly due to interface surface energy. On the other hand, if the model fits the n value of 3, it is then due to diffusion kinetics. However, since the fluorescence microscopy does not have a cold stage, the temperature at which the experiments took place changed drastically, depending on the daily weather. Besides temperature fluctuations, the humidity also made the slides foggy. Due to the low quality of the micrographs, the standard deviations for the crystal size were relatively large. The data points appeared to fit both graphs of n values 2 and 3, though the data fits the n = 2 graph a little bit better (higher R^2 value) (Figure 14). For that reason, recrystallization might have mixed rate control. However, more experiments should be conducted in a better controlled environment, so as to identify the main kinetics of recrystallization in sorbet.

5.1.2 VISCOSITY MEASUREMENTS

As mentioned above, the faster rate of change of crystal size in sorbet over longer time intervals might be due to the fact that sorbet becomes less viscous. A viscosity test with three different shear rates: 50, 100, and 150 RPM was conducted, in order to test this hypothesis.

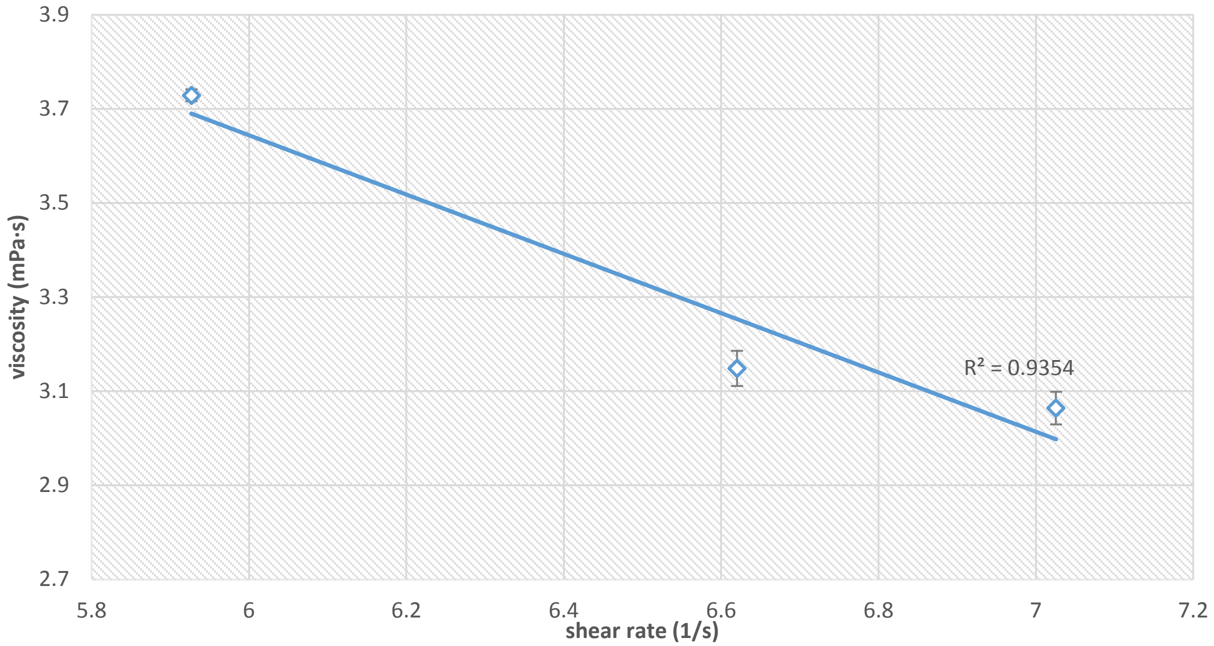

Figure 16. Viscosity measurement for Häagen-Daz mango sorbet with various shear rates.

As indicated in Figure 16, the viscosity of sorbet decreased at a higher shear rate. Since most shear-thinning fluids contain both the Power-law region and the Newtonian region, the more drastic change in the sorbet viscosity between 50 and 100 RPM shear rate in comparison to 100 and 150 RPM might be due to the fact that 50 and 100 RPM are the in Power-law region, whereas 150 RPM might belong to the Newtonian region for this sorbet solution.

Table 8. Variation in viscosity of Häagen-Daz mango sorbet for various shear rates.

Time (min)	Average viscosity (mPa·s)	n	K (Pa.s^n)
0	41.6 ± 0.5	0.4	7.6 × 10^{-6}
10	23.3 ± 0.9		
20	21.4 ± 0.7		

The fitted line for sorbet viscosity data in Figure 16 yielded a flow behavior index (n) of 0.4 and a consistency index (K) of 7.6 × 10^{-6} (Table 8). The n value less than 1 reinforced the shear-thinning behavior of sorbet. The high K value of sorbet was consistent with the high sugar concentration in the solution. Since recrystallization rate is reduced in a more viscous environment, the lower viscosity at longer time intervals indicate a faster recrystallization rate in sorbet, which is consistent with the observed trend in the ice crystal images and distribution from the previous section.

5.1.3 HARDNESS MEASUREMENTS

The hardness measurement was carried out to confirm the coarsening mechanism of sorbet over time which was observed in crystal size and distribution measurement. Below is the graph of force as a function of deformation for sorbet over time.

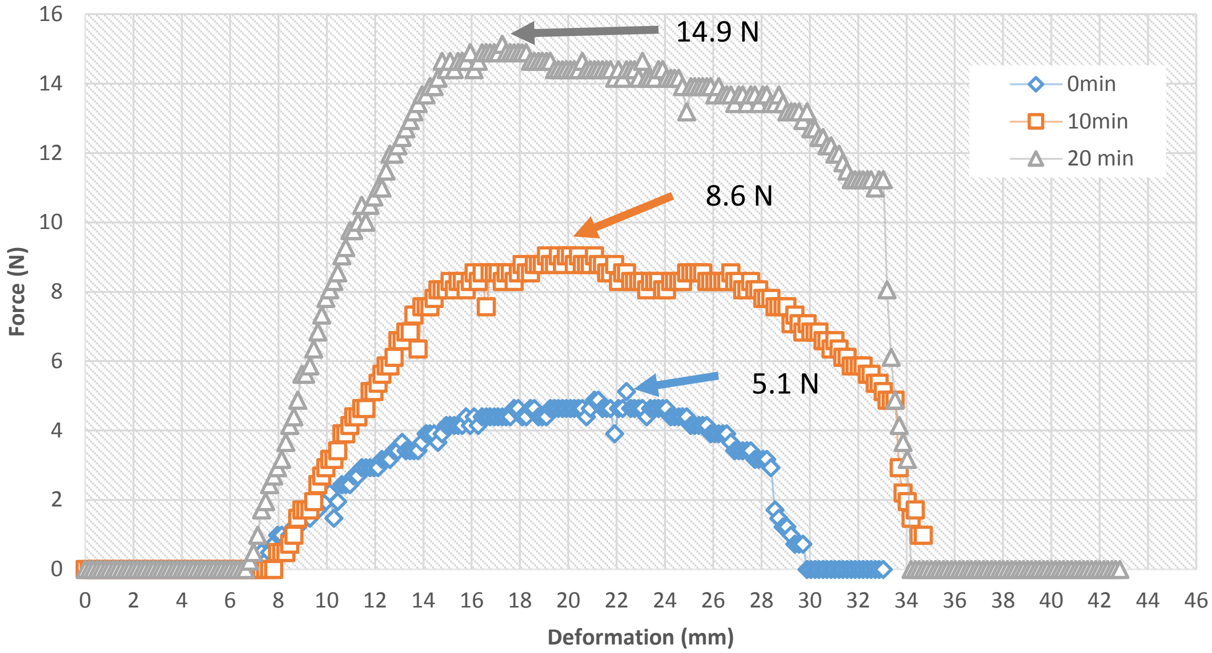

Figure 17. Hardness measurement for sorbet over coarsening time. The peak force is defined as the hardness of sorbet at time intervals of 0, 10 and 20 minutes (shown by arrow and labeled).

Hardness is the peak force of the curve, representing the mouth feel or texture of ice cream. Hardness of ice cream at 0, 10 and 20 minutes were 5.1, 8.6 and 14.9 N, respectively. As shown on the graph, the longer time sorbet was left outside at room temperature, the harder the sample. As time increased, some small crystals diffused away as large crystals grew due to Ostwald ripening mechanism. Additionally, accretion mechanism led to a formation of large ice crystal network as small crystals merged. As a result, the number of large ice crystals went up. Since hardness increased with a higher amount of large ice crystals, hardness of sorbet increased over time. This reinforced the hypothesis that samples with larger ice crystals were harder than those with smaller ice crystal by Sakurai et al. (1996). The hardness values also confirmed the coarsening effect that were observed in crystal size and distribution measurement for sorbet. The longer time the sample was left out of the fridge, the larger the ice crystals, leading to a higher hardness.

5.2 ICE CREAM ANALYSIS

5.2.1 ICE CRYSTAL SIZE AND DISTRIBUTION MEASUREMENTS

Since a longer time interval outside of the fridge indicated a larger temperature fluctuation, the ice cream samples underwent recrystallization via Ostwald ripening and accretion at a faster rate. The partially-melted smaller crystals were driven thermodynamically to diffuse to growing ice crystals, and the larger crystals grew at the expense of these small crystals.

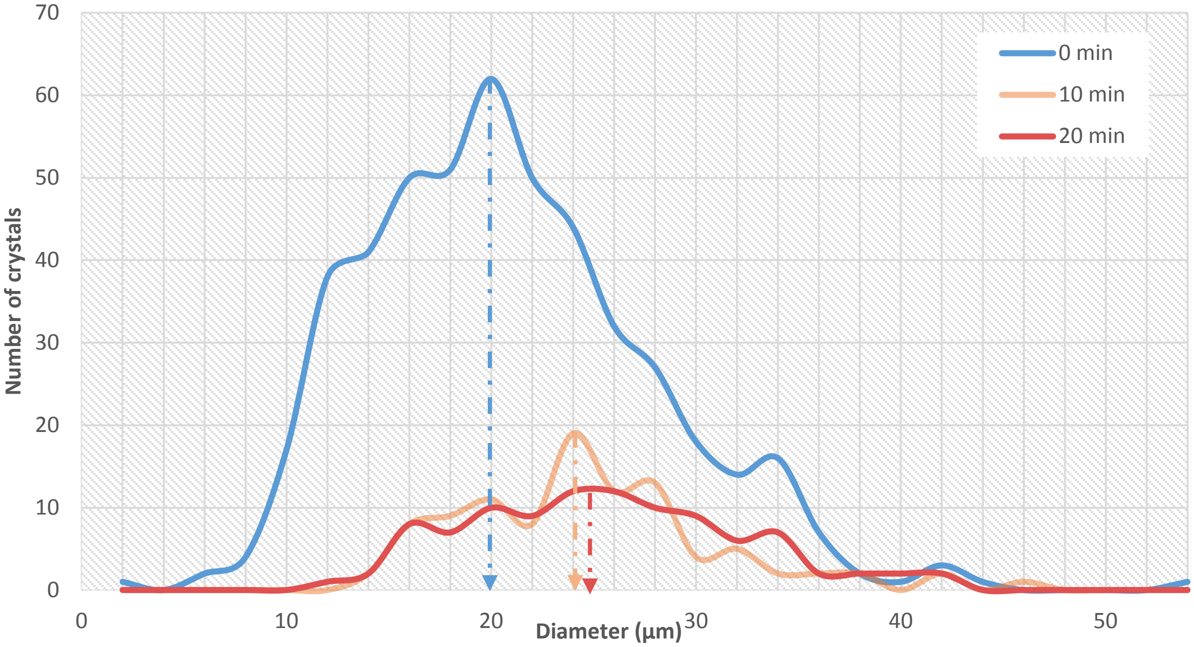

Figure 18. Typical ice crystal distributions in ice cream. Data are plotted for various recrystallization times of 0, 10, and 20 minutes. The arrows indicate the mean in the distribution.

In Figure 18, the ice crystal distribution shifted to the right and became more widespread over time. The increasing trend of ice cream weighted average crystal size over longer time intervals matched the coarsening effects in sorbet, as shown in the previous Sorbet Analysis section. The broader distribution signified that there were more crystals in the extremes of the spectrum, very large crystals and very small crystals. The lower peaks entailed that the ice cream samples at 10 and 20 minutes interval had fewer crystals. Table 9 below demonstrated that average ice crystal size increased as a function of time interval outside of fridge for both unstabilized and stabilized ice cream. On the other hand, with the addition of stabilizers in the ice cream samples, it was expected to decrease the average ice crystal size. However, the result from the microscopy indicated the reverse trend: ice cream with stabilizers had a larger average crystal size compared to that without stabilizers (Table 9).

Table 9. Variation in crystal size for ice cream with different stabilizer concentrations.

Time (min)	Ice Crystal Size (µm)			
	0.00% Stabilizer	0.05% Stabilizer	0.10% Stabilizer	0.15% Stabilizer
0	15.2 ± 4.4	20.1 ± 5.1	23.4 ± 1.4	25.7 ± 5.9
10	19.5 ± 4.9	22.8 ± 6.6	22.7 ± 2.0	27.1 ± 1.8
20	23.6 ± 6.2	23.0 ± 6.9	25.6 ± 2.1	27.5 ± 0.3

Stabilizer that were utilized in the experiments appeared to be ineffective in maintaining the crystal sizes of the ice cream samples and the number of ice crystals in the samples. Table 9 above demonstrated that the application of stabilizer increased the initial ice crystal size. Figure 19 below demonstrated that the distribution of ice crystal size shifted to the right with increasing stabilizer concentration. The mean in the ice crystal distribution was expected to be lower for higher concentration of stabilizers, and therefore representing a smaller weighted average crystal size. However, both Figure 19 and Table 9 indicates a larger average crystal size as stabilizer concentration increases.

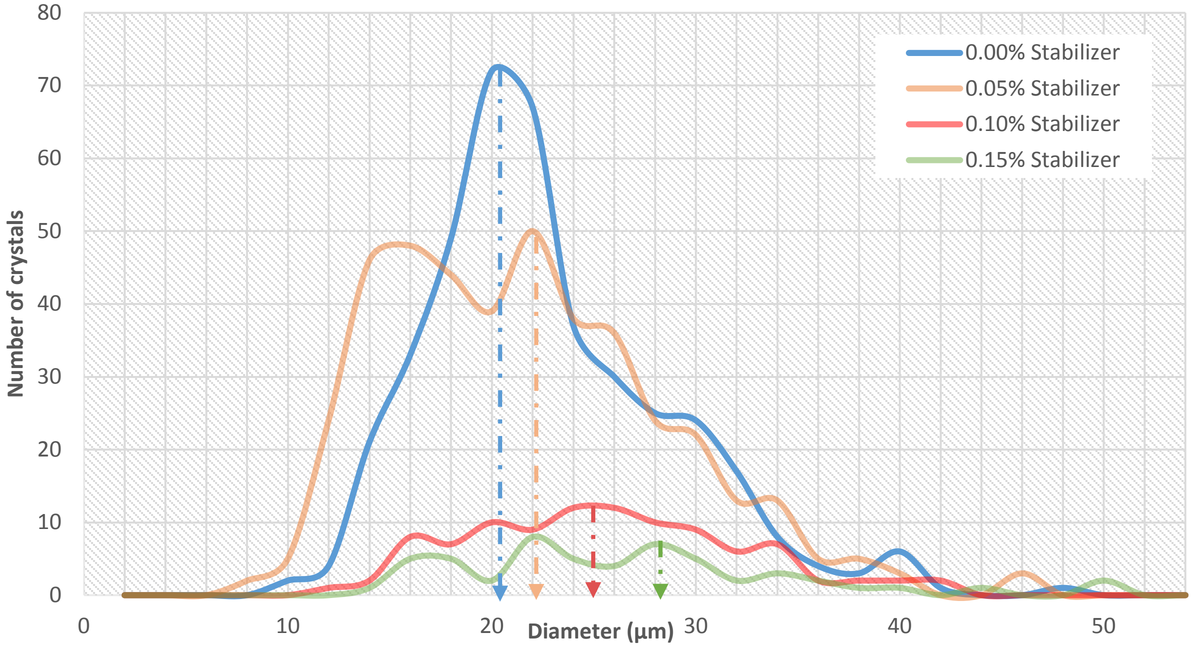

Figure 19.Typical ice crystal distribution in ice cream. Data are plotted for ice cream with various stabilizer concentration at recrystallization time of 20 minutes. The arrows represent the mean in the distribution.

This opposite trend might have been due to various reasons, including but not limited to the unhomogenized nature of the ice cream mix, the impure stabilizers, as well as the temperature and humidity fluctuations during the experiments. Nonetheless, higher stabilizer concentration samples showed the same phenomena as shown in unstabilized samples: ice crystal size increased over longer time intervals. The change in ice crystal size at different time intervals for stabilized ice cream was smaller than that in unstabilized ice cream (Table 9). For example, between 0-minute and 10-minute time interval, the change in ice crystal size for unstabilized ice cream was 4.3 µm, whereas that for 0.05% stabilized ice cream was 2.7 µm. This observation suggested that stabilizers did perform their function of reducing recrystallization rate, and therefore inhibited crystal growth rate. For 0.10% stabilized ice cream. 0-minute interval had a slightly higher average crystal size compared to 10-minute interval, which might have been caused by the unhomogenized ice cream mixture. The samples for 10-minute interval might have come from a region clustered with stabilizers, whereas those for 0-minute interval might have come from an area with more water and less solid content. Overall, the ice crystal size over different time intervals for both unstabilized and stabilized ice cream followed the expected increasing trend. Similar with sorbet's, ice cream's recrystallization was studied with the LSW kinetic model for both n values of 2 and 3 (Figure 20).

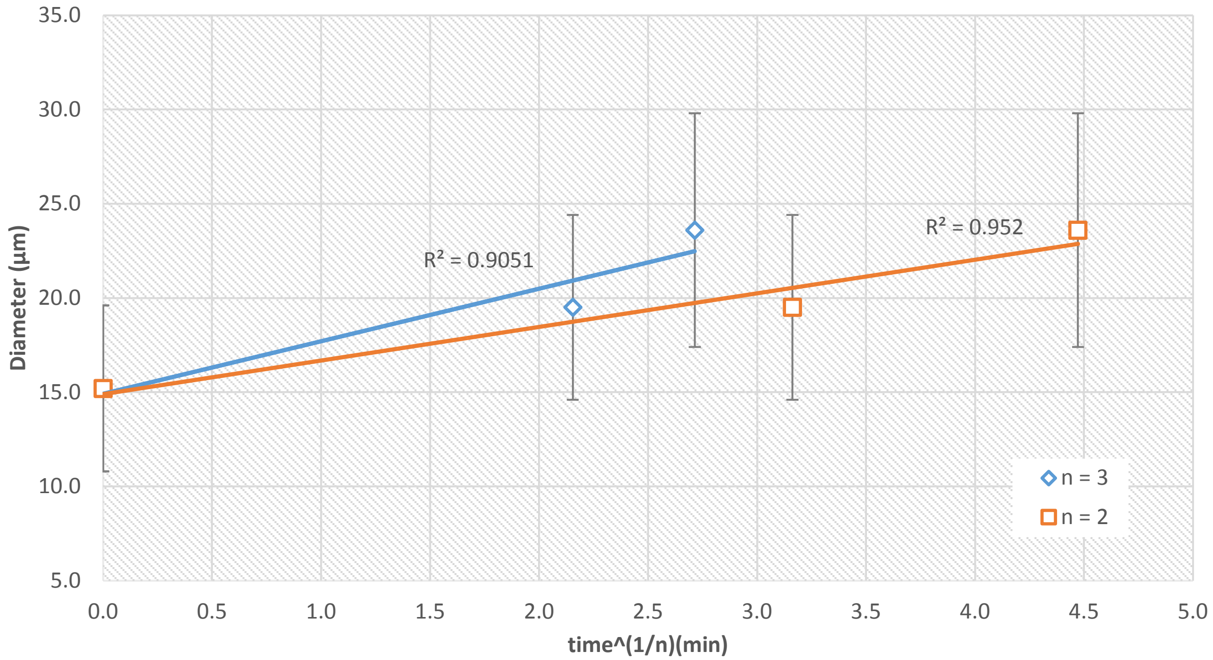

Figure 20. Kinetic models for ice cream, where n = 2 represents interface surface energy kinetic and n = 3 represents diffusion kinetic.

Recrystallization may have been due to two mechanisms: surface interface energy and diffusion kinetics. The data fit for n=2, or interface surface energy kinetics, had a higher R-square value than that for diffusion kinetics. The higher R-square value for interface surface energy kinetic may have indicated that accretion was the more prevalent rate controlling step in coarsening. Figure 21 below demonstrated that the accretion occurred in ice crystals; it was apparent that the neighboring crystals merged with one another. Additionally, the data fit for n=2 and n=3 implied that the recrystallization process could have been a mixed control step in between interface surface energy kinetics and diffusion kinetics. Nonetheless, due to the large deviation of ice crystal sizes, as shown in Figure 20, more experiments are necessary to consolidate the actual mechanism of recrystallization of ice cream.

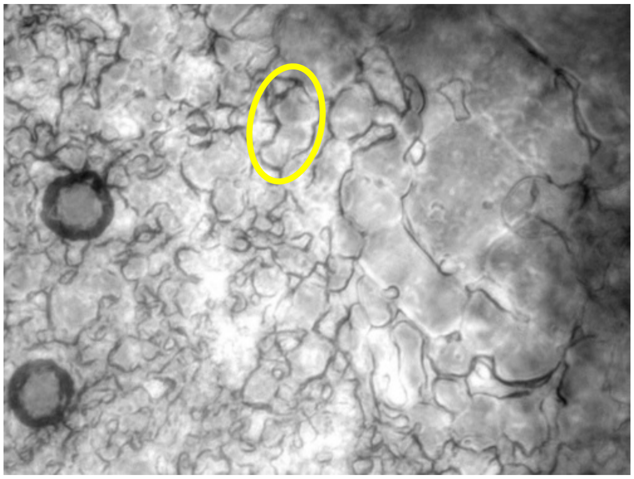

Figure 21. Ice crystal structure for 0.10% stabilized ice cream (Run 1). The yellow circles represent the typical ice crystals that were analyzed and measured.

From the result of the experiments, the average ice crystal size increased over time with increasing stabilizer. Table 9 above indicated the increasing concentration of stabilizer correlated to a higher initial crystal size. The phenomena could have been due to the low quality of the stabilizer in the recipe. The below-standard stabilizers could have served as a site for ice crystal to grow and hence increased the mean crystal sizes. Moreover, the partially undissolved stabilizer during ice cream preparation failed to function as a prohibitory agent for recrystallization. Furthermore, the undissolved stabilizers were unable to disperse uniformly, or homogenize, in the ice cream mix and thus slowed down crystal growth rate in the diffusive medium. This also contributed to the reasons why the distribution of ice crystals became more widely spread-out. However, stabilizers did perform their function in lowering the recrystallization rate. The effect was demonstrated in Figure 22 for diffusion kinetics and Figure 23 for interface surface energy kinetics. The slopes of the kinetic models for each stabilizer concentration had decreasing trends with increasing stabilizer concentration. However, the rate of recrystallization of 0.15% stabilized ice cream was higher in comparison with that of 0.10%

stabilized ice cream. The reverse trend might have been an indication of an optimal concentration of stabilizer in this particular ice cream formula. In order to achieve the lowest recrystallization rate, the concentration of combined locust bean gum and gum was predicted to be between 0.10% and 0.15%. Nonetheless, due to the large deviations in the obtained data, further testing is required to confirm this hypothesis.

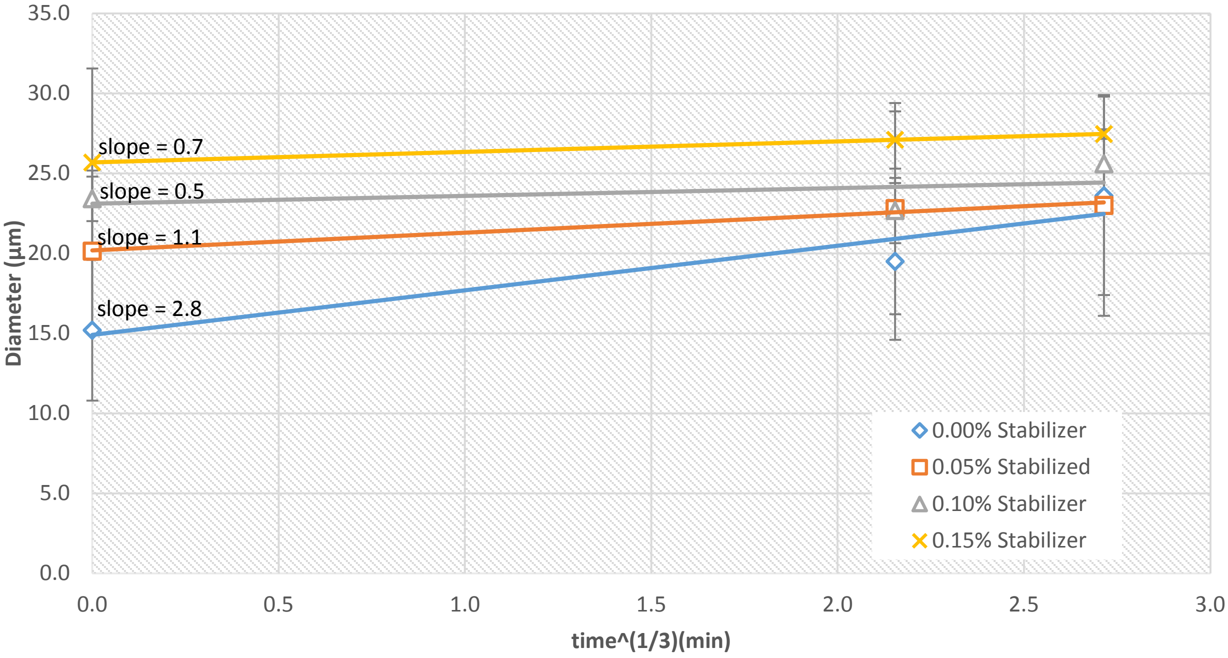

Figure 22. Diffusion kinetic model for ice cream at different stabilizers concentration.

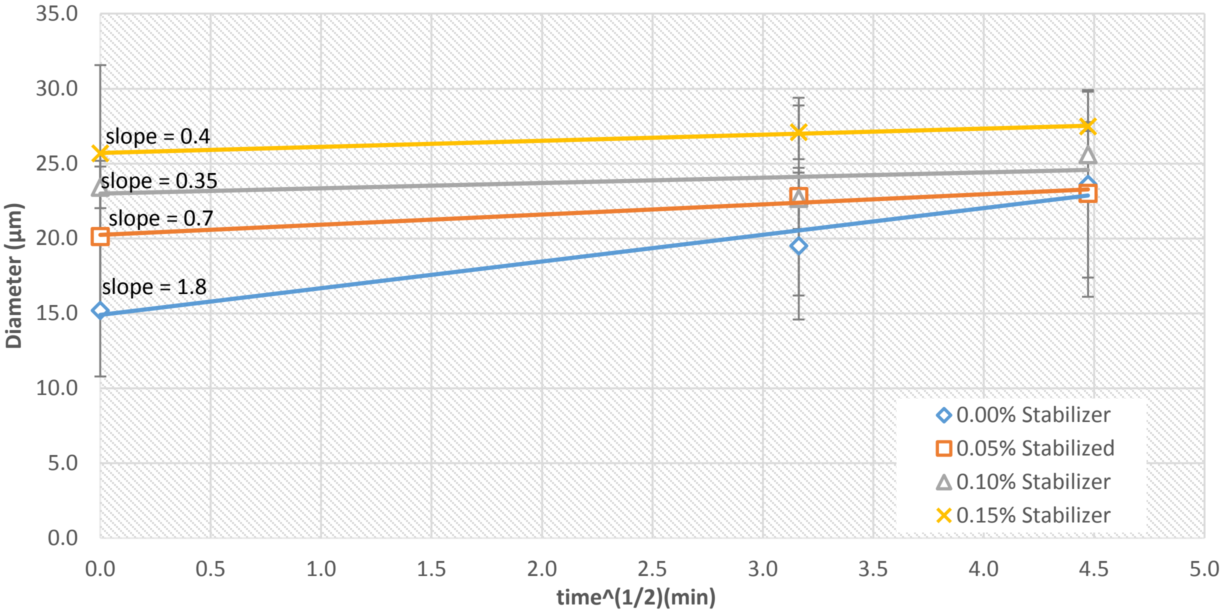

Figure 23. Interface surface energy kinetic model for ice cream with different stabilizers concentration.

5.2.2 VISCOSITY MEASUREMENTS

Similar with sorbet, ice cream should exhibit a shear-thinning non-Newtonian behavior. The higher the shear rate, the less viscous the ice cream solution, as indicated in Figure 24.

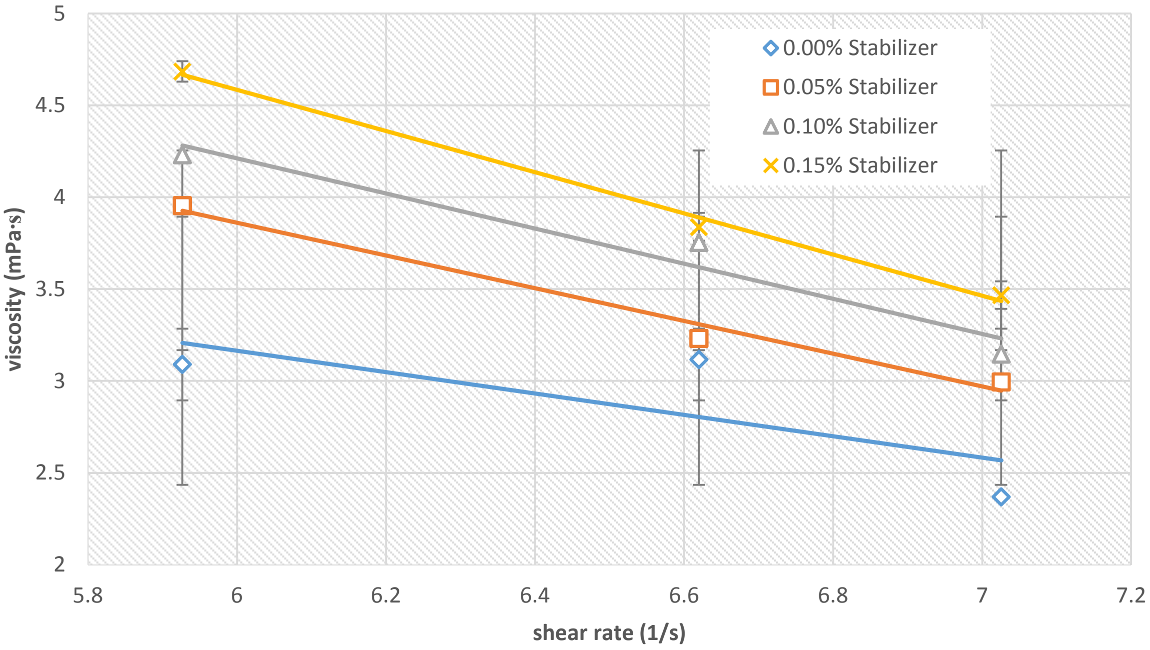

Figure 24. Variation of viscosity of ice cream with different stabilizer concentrations.

At a higher stabilizer concentration, the viscosity of the ice cream mix became higher when applied a constant shear rate, consistent with the literature conclusion that stabilizers should inhibit recrystallization rate (Table 10). Since the higher the viscosity, the slower the diffusion rate should be, ice cream with a higher concentration of stabilizers should have a smaller weighted average crystal size. However, the ice crystal size had an opposite trend as shown earlier, which might have been due to the inhomogeneity of the ice cream mix as well as the lack of controls in the conducted experiments. Under the microscope, depending on the regions where the micrograph photos were taken, the ice crystal size might have varied significantly. Even though ice cream became more viscous with higher stabilizer concentrations, the unhomogenized nature of the mixture might have led to a lower viscosity regionally. The ice crystal size therefore was formed with a larger initial size, leading to an overall larger crystal size when compared with unstabilized ice cream.

Table 10. Viscosity measurements for ice cream with different stabilizer concentrations.

Shear rate		Viscosity (mPa·s)			
RPM	1/s	0.00% stabilizer	0.05% stabilizer	0.10% stabilizer	0.15% stabilizer
50	375	22.0 ± 5.0	52.2 ± 13.3	68.9 ± 10.0	108.3 ± 6.0
100	750	22.6 ± 5.0	25.3 ± 3.0	42.7 ± 5.3	46.5 ± 3.5
150	1125	10.7 ± 2.0	20.0 ± 1.0	23.3 ± 0.5	32.0 ± 2.4

Furthermore, as the shear rate increased, the fluctuation in viscosity measurement decreased, because the ice cream solution became more homogenous at a faster rate. The fact that the viscosity of unstabilized ice cream at 50 RPM WAS slightly smaller than that at 100 RPM might have been caused by a measurement error or the temperature difference between two runs. Since viscosity is dependent on temperature, the data point at 50 RPM was taken at a temperature of 23.5°C while that at 100 RPM was taken at a temperature of 22.4°C, indicating that the viscosity at 50 RPM should have been higher than that at 100 RPM. Also, because a higher concentration of stabilizers yielded a more viscous ice cream solution, an increase in stabilizers concentration should have increased the K value and decreased the n value (the ice cream behavior deviated further away from Newtonian fluid), as demonstrated in Table 11.

Table 11. Summary table for n (flow behavior index) and K (consistency index) for ice cream with different stabilizer concentrations.

Stabilizer concentration	n	K (Pa.s^n)
0.00% stabilizer	0.4	1×10^{-5}
0.05% stabilizer	0.1	3×10^{-5}
0.10% stabilizer	0.04	3×10^{-5}
0.15% stabilizer	-0.12	4×10^{-5}

All the n values were less than 1, again confirming the shear-thinning behavior of ice cream. The rates of change in both the n and K values became smaller as more stabilizers were added into the ice cream mix. As mentioned above, the stabilizer concentrations might have been approaching a threshold limit where further addition of stabilizers would not have slowed down the recrystallization anymore, and in fact, might have worked in the opposite direction. The smaller rate of change in both n and K values further suggested the above hypothesis. For 0.15% stabilized ice cream, the measured data generated a negative n value (-0.12), indicating a measurement error for this particular ice cream mix.

5.2.3 HARDNESS MEASUREMENTS

The hardness measurement was carried out to confirm the coarsening mechanism of sorbet over time which was observed in crystal size and distribution measurement. Shown below is the graph of force as a function of deformation for sorbet over time.

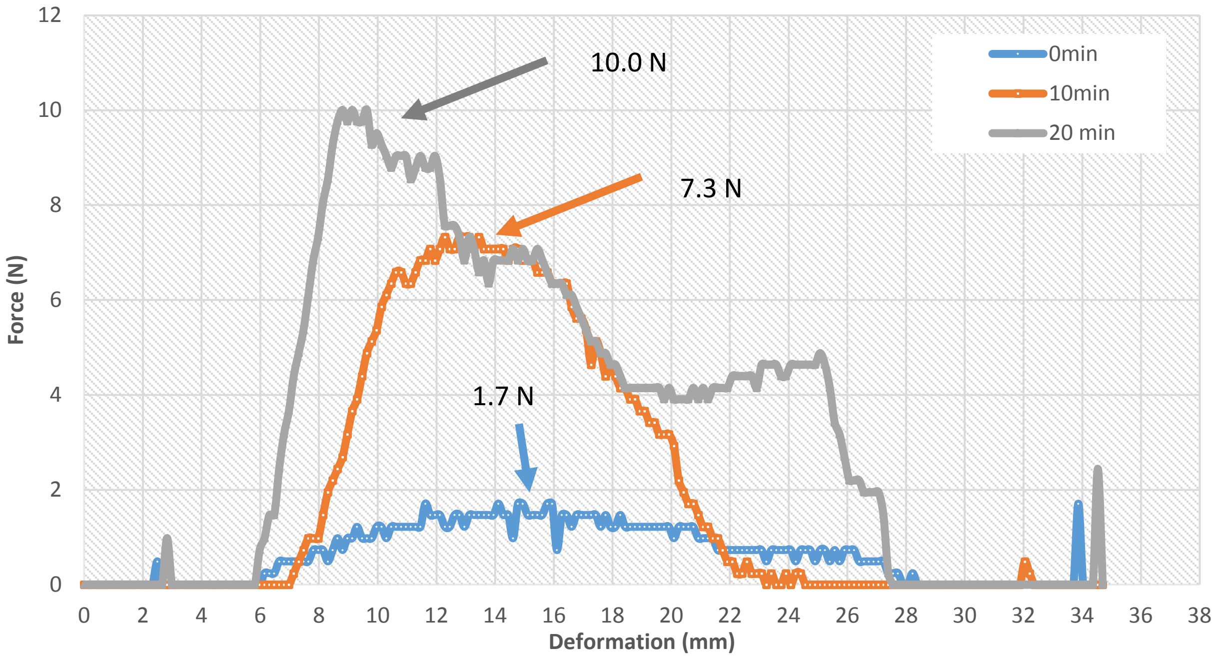

Figure 25. Hardness measurement for 0.00% stabilized ice cream over coarsening time. The peak force is defined as the hardness of sorbet at time intervals of 0, 10 and 20 minutes (shown by arrow and labeled).

As in the graph, the hardness for the ice cream sample for the time interval of 0, 10 and 20 minutes were 1.7, 7.3 and 10.0 N, respectively. When the ice cream was left outside of the fridge for longer time, it became harder due to the increasing number of large ice crystals according to Ostwald ripening and accretion mechanisms. Lower viscosity also contributed to the lower harness of ice cream sample over time. The data depicted the same trend between crystal size and ice cream hardness as Muse and Hartel (2004) found. Additionally, the hardness values confirmed the coarsening mechanism that was observed in crystal size and distribution measurement for ice cream. The longer time the sample was left out of the fridge, the larger the ice crystals, leading to higher hardness. This trend was also observed in hardness measurement of ice cream with different amount of stabilizers.

Additionally, the effect of stabilizers on the hardness of the ice cream was also investigated. A typical graph of the hardness measurement between unstabilized ice cream and ice cream with stabilizer would look like Figure 26. In this figure, the hardness measurement of unstabilized ice cream and ice cream with 0.05% stabilizer were shown.

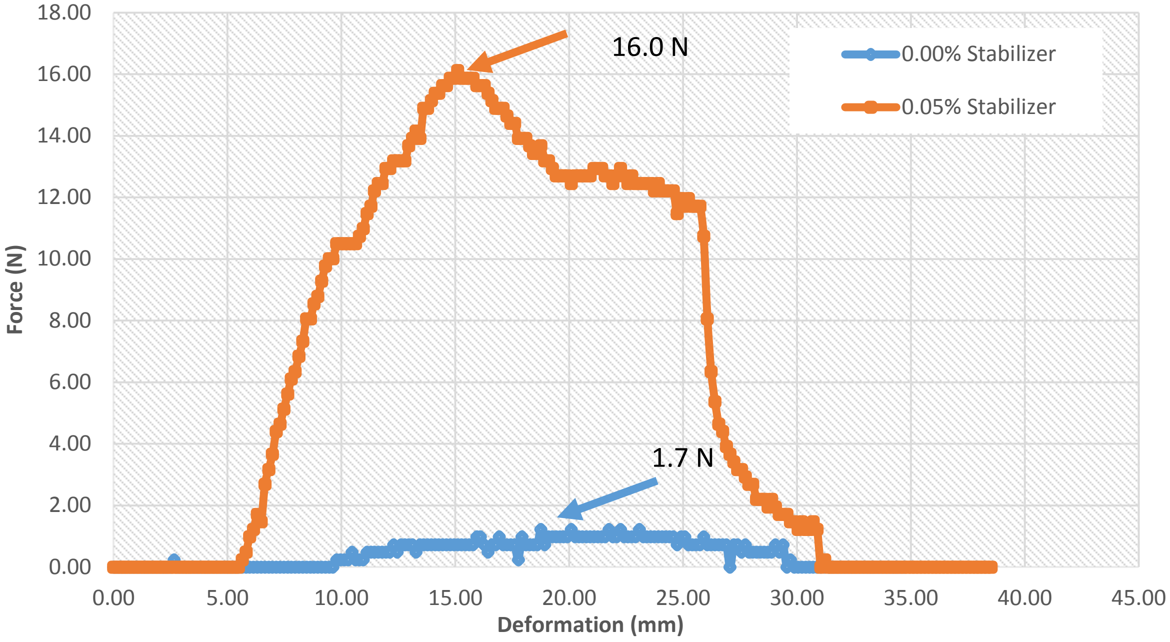

Figure 26. Hardness test for ice cream with and without stabilizer at 0 minute.

The hardness of ice cream with stabilizers was supposed to be higher than that of unstabilized ice cream since stabilizers retarded recrystallization process, leading to smaller ice crystals. However, the graph showed the opposite trend: the hardness of ice cream with stabilizers was smaller than that of unstabilized ice cream (1.7 N < 16.0 N). Since these data were at time interval of 0 min, the reason might have been that the stabilizers were not fully dissolved in ice cream mix and clustered together, creating the reverse effects on initial ice crystals. Thus, the initial ice crystals of stabilized ice cream were larger than those of unstabilized ice cream, which was confirmed in the crystals size and distribution measurement. As a result, the number of large ice crystals in stabilized ice cream was higher, leading to higher hardness. Additionally, due to the limitation of the equipment, only one ice cream batch could have been made per day, so unstabilized ice cream and stabilized ice cream were tested on different days. Therefore, the difference in temperature and humidity between days could have contributed to the opposite trend of the hardness measurement.

5.2.4 DSC MEASUREMENTS

To further confirm what was observed from microscope and hardness measurement, DSC was used to determine the heat of fusion and crystallinity of ice cream. These values for unstabilized and stabilized ice cream were shown in the following table.

Table 12. Heat of fusion and crystallinity of unstabilized and stabilized ice cream.

	Heat of fusion (J/g)	Crystallinity (%)
Ice cream without stabilizers	80.11	64
Ice cream with 0.05% stabilizers	91.43	73
Ice cream with 0.10% stabilizers	101.7	81
Ice cream with 0.15% stabilizers	110.8	88

As seen in the table, the ice cream without stabilizers had smaller heat of fusion compared to the ice cream with stabilizers. This meant that ice cream mix with stabilizer required higher energy to change the phase from liquid to solid. Additionally, the more stabilizers were added in the ice cream mix, the higher the heat of fusion was. Since crystallinity is the percentage of heat of fusion of ice cream over heat of fusion of water, higher heat of fusion results in higher crystallinity. From what was observed in microscope and hardness experiments, it was concluded that these values were higher because of the increase in size of ice crystals. As mentioned earlier, due to the equipment limitation, the stabilizers were not fully dissolved in the ice cream mix, leading to an inhomogeneous nature of ice cream. Hence, the stabilizers increased instead of reduced the initial crystals size.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The coarsening of sorbet and ice cream over time was clearly observed through microscopic images. The crystals size of both sorbet and ice cream increased with increasing time that the sample was left outside of the fridge. Since coarsening is a time-dependent process, coarsening increased with increasing time of temperature fluctuations. Additionally, since hardness is an indirect measure of ice crystal size, the hardness test was also conducted. At a longer time interval, hardness increased, indicating that the size of crystals increased over time. This further confirmed the coarsening process occurred in sorbet and ice cream. Furthermore, the weighted average crystal size over time fitted in between interface surface energy and diffusion kinetic model, suggesting that the ice cream coarsening effect might have been mixed control. However, due to the large standard deviations of the weighted average crystal size, more experiments should be conducted to confirm the dominant coarsening kinetics in this particular ice cream.

The data obtained from microscopy experiments shows that the coarsening rate of stabilized ice cream was smaller than that of unstabilized ice cream. This implied that the combination of locust bean gum and guar gum did reduce the coarsening rate in ice cream. Moreover, the data from viscosity measurement also reinforced the effects of stabilizers on ice cream coarsening. Compared to unstabilized ice cream, stabilized ice cream had a higher viscosity, and thus, inhibited crystals mobility and decreased the diffusion rate of ice crystals. As a result, adding stabilizers in ice cream mix diminished the coarsening rate.

Even though stabilizers carried out their function, which is to decrease coarsening rate, the ice crystals size was observed to be larger in stabilized ice cream than in unstabilized ice cream. The main reason could be that the stabilizers were not fully dissolved in the ice cream mix due to the equipment limitation. As a result, even though stabilizers reduced the coarsening rate, since the initial ice crystals in the mix were already big, the weighted average crystal size for each time interval of stabilized ice cream were larger than that of unstabilized ice cream. Additionally, at 0 minute, the hardness was also higher for stabilized ice cream, confirming that the initial crystal size of stabilized ice cream was larger than that of unstabilized ice cream. Moreover, the crystallinity of stabilized ice cream was found to be higher, which further supported this conclusion.

Hardness of sorbet was determined to higher than that of ice cream at all time intervals of 0, 10, and 20 minutes, which is consistent with the nature of sorbet. However, sorbet average crystal size was found to be smaller than that of both unstabilized and stabilized ice cream. This reverse trend might have been due to the more controlled environment that Häagen-Dazs sorbet was manufactured in.

Since the accuracy of the data was significantly affected by the conditions of the experiments, it is recommended to obtain data under a better controlled environments and equipment. A fluorescence microscope with a cold stage is required for better results. Ice cream and sorbet should also be prepared in a temperature-controlled environment to prevent temperature fluctuations. Higher quality stabilizers should be ensured for ice cream preparation, and the ice cream solution should be better-mixed.

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8.0 APPENDIX

8.1 ICE CREAM FORMULATIONS

Following the ice cream formula of 10% fat, 12% milk-solids-not-fat (MSNF), 15% dextrose, 0.15% mono-diglycerides (MNG), and 0.05 to 0.15% stabilizers, the following calculations yield the component mass for each ice cream batch of 938.39g.

$$Mass\ of\ fat = (1000)(0.10) = 100g$$

$$Mass\ of\ MSNF = (1000)(0.12) = 120g$$

$$Mass\ of\ dextrose = (1000)(0.15) = 150g$$

$$Mass\ of\ MNG = (1000)(0.0015) = 1.5g$$

$$Minimum\ mass\ of\ stabilizers = (1000)(0.0005) = 0.5g$$

$$Minimum\ mass\ of\ locust\ bean\ gum = (0.5)(0.75) = 0.375g$$

$$Minimum\ mass\ of\ guar\ gum = (0.5)(0.25) = 0.125g$$

In every 15mL of heavy cream, there are 5g of fat and 1g of sugar. Since heavy cream is the only ingredient that contributes to the fat content of the ice cream, its required volume is calculated first.

$$V_{heavy\ cream} = \frac{(15mL\ heavy\ cream)(100g\ fat)}{5g\ fat} = 300mL$$

Since 300mL is used for the ice cream recipe, the amount of sugar from heavy cream is then determined.

$$m_{sugar} = \frac{(300mL\ heavy\ cream)(1g\ sugar)}{15mL\ heavy\ cream} = 20g$$

In every 23g of MSNF, there is 12g of sugar. When 120g of MSNF is used per ice cream batch, the amount of added sugar from MSNF is calculated.

$$m_{sugar} = \frac{(120g\ MSNF)(12g\ sugar)}{23g\ sugar} = 62.61g$$

Then, the total amount of dextrose to be added in each ice cream batch is as follows.

$$m_{dextrose} = 150g - 20g - 62.61g = 67.39g$$

Since every 50mL of heavy cream weighs about 53.80g, density of heavy cream is generated.

$$\rho_{heavy\ cream} = \frac{53.80g}{50mL} = 1.076\frac{g}{mL}$$

The mass of heavy cream per ice cream batch,

$$m_{heavy\ cream} = (300mL)\left(1.076\frac{g}{mL}\right) = 322.8g$$

Therefore, the maximum mass of water per ice cream batch,

$$m_{water} = 938.39 - m_{heavy\ cream} - m_{MSNF} - m_{dextrose} - m_{MNG} - m_{stabilizers}$$

$$m_{water} = 938.39g - 322.8g - 120g - 67.39g - 1.5g - 0.5g = 426.2g$$

Table 13. Summary of different ice cream formulations.

		0.00% stabilizers	0.05% stabilizers	0.10% stabilizers	0.15% stabilizers
Heavy cream (mL)		300	300	300	300
Dextrose (g)		67.39	67.39	67.39	67.39
MNF (g)		1.5	1.5	1.5	1.5
MSNF (g)		120	120	120	120
Water (g)		426.2	425.7	425.2	424.7
Stabilizers (g)	Locust Bean Gum	0	0.375	0.75	1.125
	Guar Gum	0	0.125	0.25	0.38

8.2 CALCULATION OF WEIGHT AVERAGE CRYTAL SIZE

A typical calculation of weight average crystal size was shown below using the data for sorbet for run 1 of 0 minute. Firstly, the weight average crystal size was calculated as in the figure below in which N is the number of crystals that have the same size and D is the crystal size.

$$\overline{D_w} = \frac{\sum_{i=1}^{\infty} N_i\, D_i^2}{\sum_{i=1}^{\infty} N_i\, D_i} = \frac{\sum_{i=1}^{217} N_i\, D_i^2}{\sum_{i=1}^{217} N_i\, d_i} = 18.4\ \mu m$$

The crystal size fraction of ice crystal i was then determined by dividing the size of crystal i to the sum of all crystal size. For example, the crystal size fraction of ice crystal with the size of 18.31 µm was calculated as below.

$$w_i = \frac{N_i D_i}{\sum_{i=1}^{\infty} N_i\, D_i} = \frac{1 * 18.35}{\sum_{i=1}^{217} N_i\, D_i} = 5.88 * 10^{-3}$$

Other crystal size fractions were also obtained using the equation above. All the crystal size fractions were then used to calculate$\overline{M_N}$.

$$\overline{D_N} = \frac{1}{\sum_{i=1}^{\infty} \frac{w_i}{D_i}} = \frac{1}{\sum_{i=1}^{217} \frac{w_i}{D_i}} = 14.4\ \mu m$$

Finally, the standard deviation of the weight average crystal size for run 1 of 0 min was carried out.

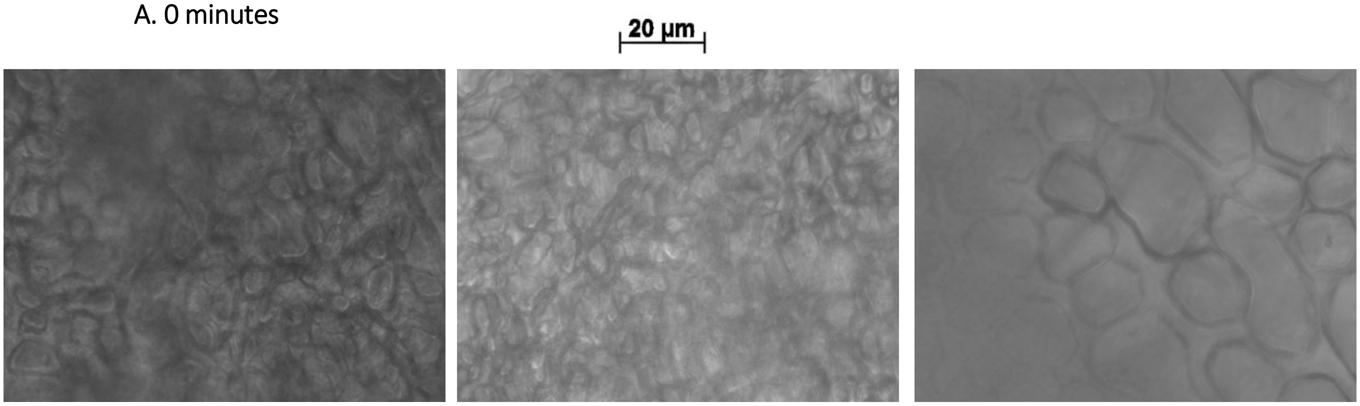
$$\sigma = \overline{D_N} \sqrt{\frac{\overline{D_W}}{\overline{D_N}} - 1} = 14.4 \sqrt{\frac{18.4}{14.4} - 1} = 7.6$$

The same method was repeated for all the runs of sorbet and ice cream.

8.3 SORBET ICE CRYSTAL ANALYSIS

8.3.1 ICE CRYSTAL STRUCTURE

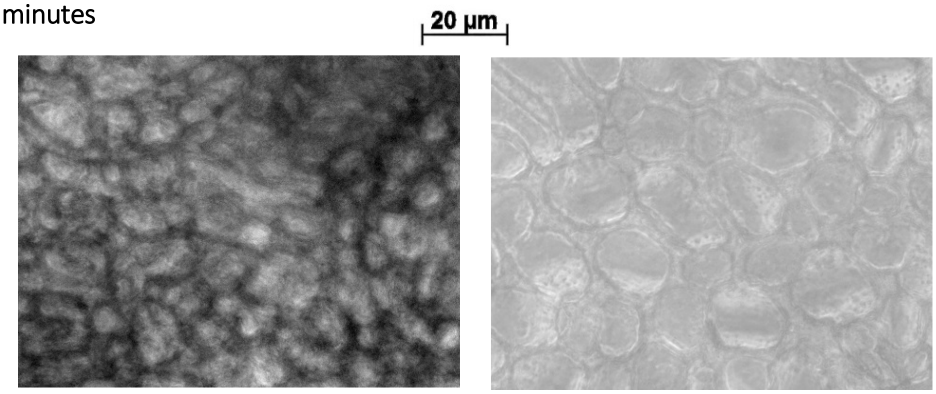
A. 0 minutes



Run 1 Run 2 Run 3

Figure 27. Crystal images for sorbet samples at 0 min for three runs.

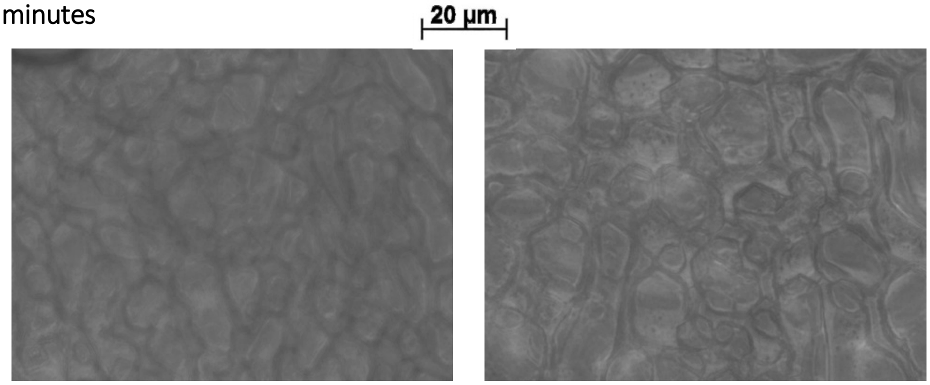
B. 10 minutes



Run 1 Run 2

Figure 28. Crystal images for sorbet samples at 10 min for two runs.

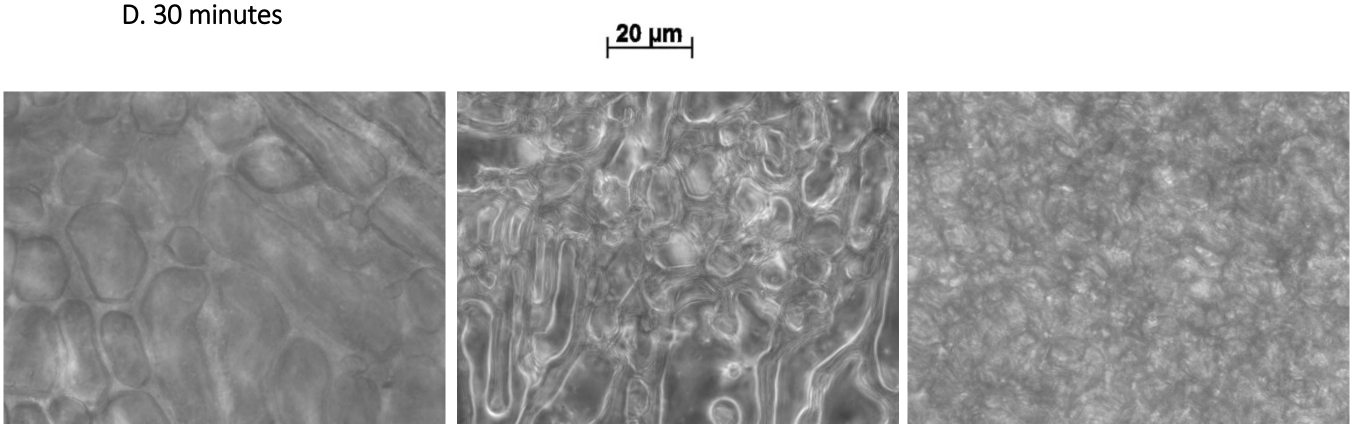
C. 20 minutes



Run 1 Run 2

Figure 29. Crystal images for sorbet samples at 20 min for two runs.

D. 30 minutes



Run 1 Run 2 Run 3

Figure 30. Crystal images for sorbet samples at 30 min for three runs.

E. 40 minutes

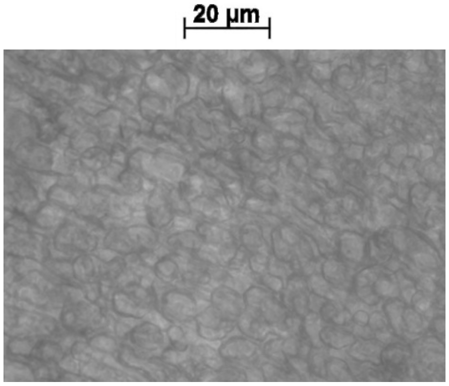


Figure 31. Crystal images for sorbet samples at 40 min.

F. 50minutes

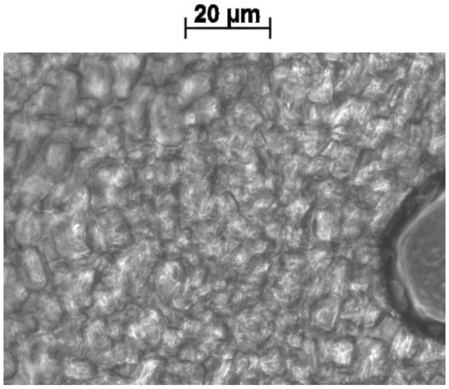


Figure 32. Crystal images for sorbet samples at 50 min.

8.3.2 ICE CRYSTAL DISRIBUTION

A. 0 minutes

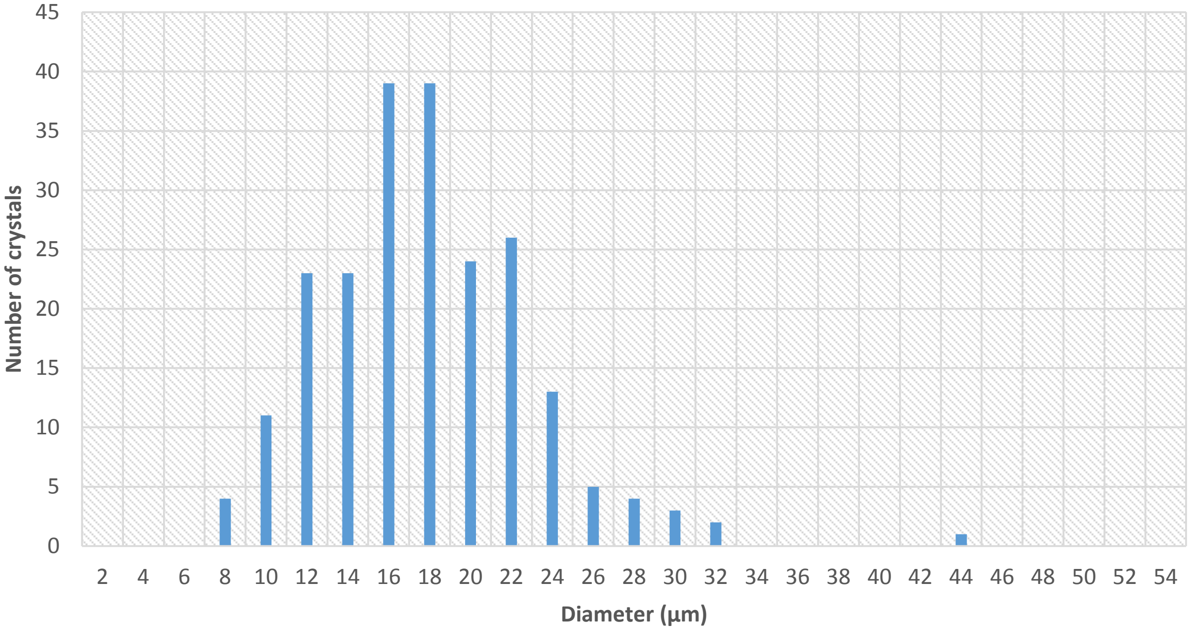


Figure 33. Ice crystal distribution of sorbet at 0 min (Run 1).

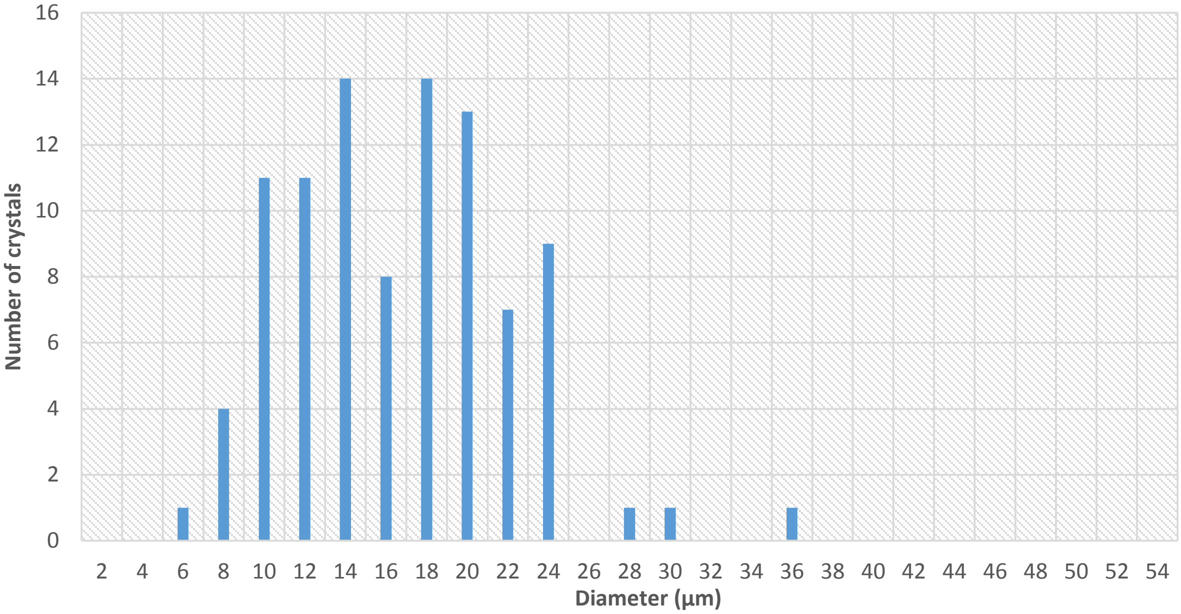


Figure 34. Ice crystal distribution of sorbet at 0 min (Run 2).

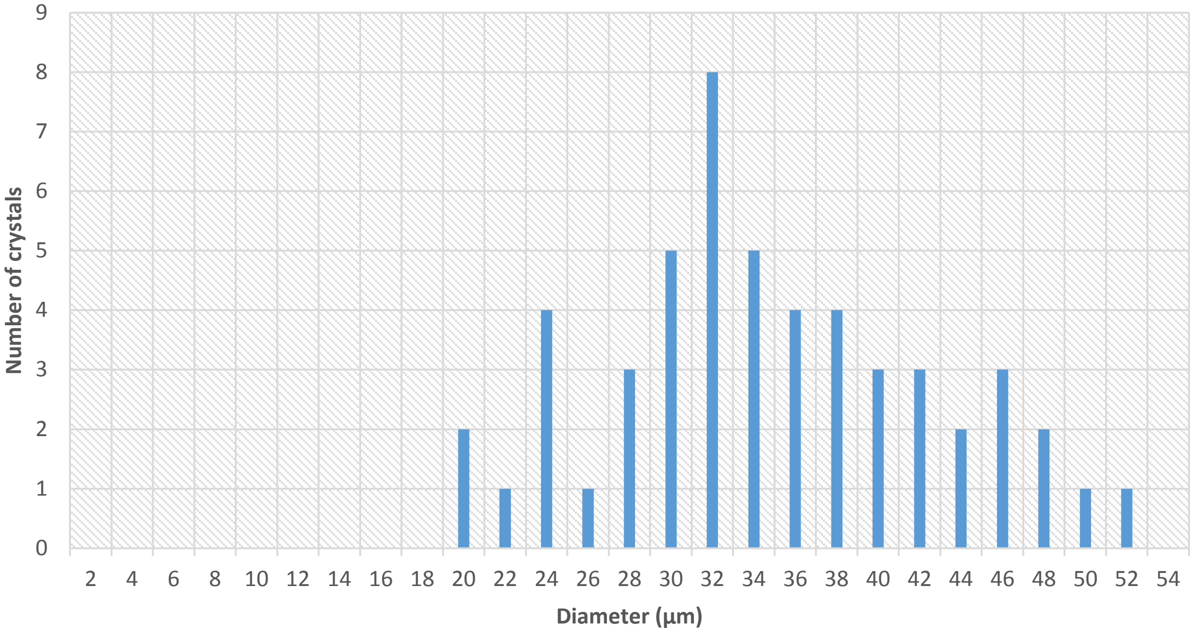


Figure 35. Ice crystal distribution of sorbet at 0 min (Run 3).

B. 10 minutes

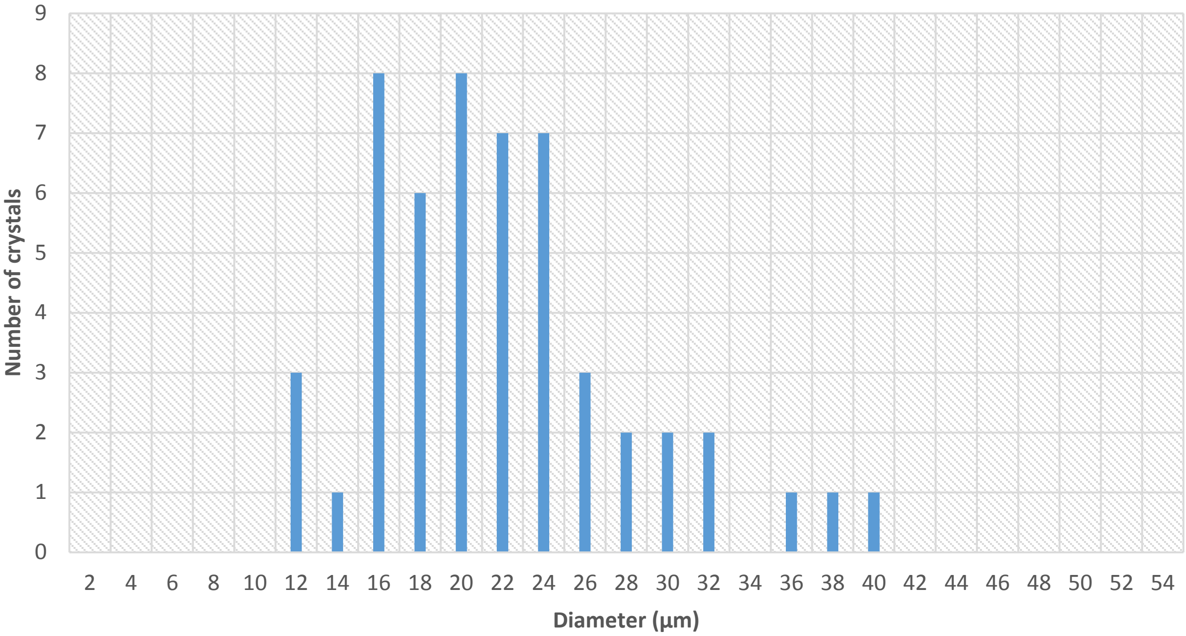


Figure 36. Ice crystal distribution of sorbet at 10 min (Run 1).

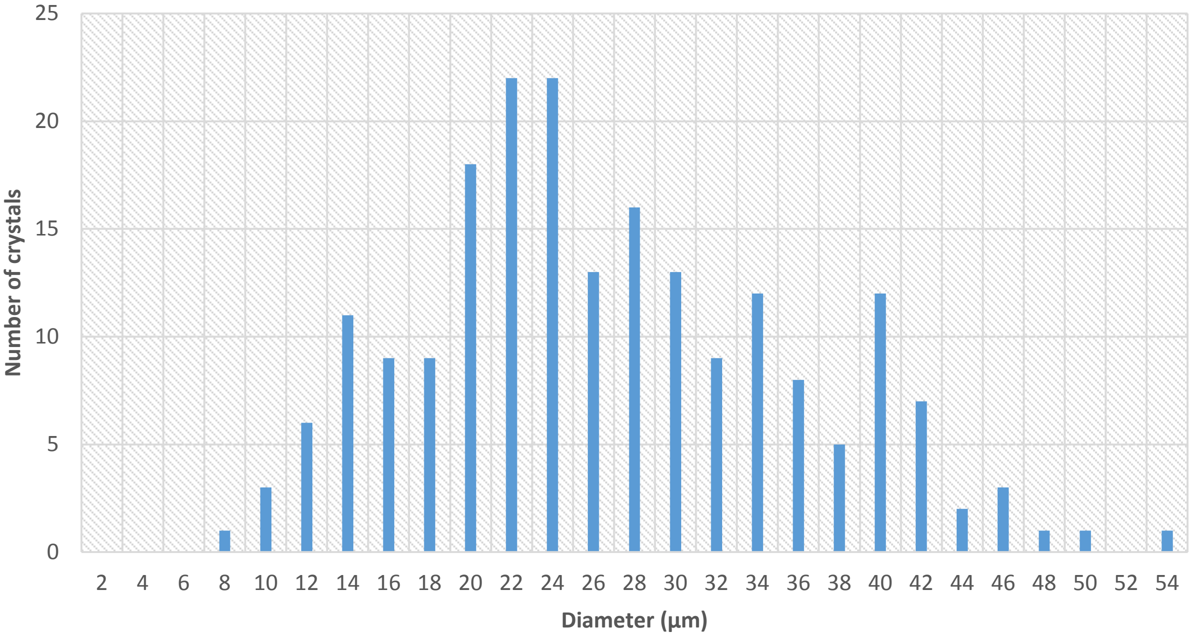


Figure 37. Ice crystal distribution of sorbet at 10 min (Run 2).

C. 20 minutes

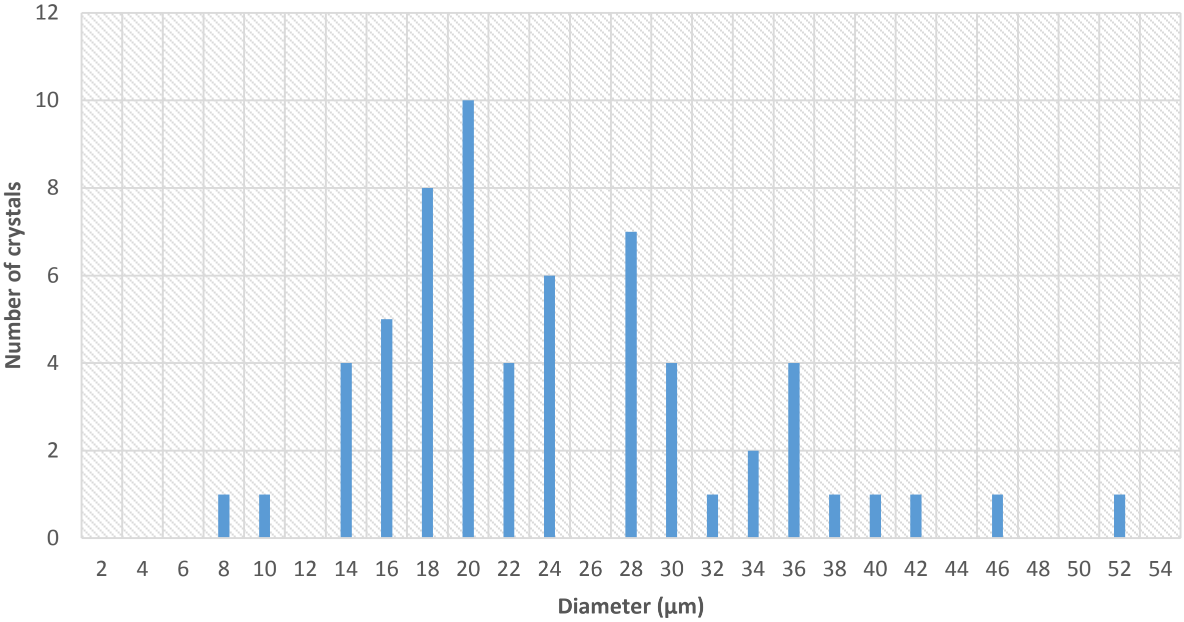


Figure 38. Ice crystal distribution of sorbet at 20 min (Run 1).

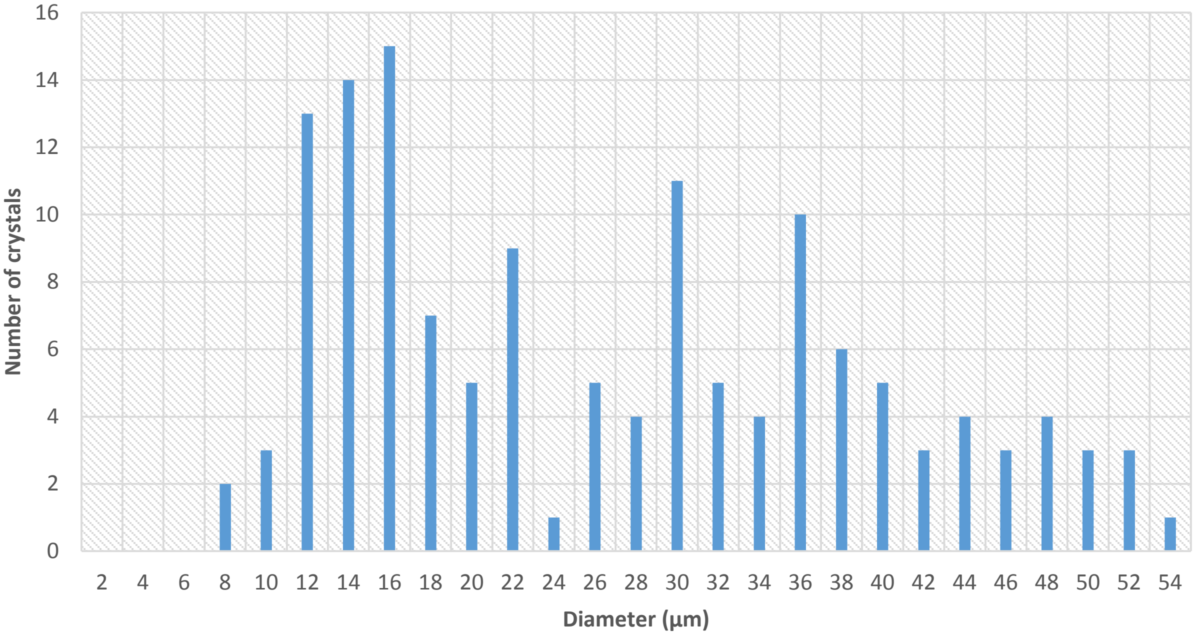


Figure 39. Ice crystal distribution of sorbet at 20 min (Run 2).

D. 30 minutes

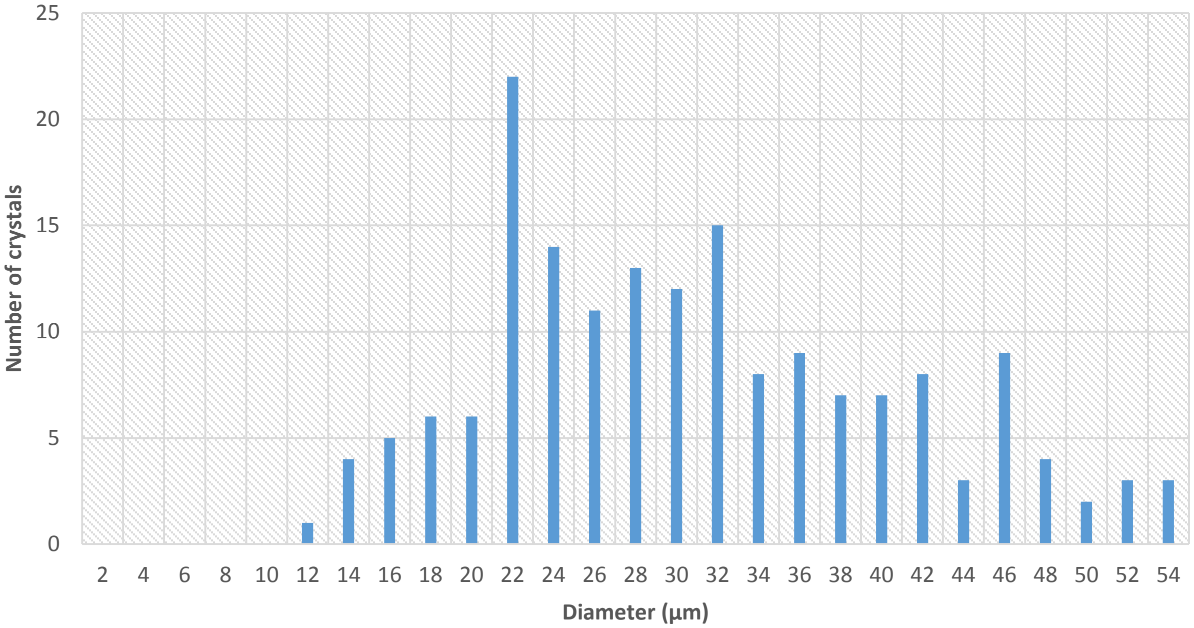


Figure 40. Ice crystal distribution of sorbet at 30 min (Run 1).

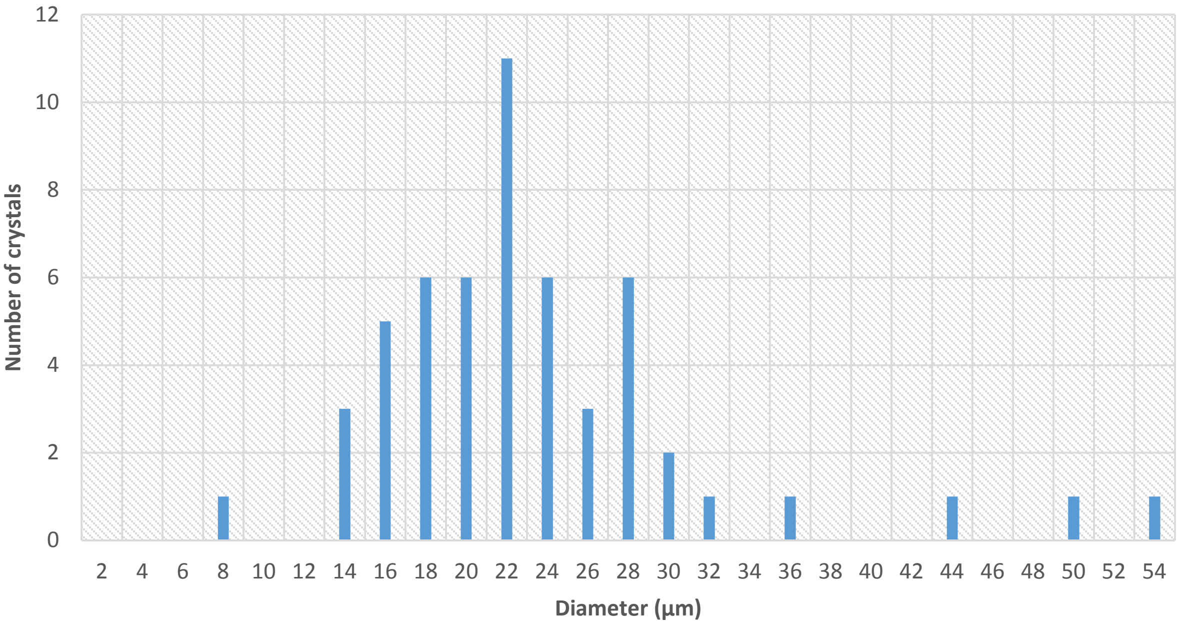


Figure 41. Ice crystal distribution of sorbet at 30 min (Run 2).

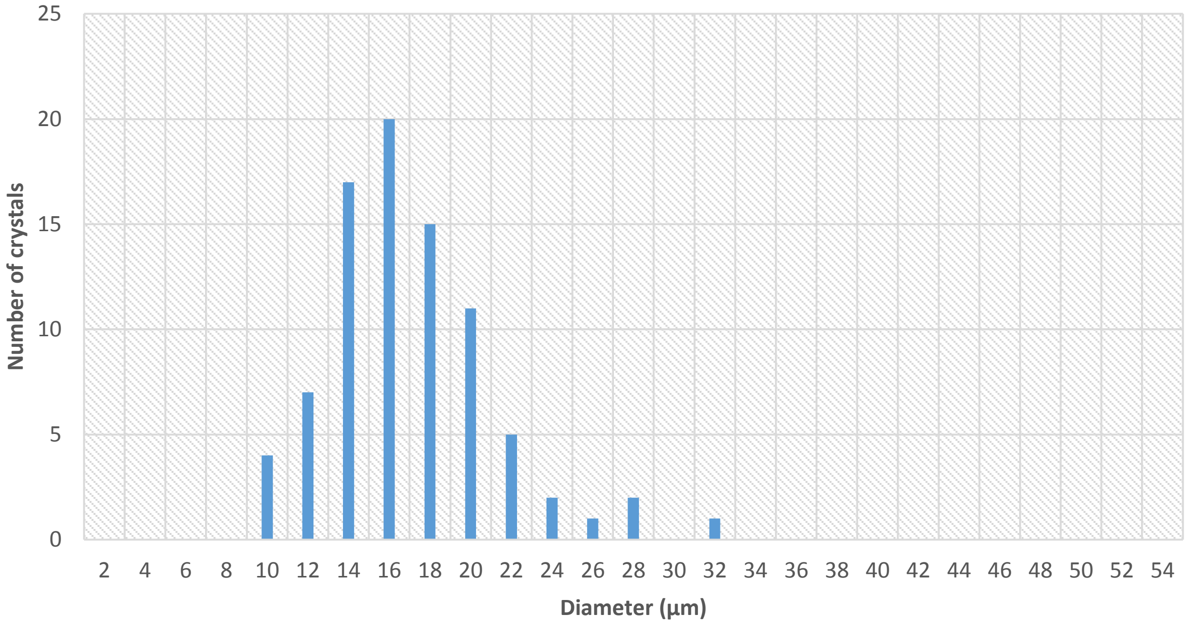


Figure 42. Ice crystal distribution of sorbet at 30 min (Run 3).

E. 40 minutes

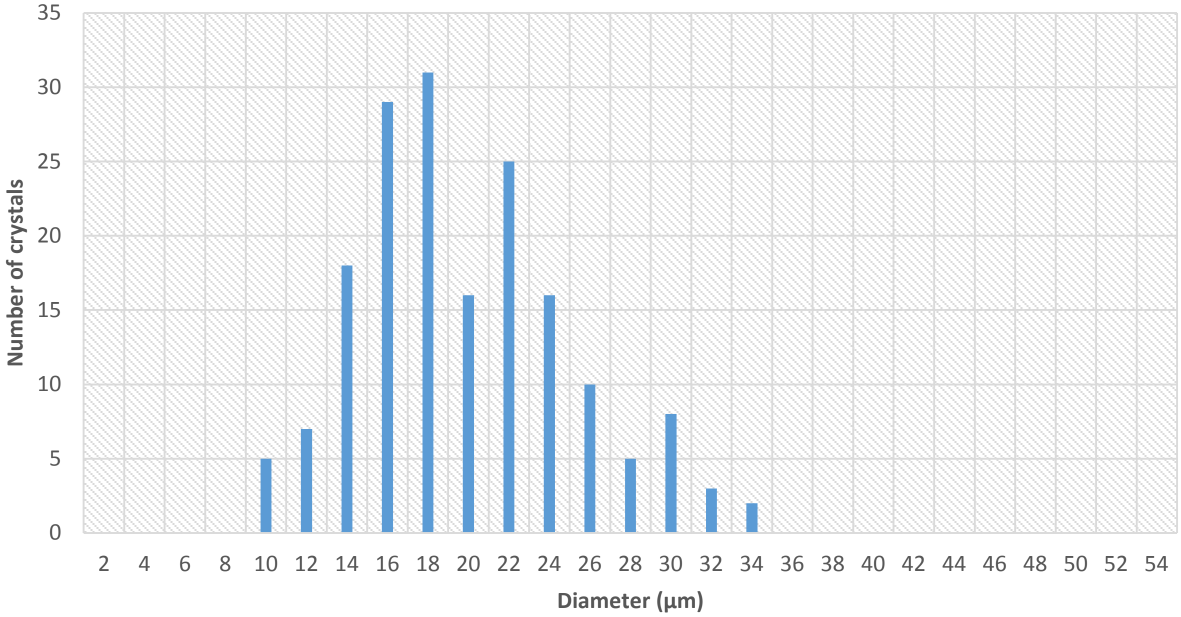


Figure 43. Ice crystal distribution of sorbet at 40 min.

F. 50 minutes

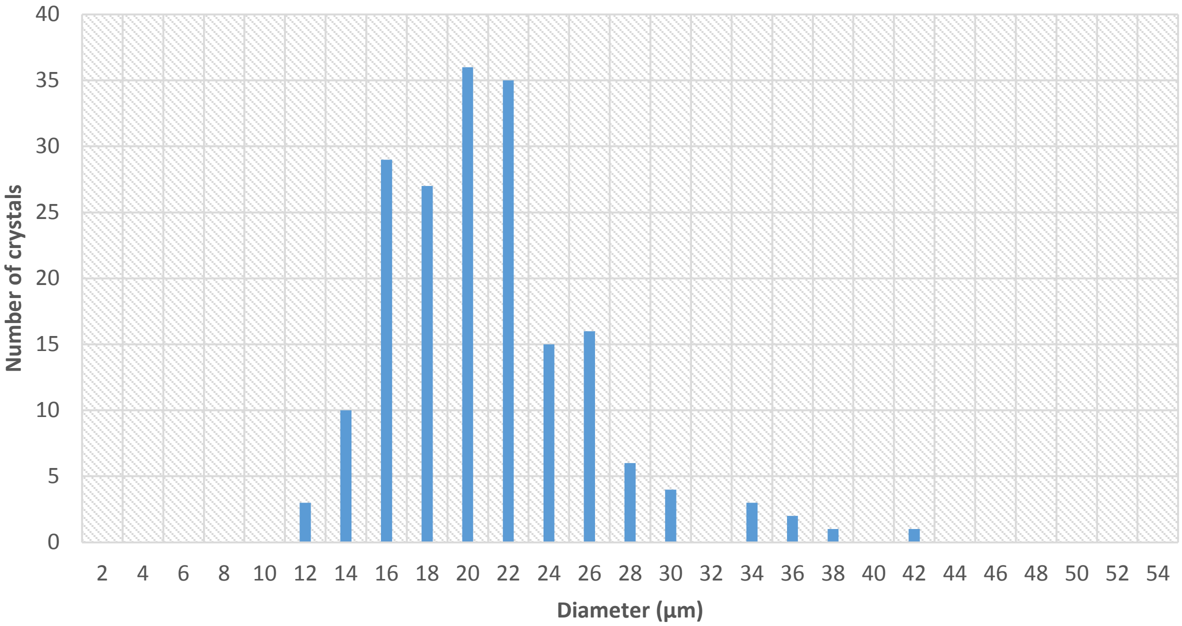


Figure 44 . Ice crystal distribution of sorbet at 50 min.

8.3.3 ICE CRYSTAL MELTING MECHANISM

A. 0 minutes

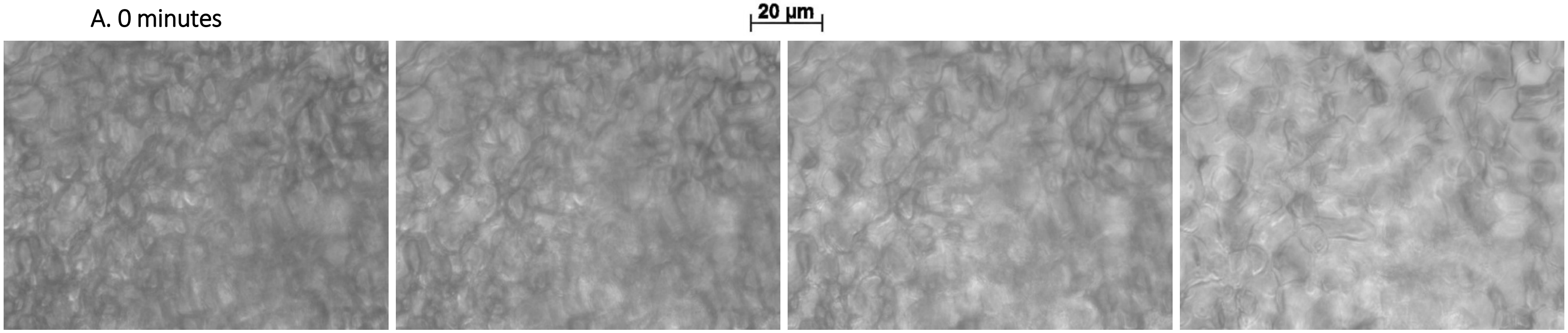


Figure 45. Ostwald ripening for sorbet at 0 min (Run 2).

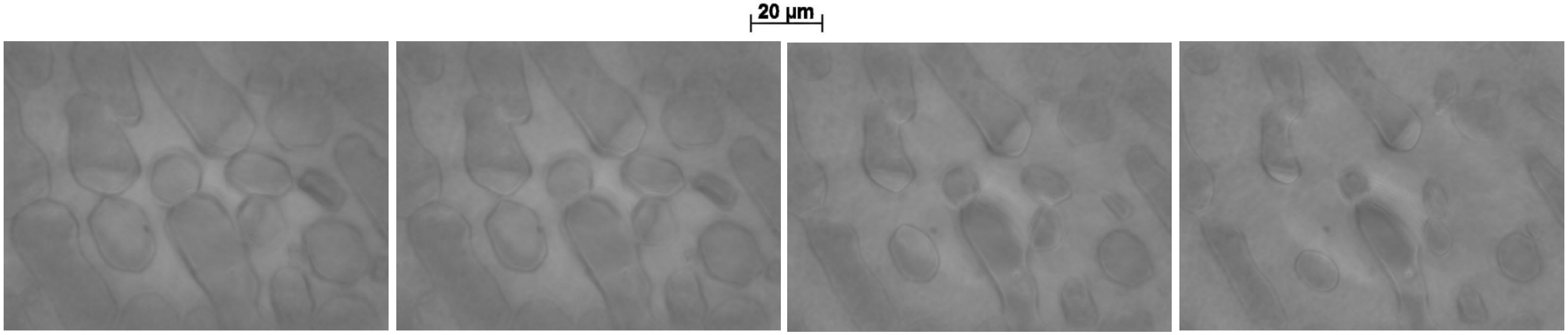


Figure 46. Ostwald ripening for sorbet at 0 min (Run 3).

B. 10 minutes

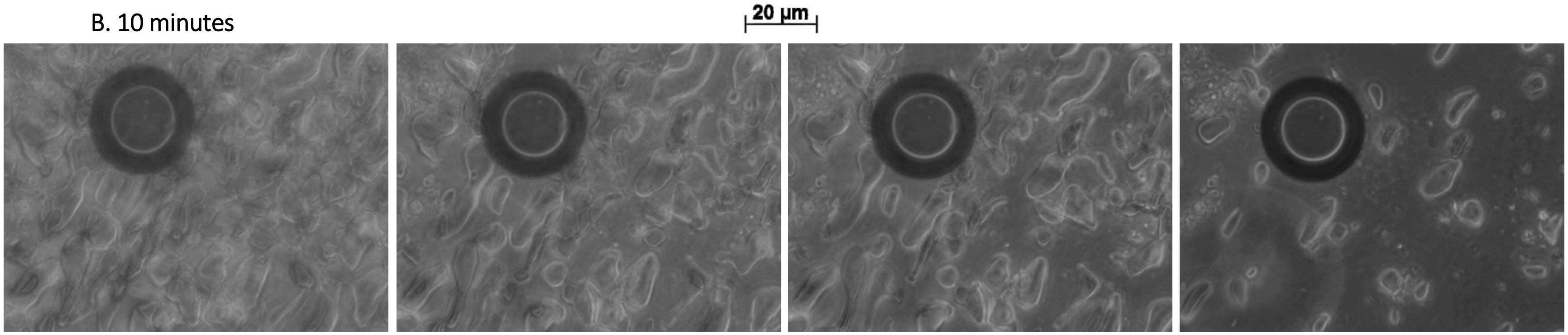


Figure 47. Ostwald ripening for sorbet at 10 min (Run 1).

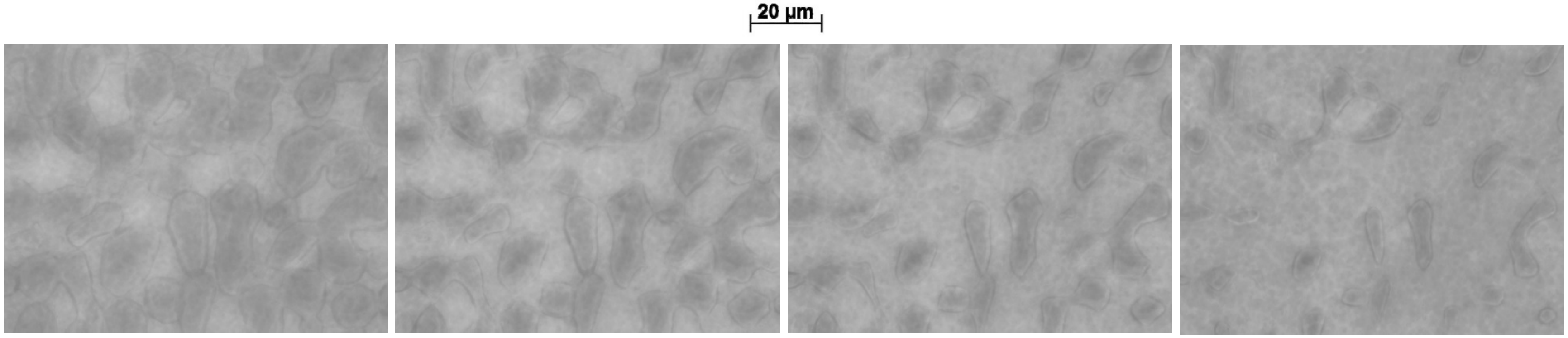


Figure 48. Ostwald ripening for sorbet at 10 min (Run 2).

C. 20 minutes

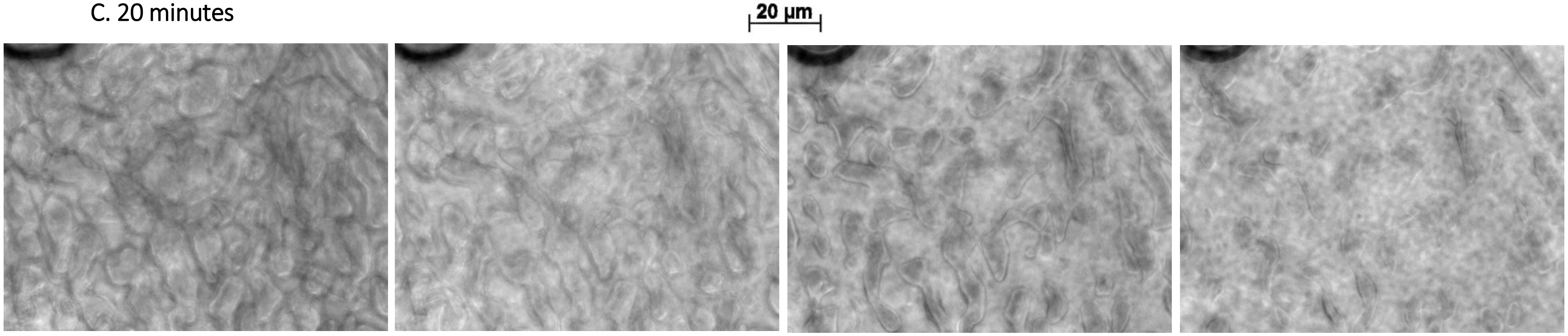


Figure 49.Ostwald ripening for sorbet at 20 min (Run 1).

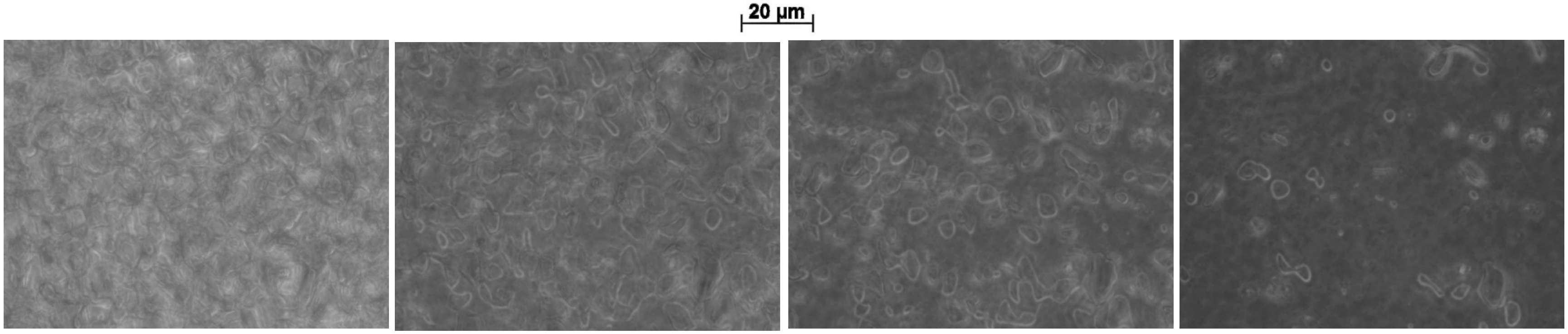


Figure 50. Ostwald ripening for sorbet at 20 min (Run 2).

D. 30 minutes

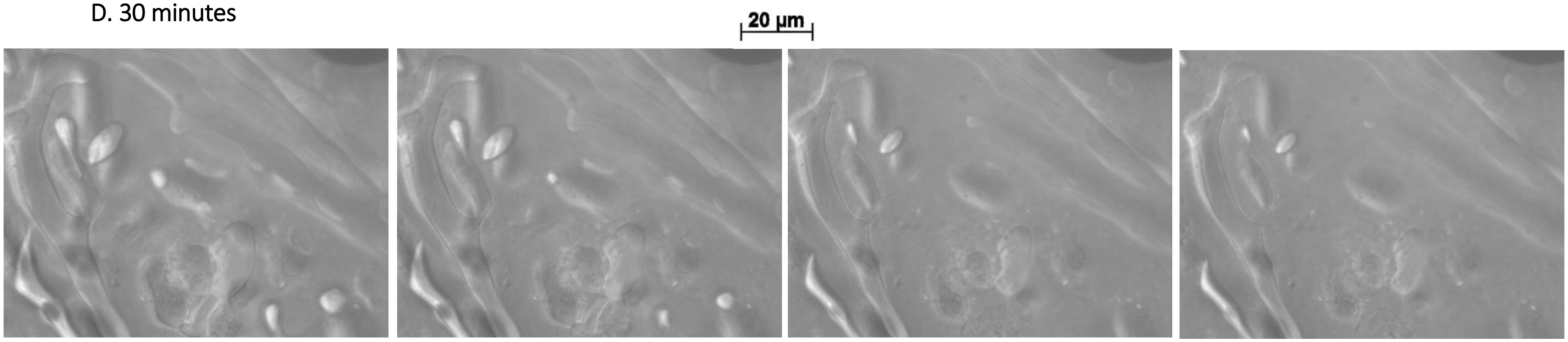


Figure 51. Ostwald ripening for sorbet at 30 min (Run 1).

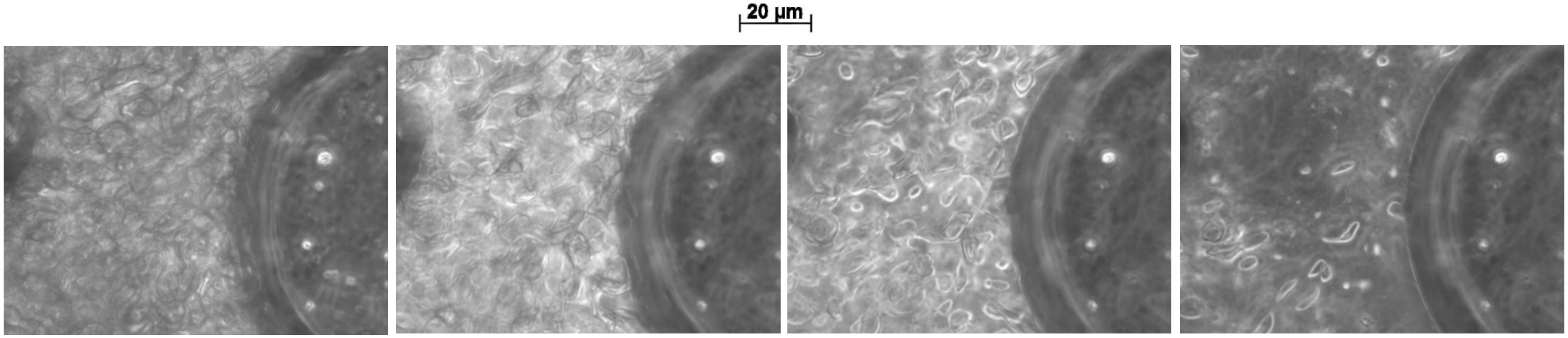


Figure 52. Ostwald ripening for sorbet at 30 min (Run 2).

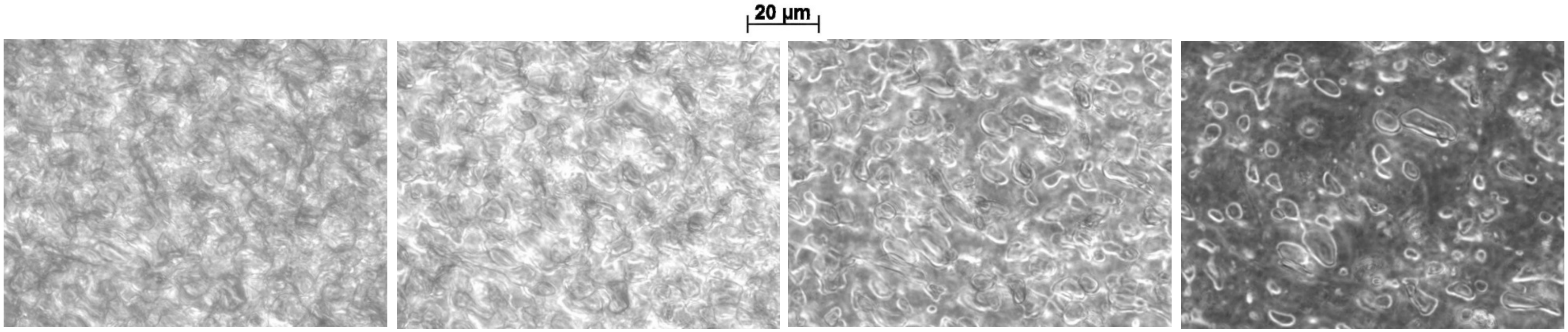


Figure 53. Ostwald ripening for sorbet at 30 min (Run 3).

E. 40 minutes

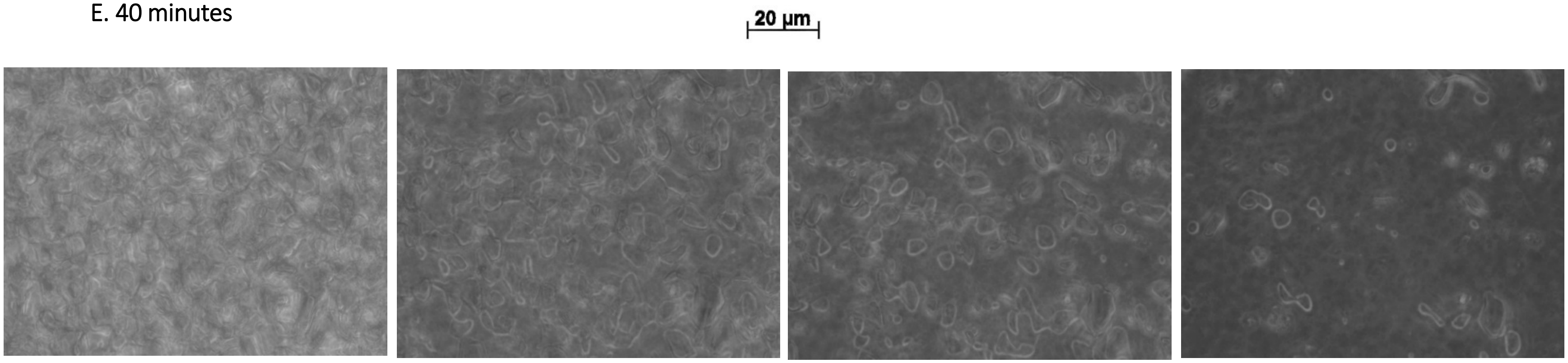


Figure 54. Ostwald ripening for sorbet at 40 min.

F. 50 minutes

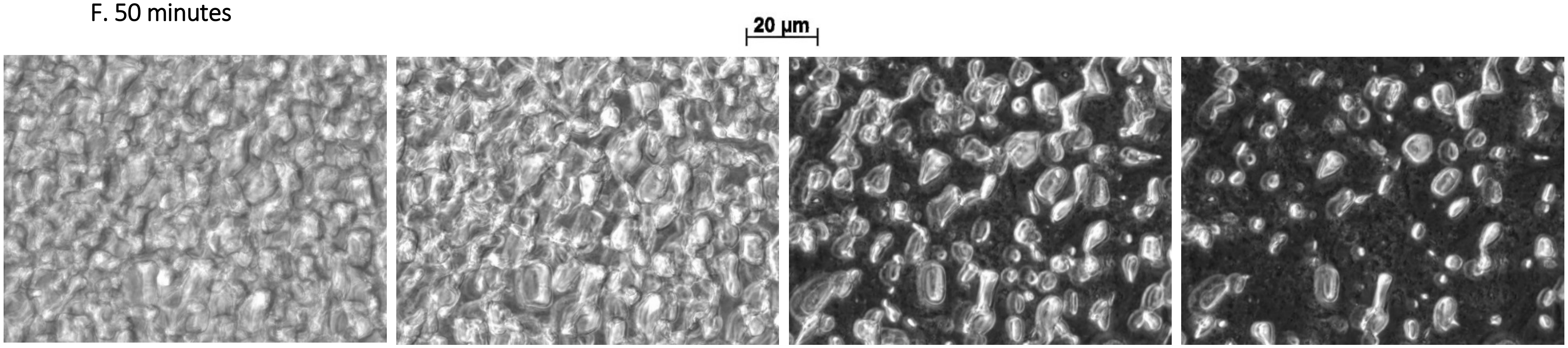
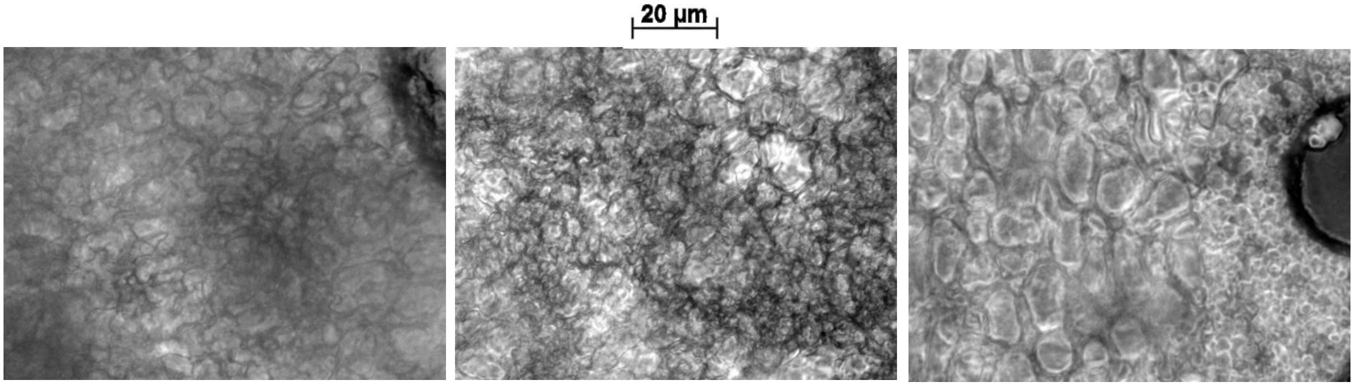


Figure 55. Ostwald ripening for sorbet at 50 min.

8.4 ICE CREAM ICE CRYSTAL ANALYSIS

8.4.1 ICE CRYSTAL STRUCTURE

A. 0.00% stabilized ice cream



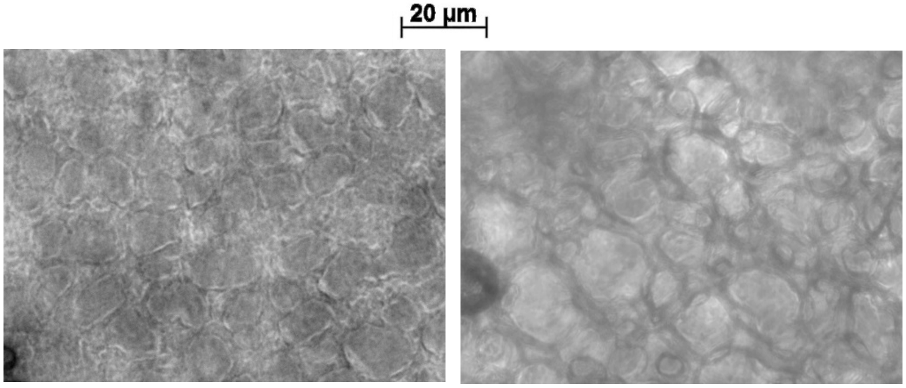
0 min

10 min

20 min

Figure 56. Crystal images for 0.00% stabilized samples (Run 1).

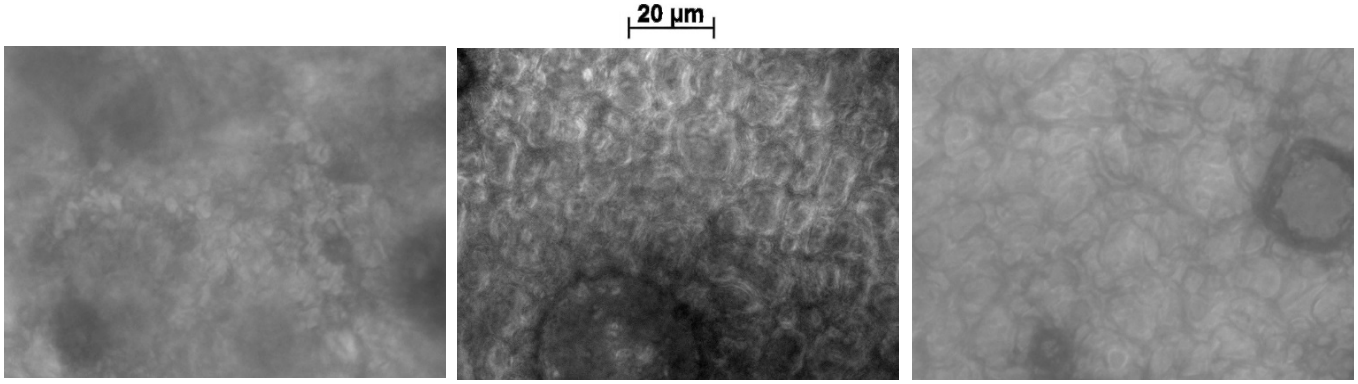
B. 0.05% stabilized ice cream



0 hour

1 hour

Figure 57. Crystal images for 0.05% stabilized ice cream samples (Run 1).



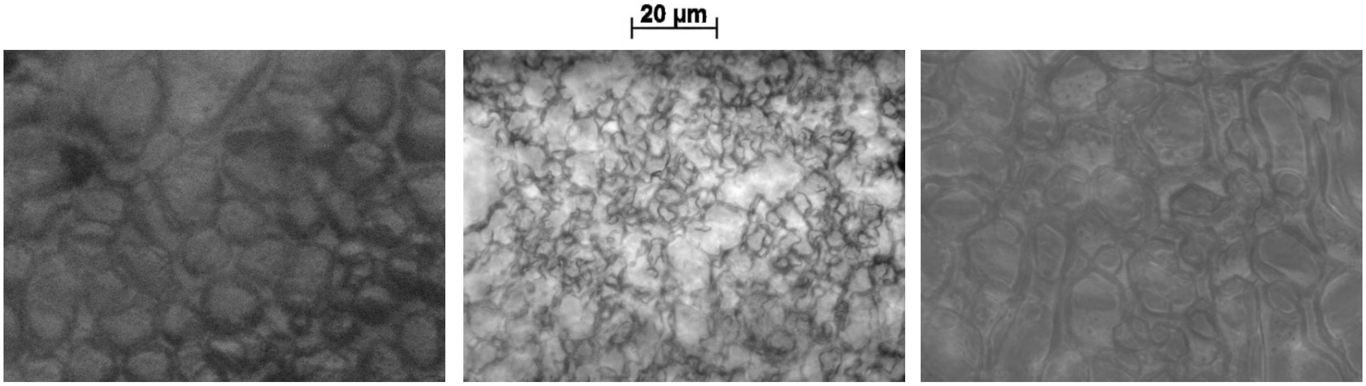
0 min

10 min

20 min

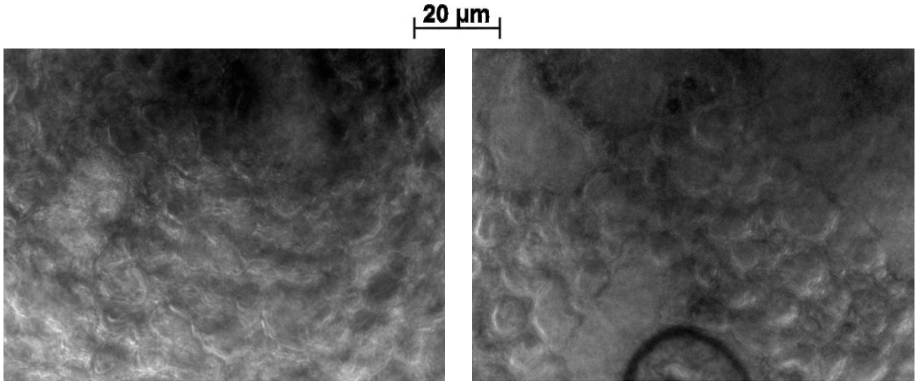
Figure 58. Crystal images for 0.05% stabilized ice cream samples (Run 2).

C. 0.10% stabilized ice cream



0 min 10 min 20 min

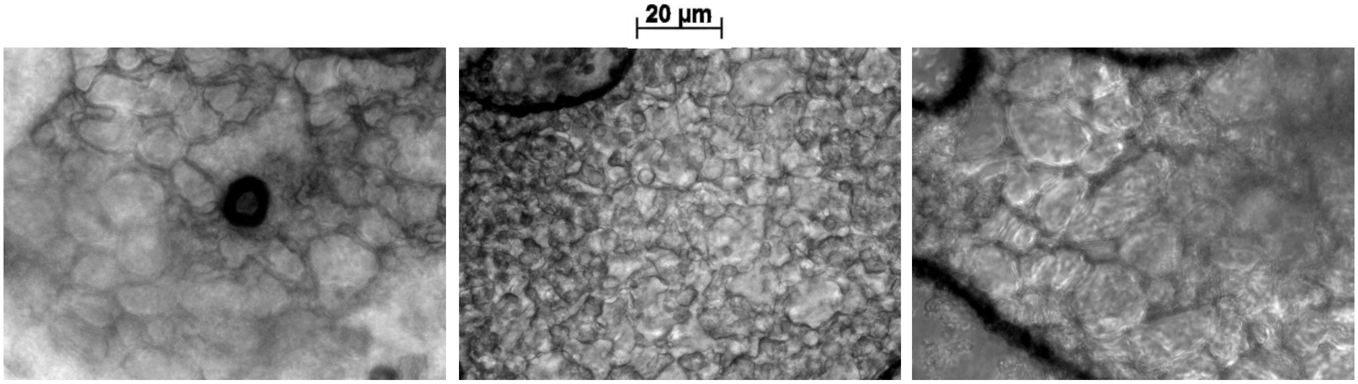
Figure 59. Crystal images for 0.10% stabilized ice cream samples (Run 1).



10 min 20 min

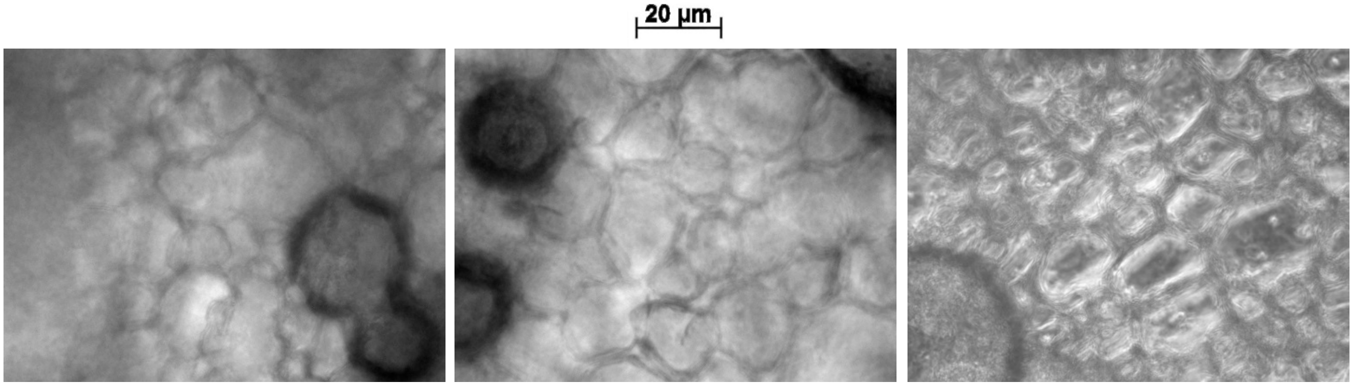
Figure 60. Crystal images for 0.10% stabilized ice cream samples (Run 2).

D. 0.15% stabilizer ice cream



0 min 10 min 20 min

Figure 61. Crystal images for 0.10% stabilized ice cream samples (Run 3).

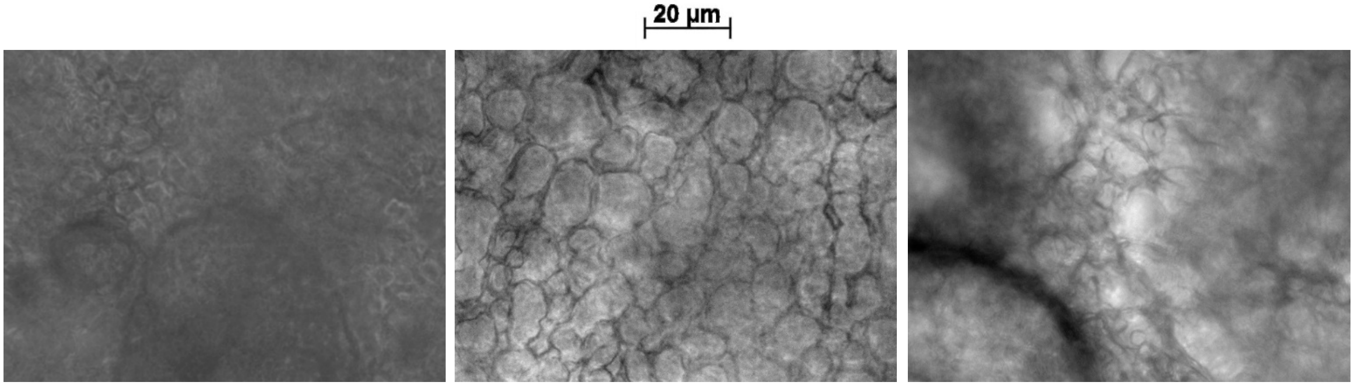


0 min

10 min

20 min

Figure 62. Crystal images for 0.15% stabilized ice cream samples (Run 1).



0 min

10 min

20 min

Figure 63. Crystal images for 0.15% stabilized ice cream samples (Run 2).

8.4.2 ICE CRYSTAL DISTRIBUTION

A. 0.00% stabilized ice cream

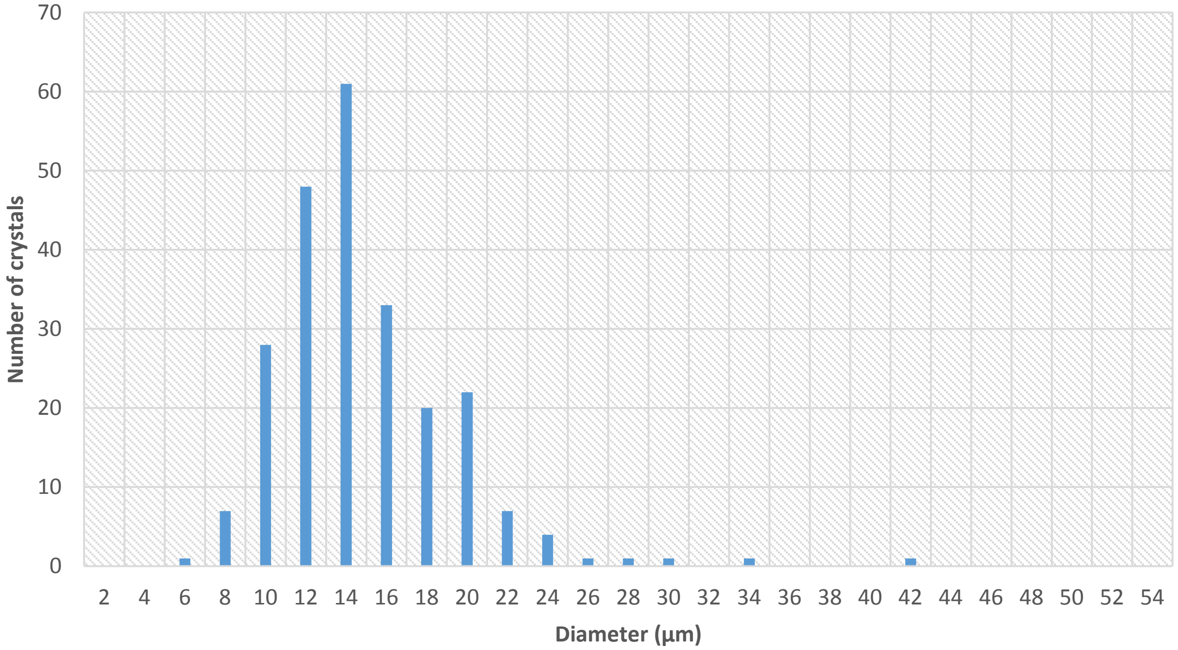


Figure 64. Ice crystal distribution of 0.00% stabilized ice cream at 0 min (Run 1).

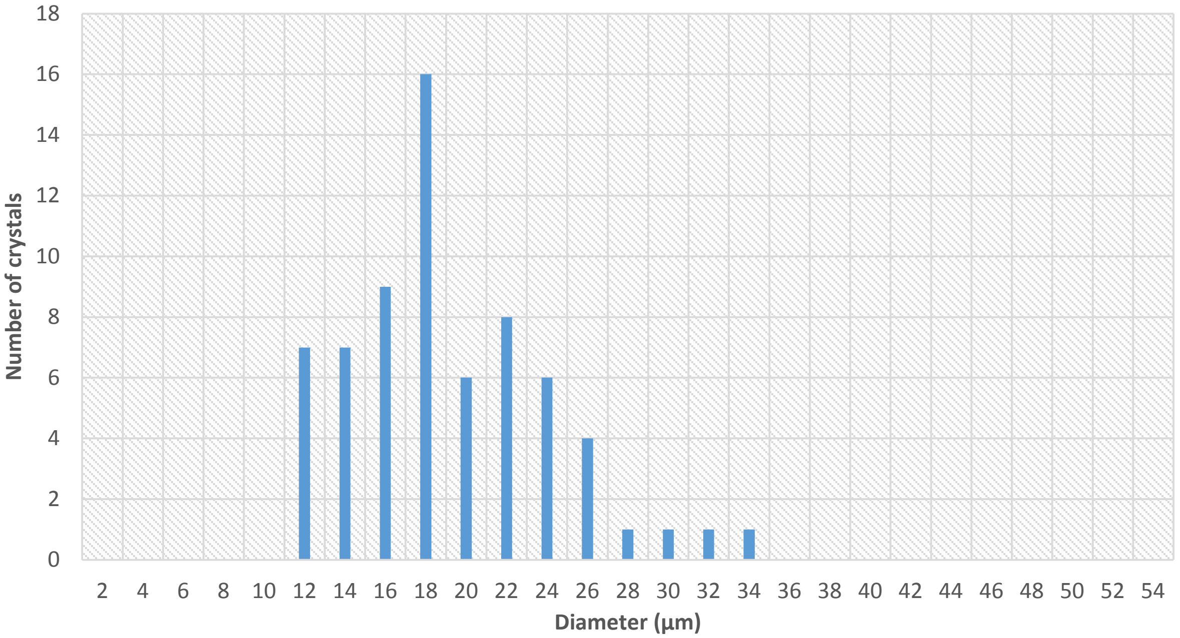


Figure 65. Ice crystal distribution of 0.00% stabilized ice cream at 10 min (Run 1).

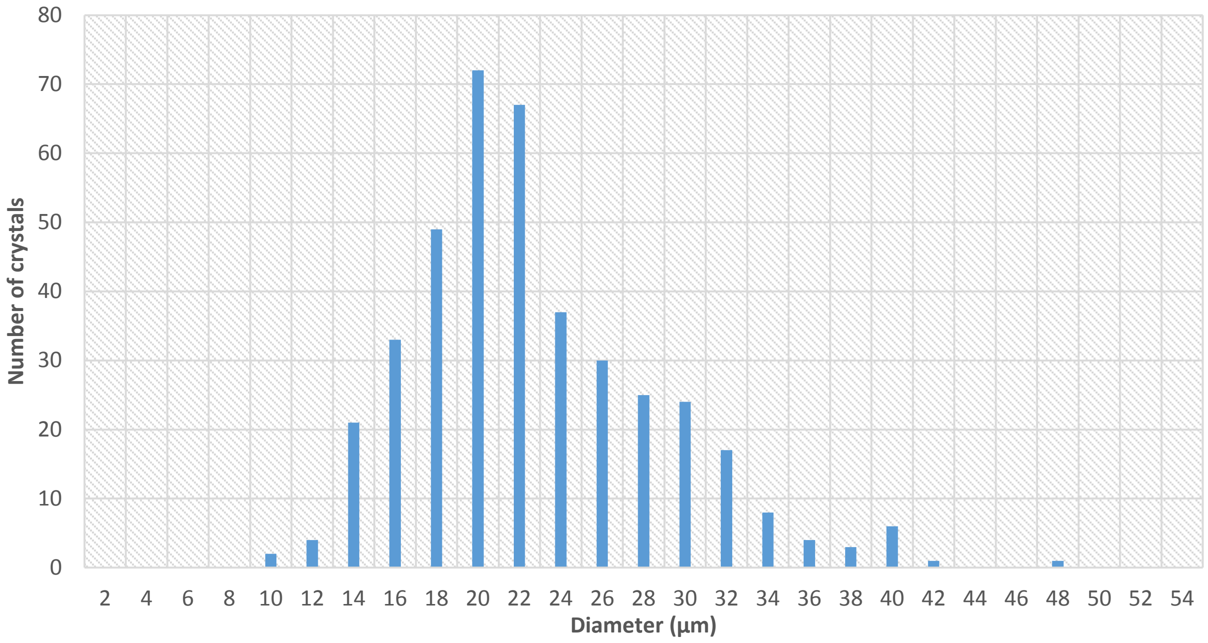


Figure 66. Ice crystal distribution of 0.00% stabilized ice cream at 20 min (Run 1).

B. 0.05% stabilized ice cream

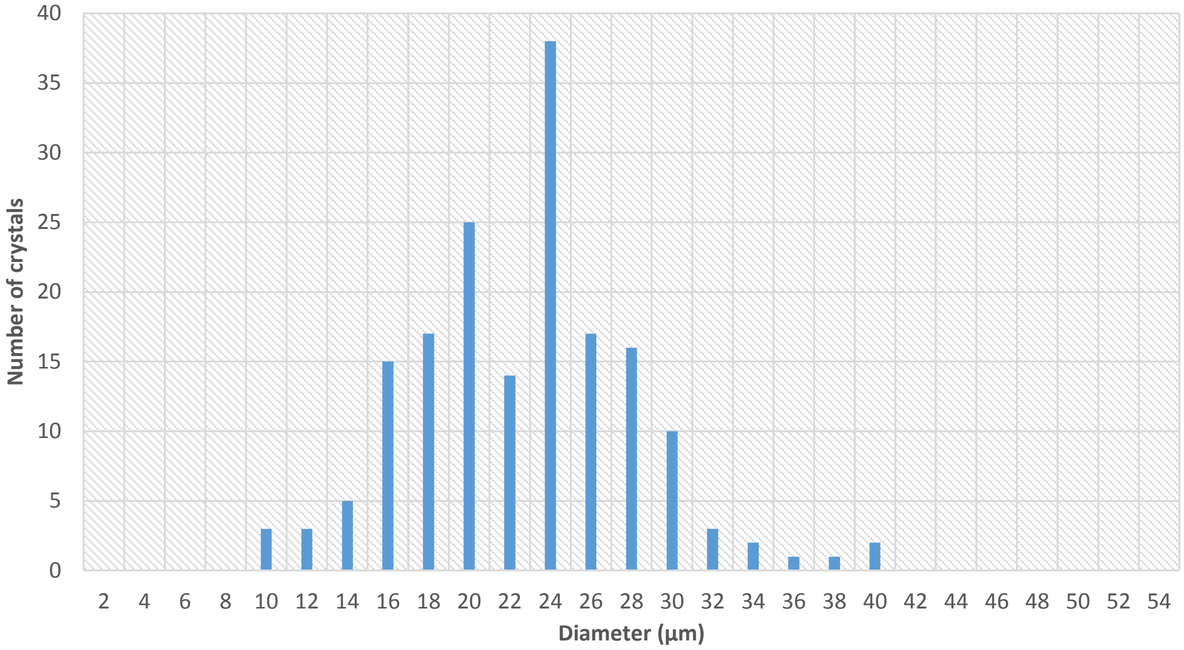


Figure 67. Ice crystal distribution of 0.05% stabilized ice cream at 0 min (Run 1).

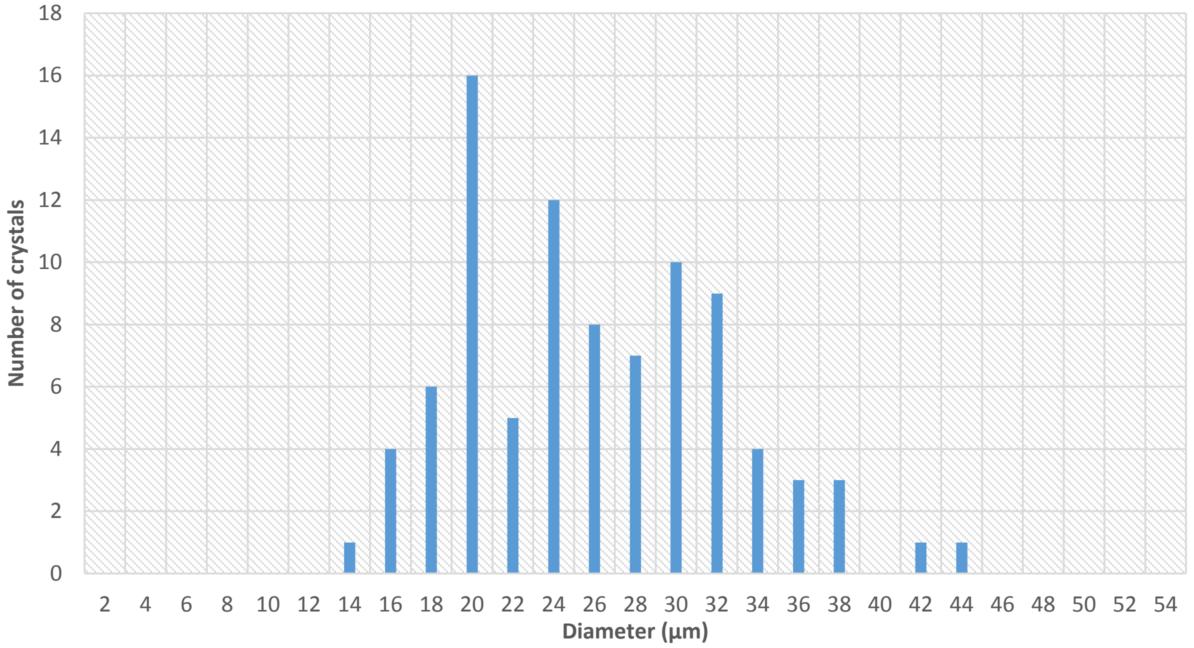


Figure 68. Ice crystal distribution of 0.05% stabilized ice cream at 60 min (Run 1).

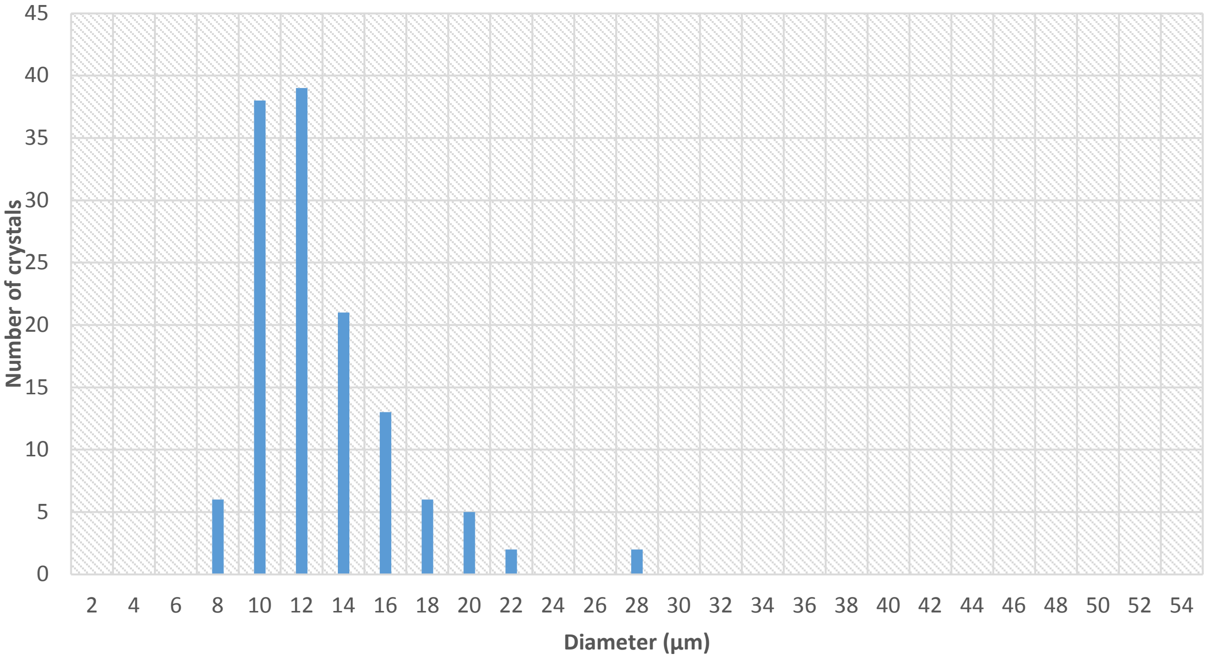


Figure 69. Ice crystal distribution of 0.05% stabilized ice cream at 0 min (Run 2).

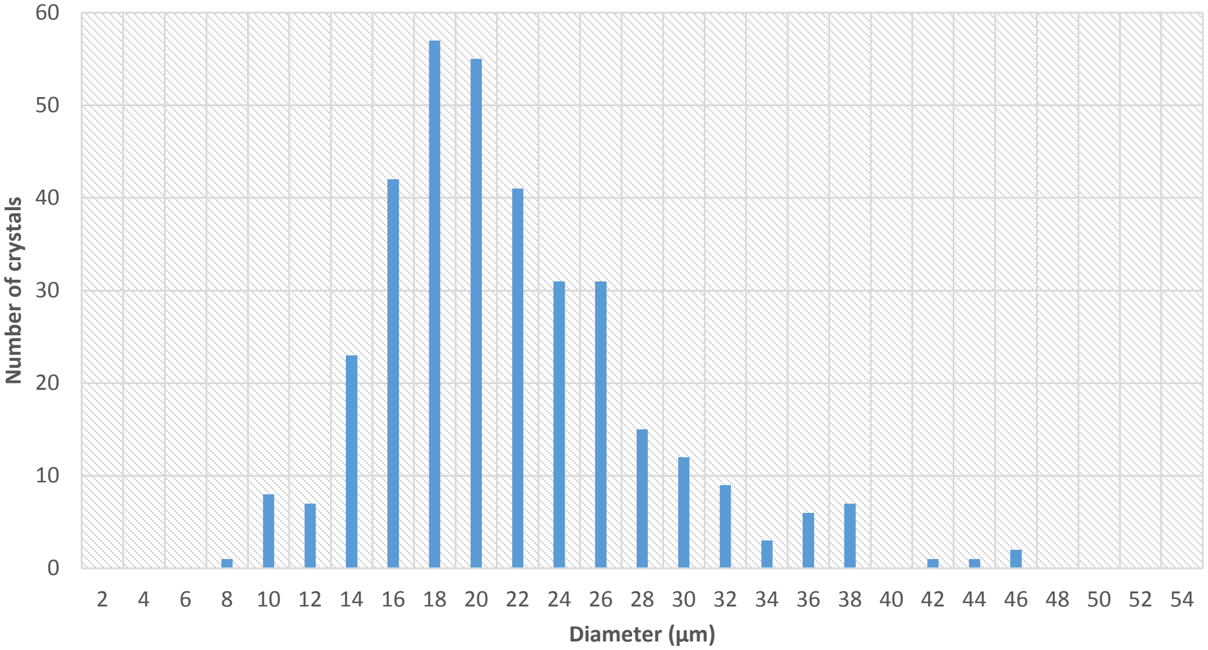


Figure 70. Ice crystal distribution of 0.05% stabilized ice cream at 10 min (Run 2).

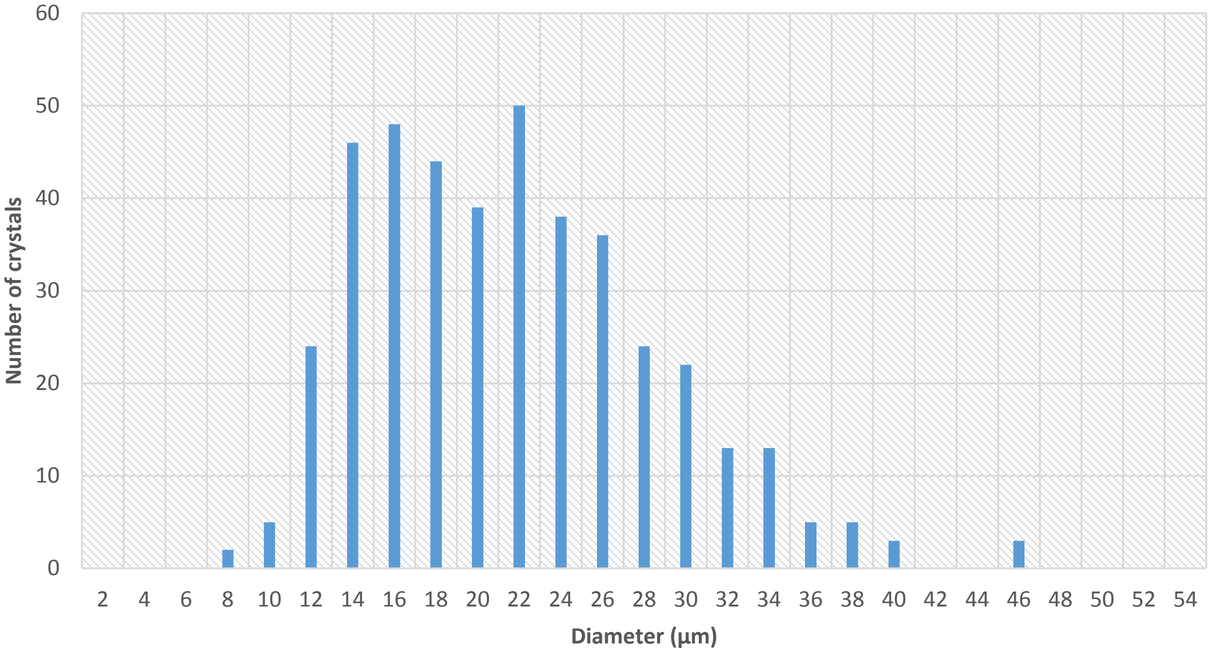


Figure 71. Ice crystal distribution of 0.05% stabilized ice cream at 20 min (Run 2).

C. 0.10% stabilized ice cream

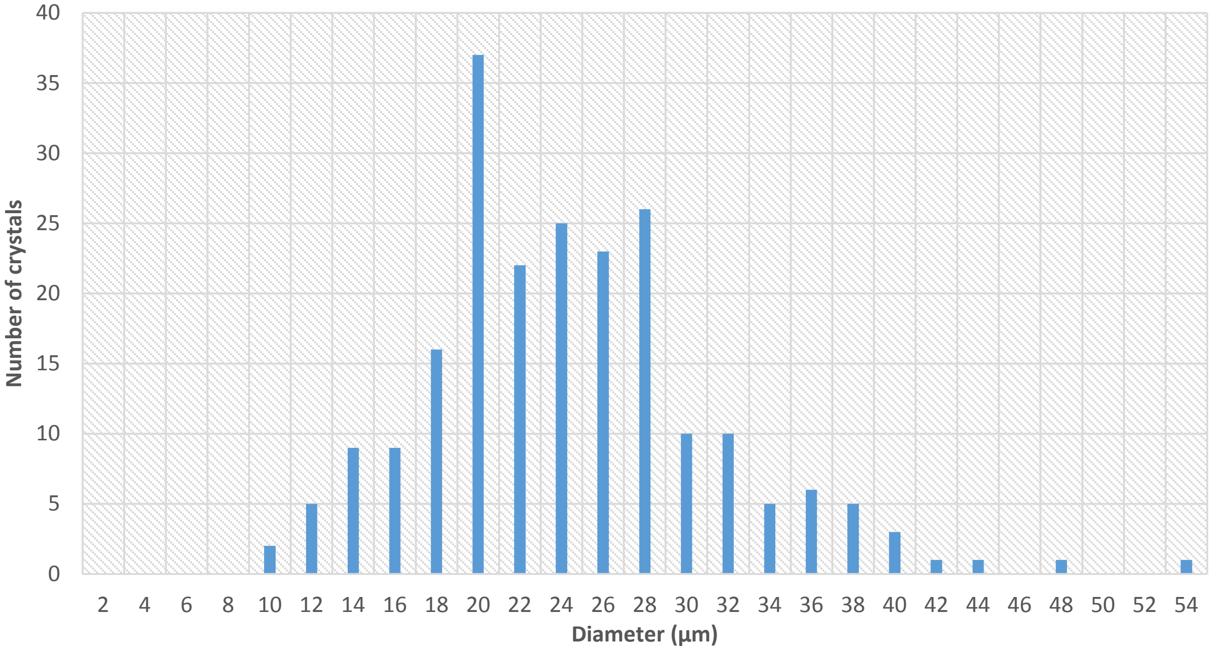


Figure 72. Ice crystal distribution of 0.10% stabilized ice cream at 0 min (Run 1).

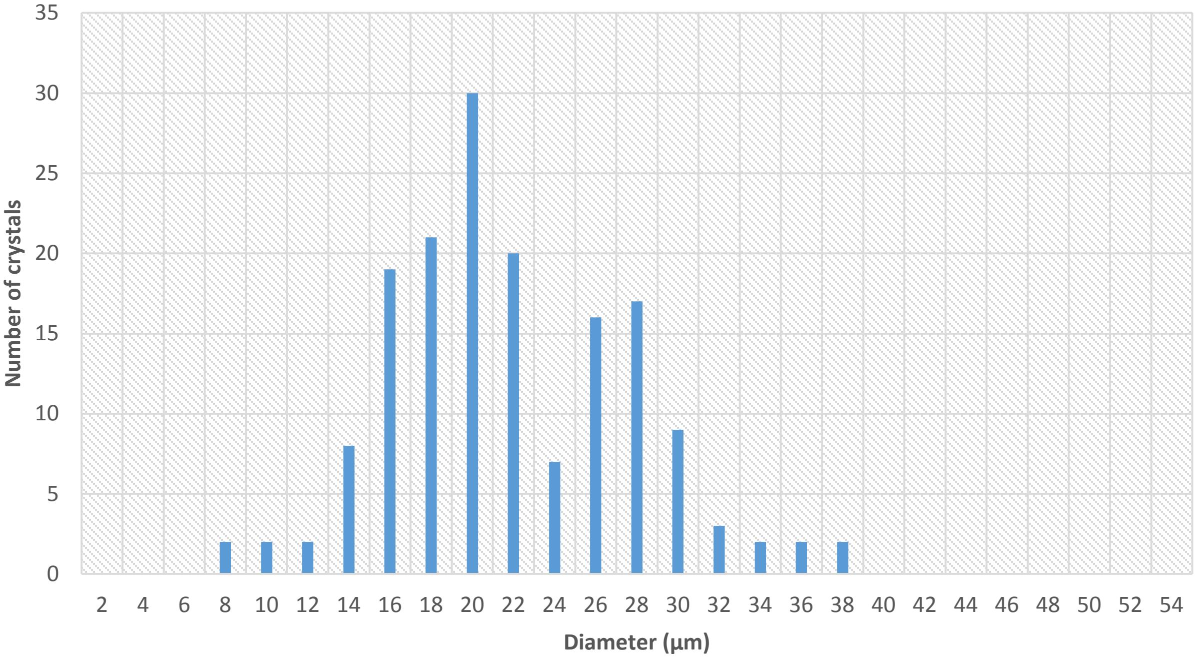


Figure 73. Ice crystal distribution of 0.10% stabilized ice cream at 10 min (Run 1).

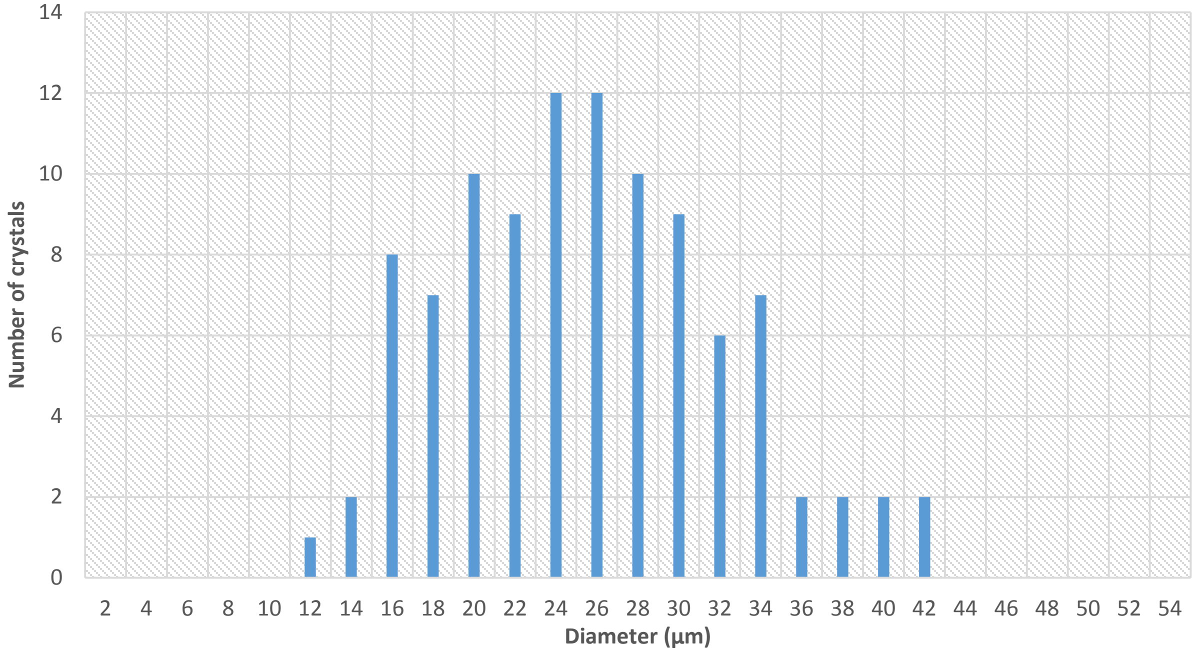


Figure 74. Ice crystal distribution of 0.10% stabilized ice cream at 20 min (Run 1).

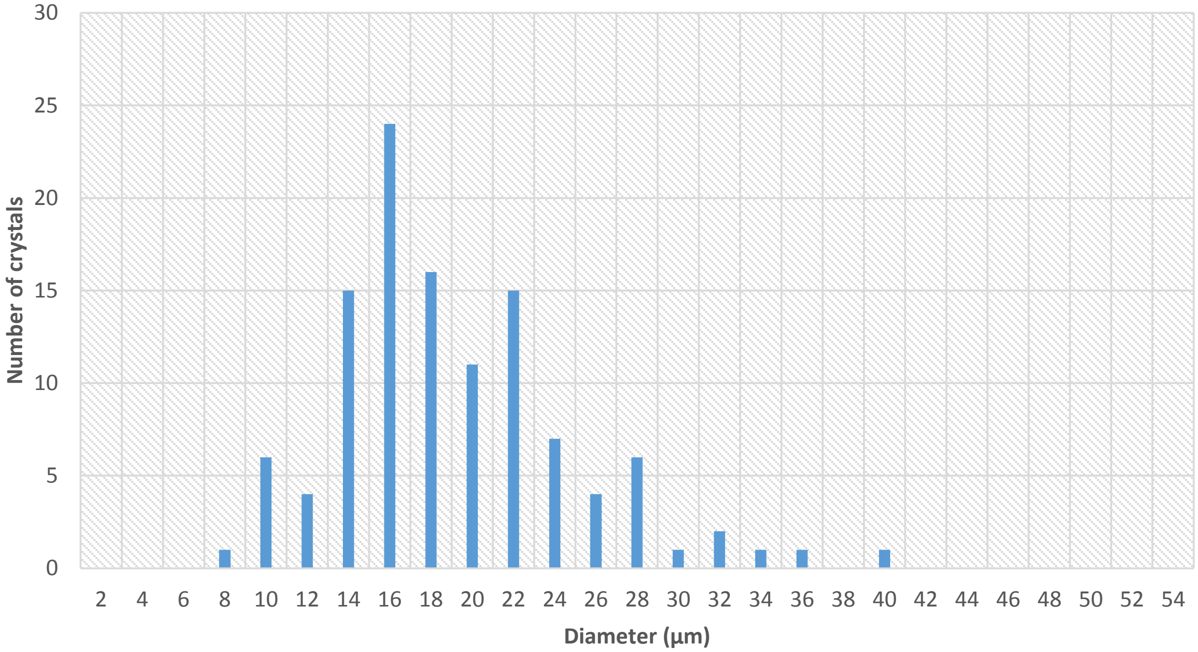


Figure 75. Ice crystal distribution of 0.10% stabilized ice cream at 10 min (Run 2).

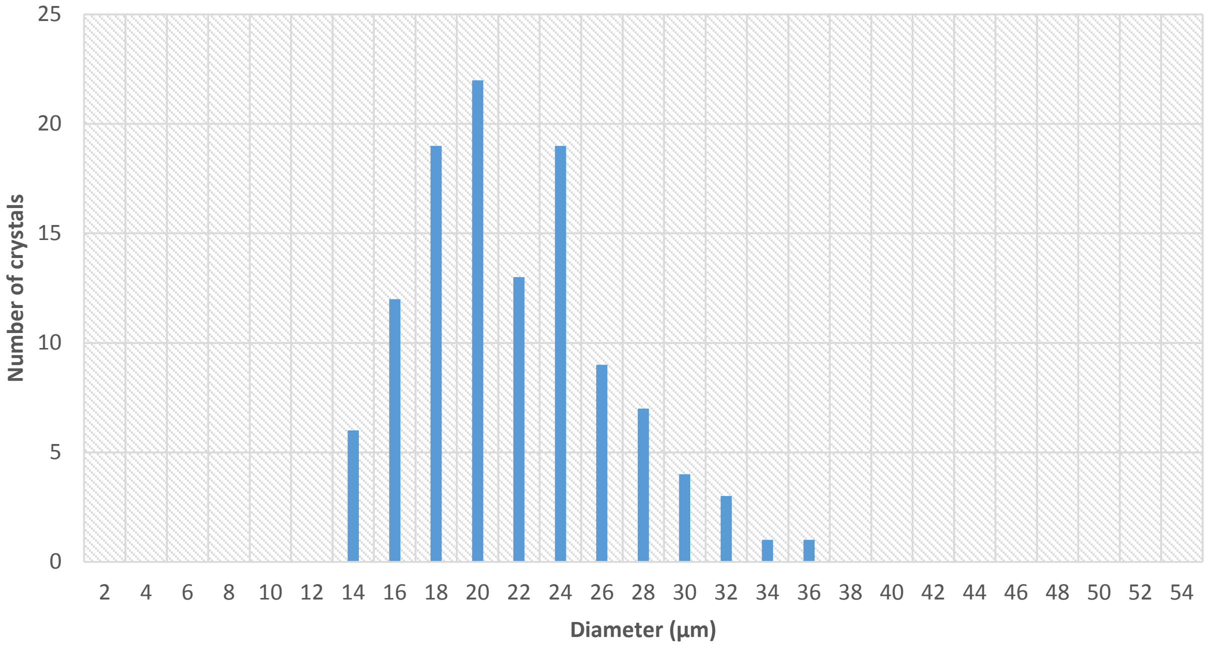


Figure 76. Ice crystal distribution of 0.10% stabilized ice cream at 20 min (Run 2).

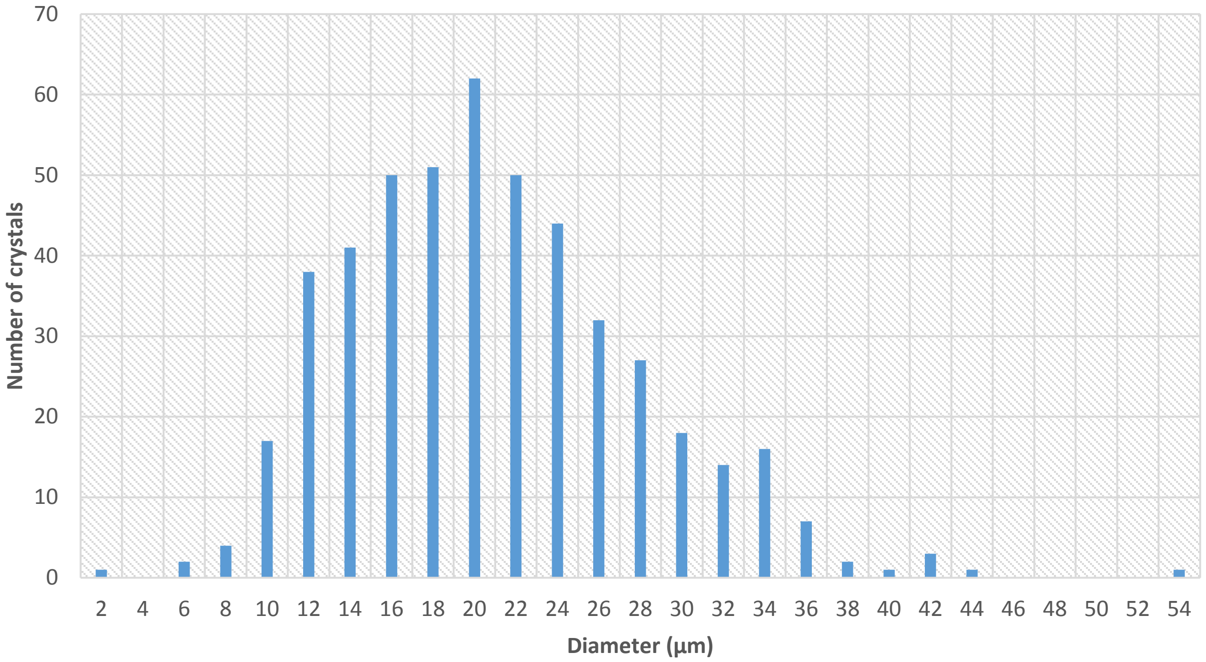


Figure 77. Ice crystal distribution of 0.10% stabilized ice cream at 0 min (Run 3).

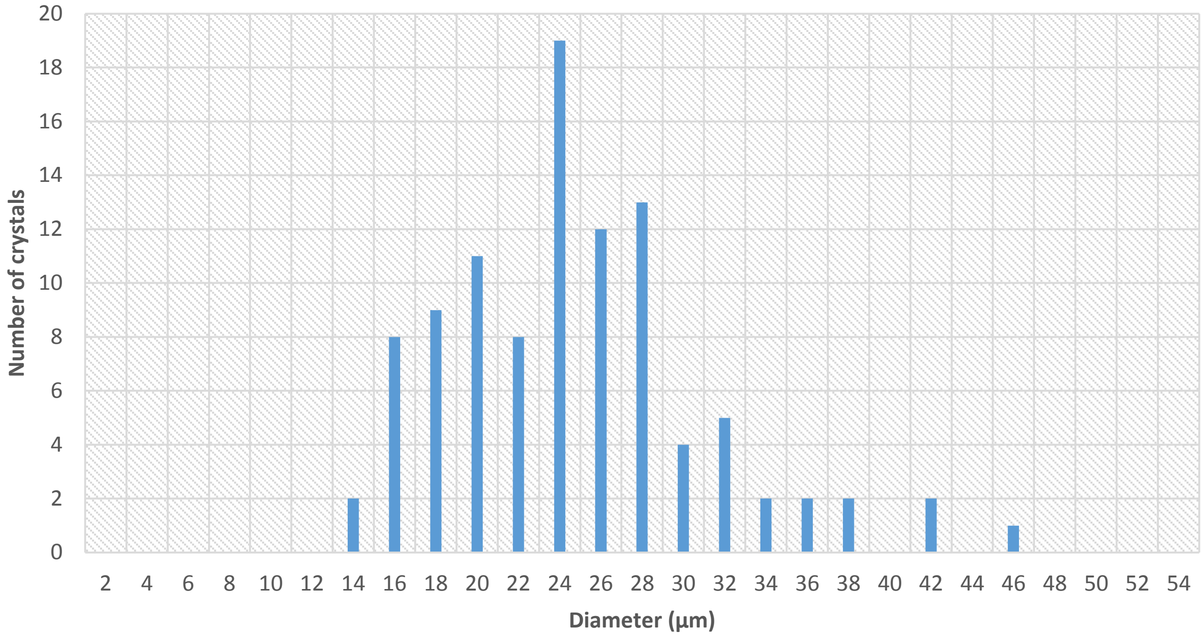


Figure 78. Ice crystal distribution of 0.10% stabilized ice cream at 10 min (Run 3).

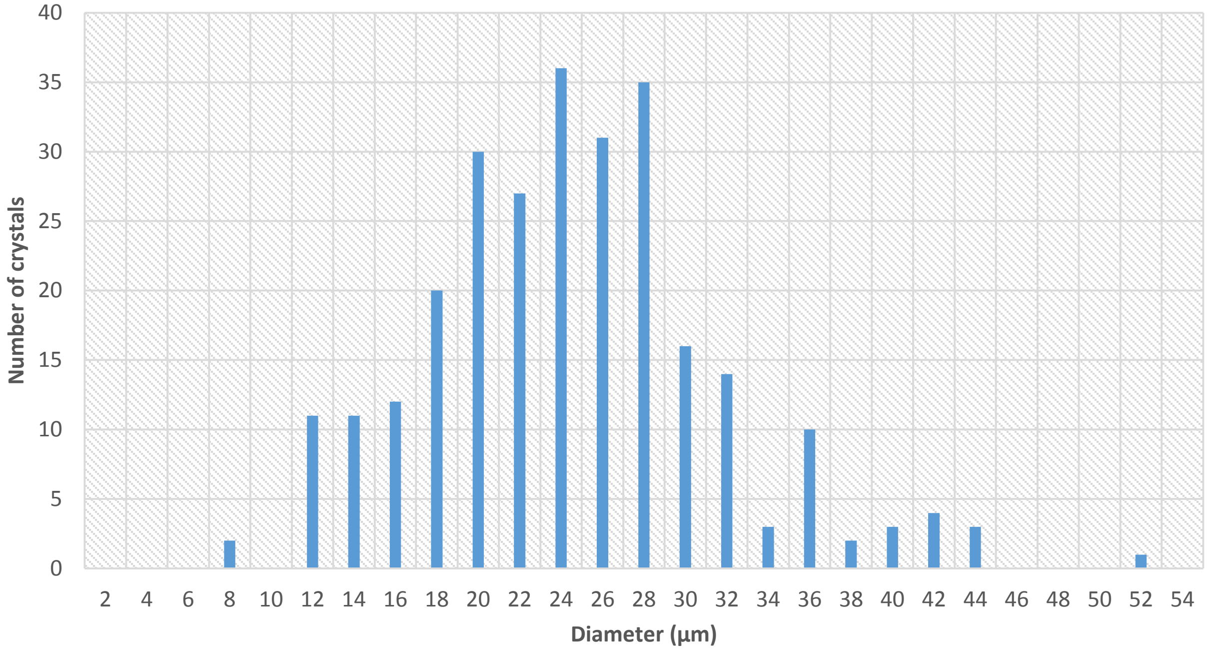


Figure 79. Ice crystal distribution of 0.10% stabilized ice cream at 20 min (Run 3).

D. 0.15% stabilized ice cream

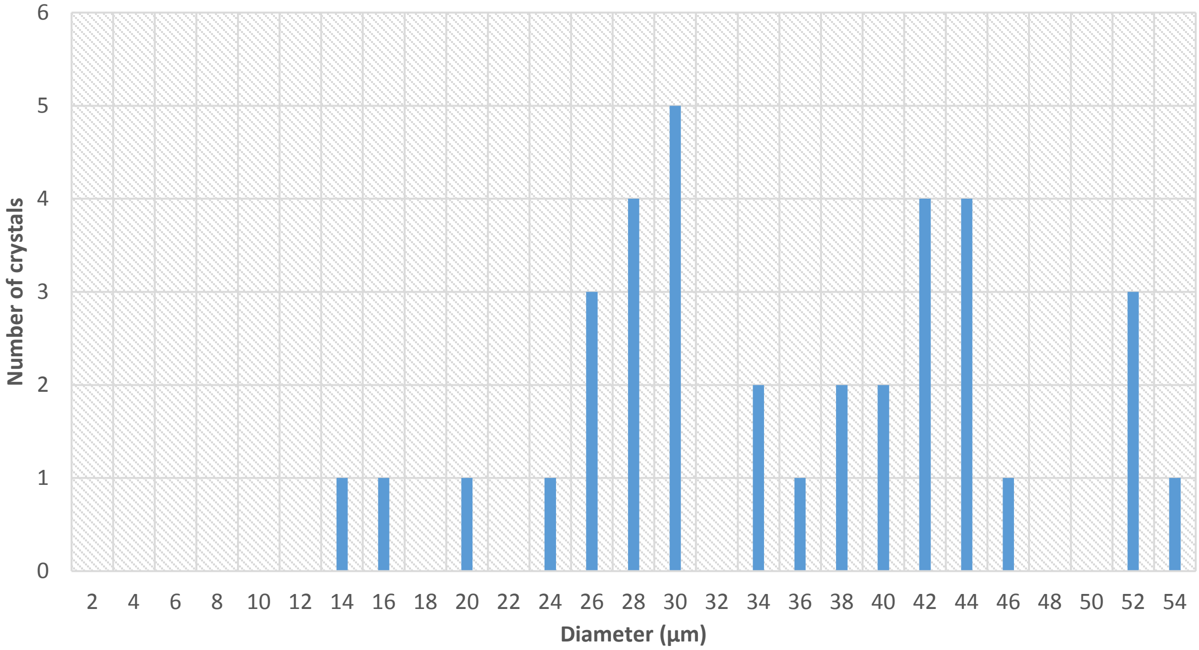


Figure 80. Ice crystal distribution of 0.15% stabilized ice cream at 0 min (Run 1).

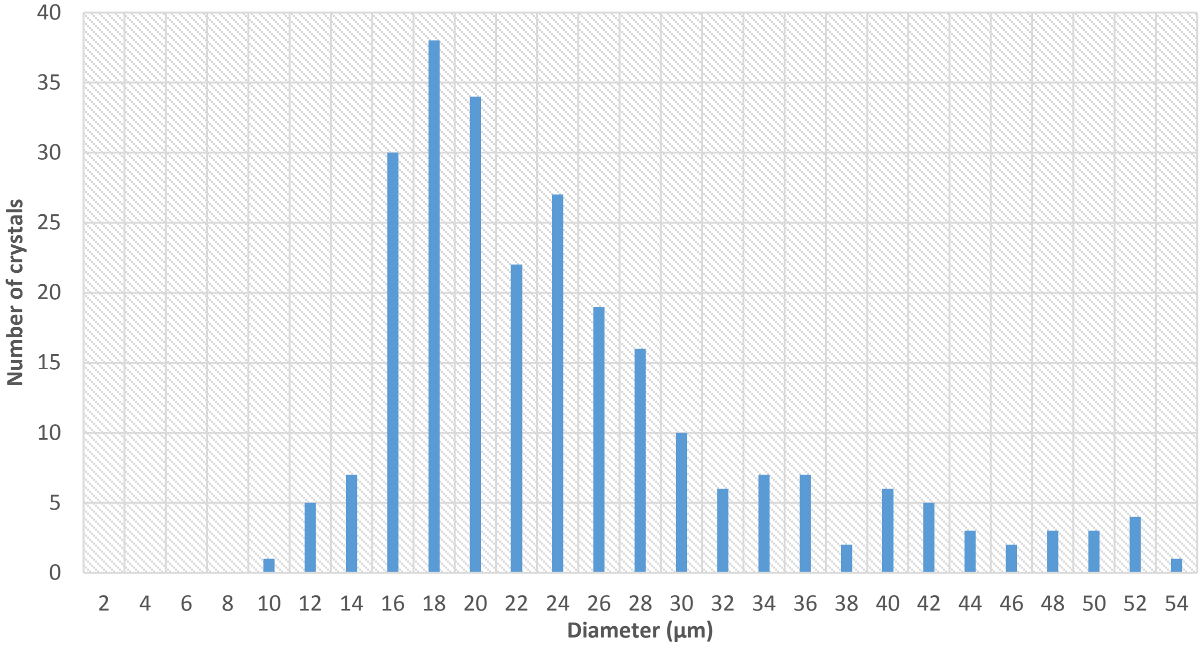


Figure 81. Ice crystal distribution of 0.15% stabilized ice cream at 10 min (Run 1).

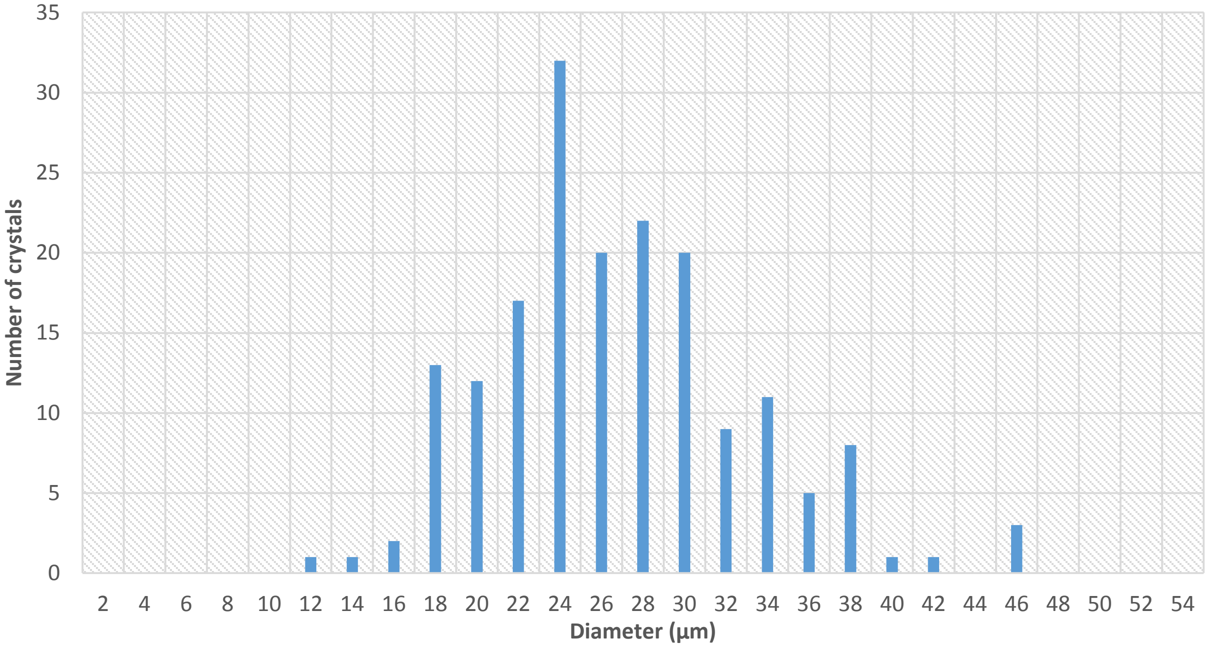


Figure 82. Ice crystal distribution of 0.15% stabilized ice cream at 20 min (Run 1).

8.4.3 ICE CRYSTAL MELTING MECHANISM

A. 0.00% stabilized ice cream

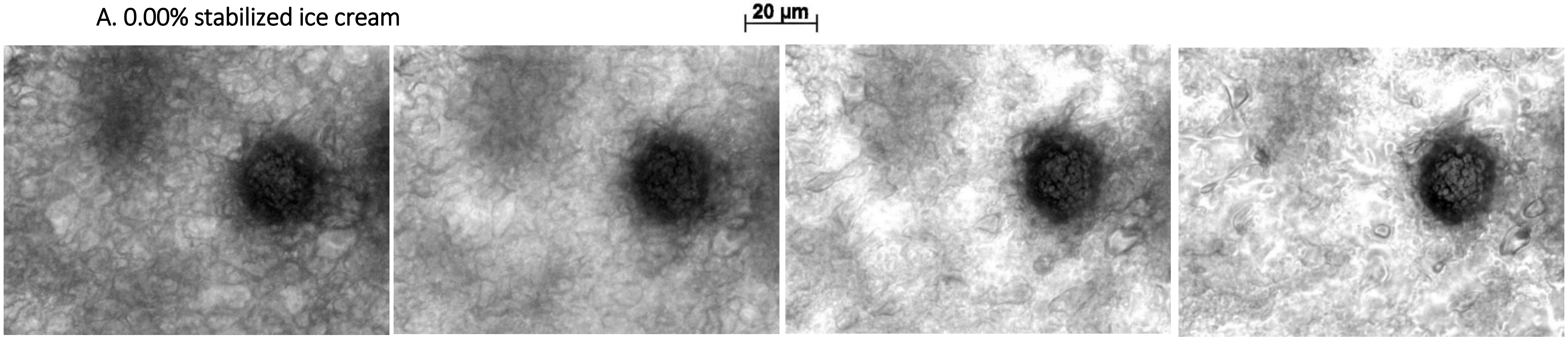


Figure 83. Ostwald ripening for 0.00 % stabilized ice cream at 0 min (Run 1).

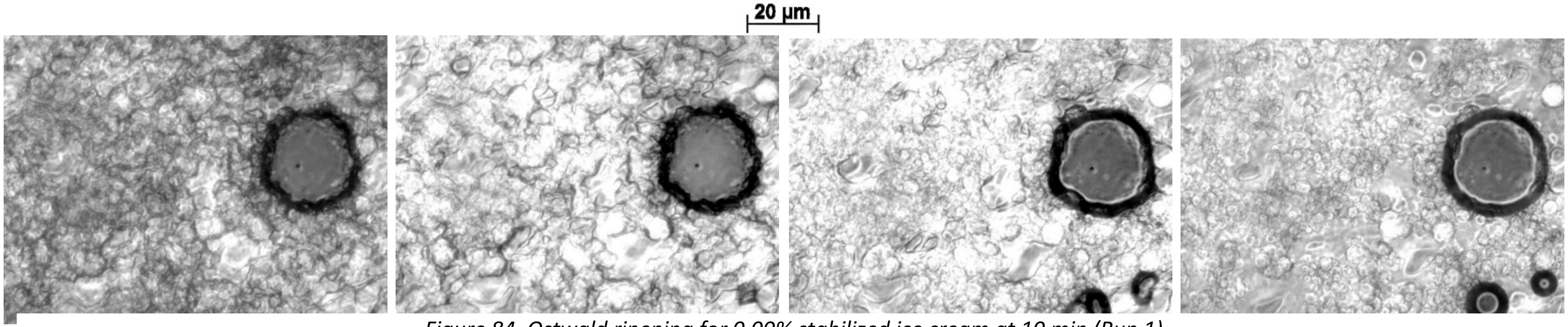


Figure 84. Ostwald ripening for 0.00% stabilized ice cream at 10 min (Run 1).

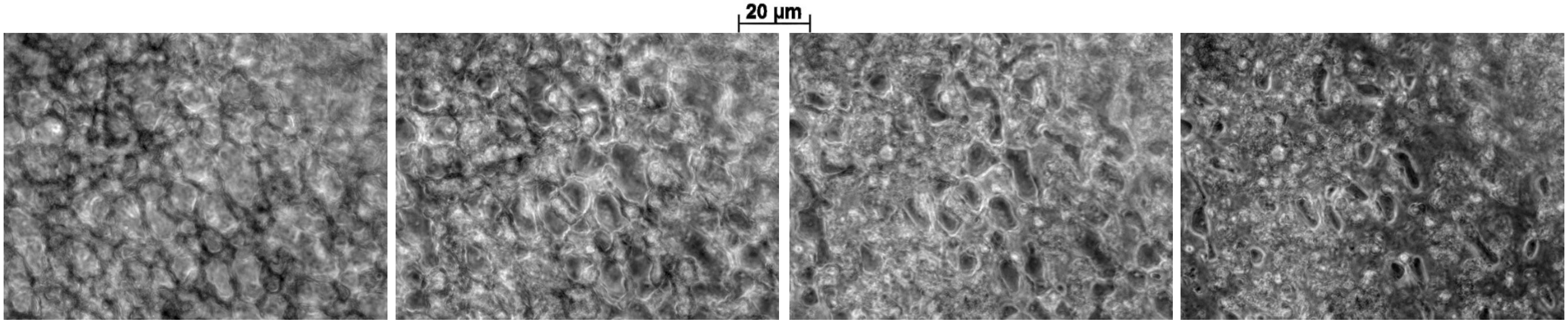


Figure 85. Ostwald ripening for 0.00% stabilized ice cream at 20 min (Run 1).

B. 0.05% stabilized ice cream

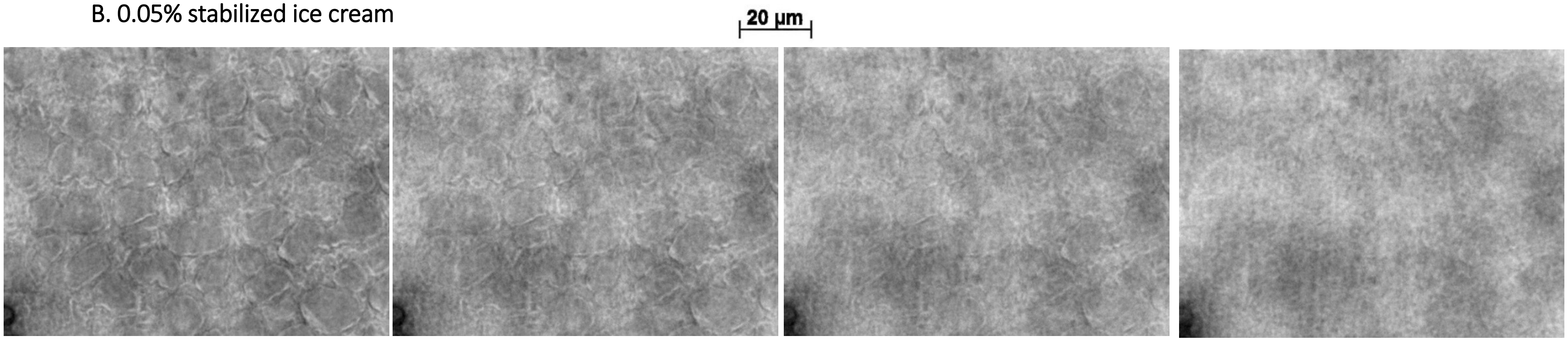


Figure 86. Ostwald ripening for 0.05% stabilized ice cream at 0 min (Run 1).

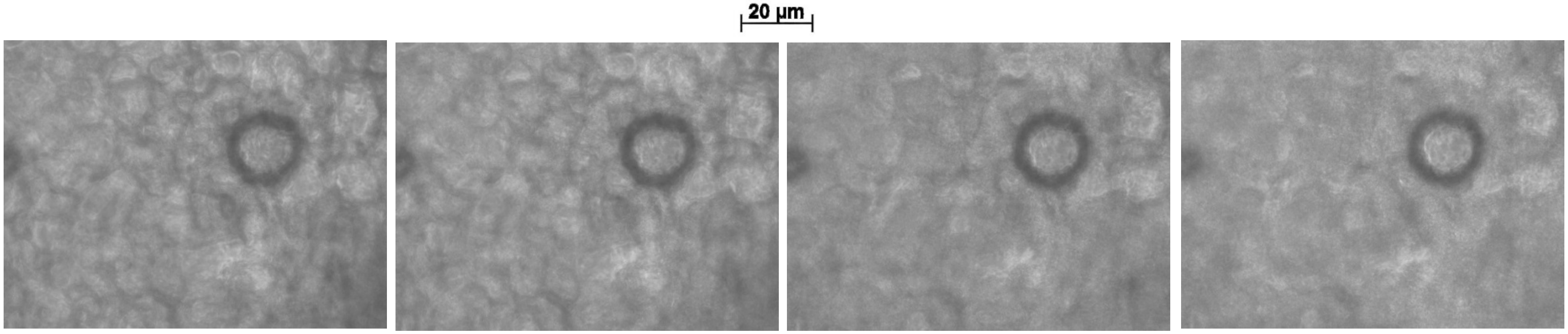


Figure 87. Ostwald ripening for 0.05% stabilized ice cream at 60 min (Run 1).

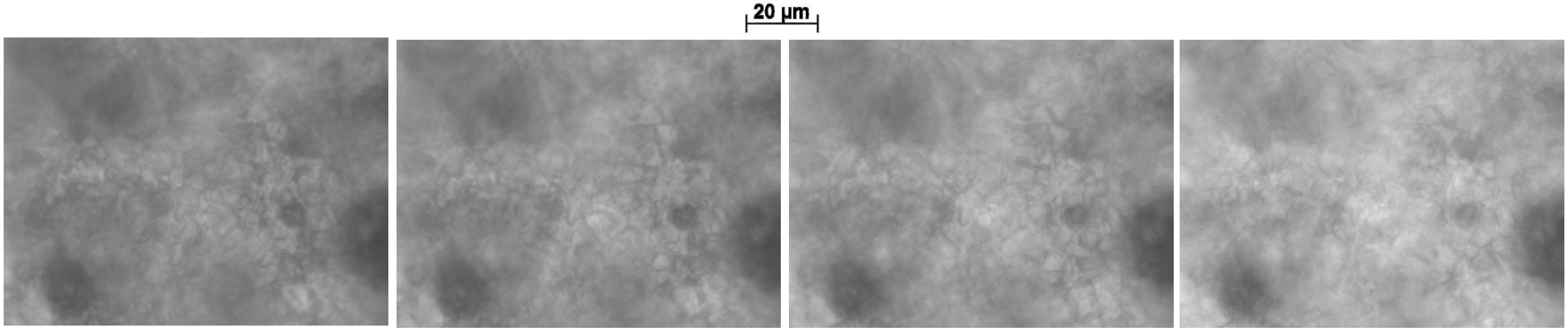


Figure 88. Ostwald ripening for 0.05% stabilized ice cream at 0 min (Run 2).

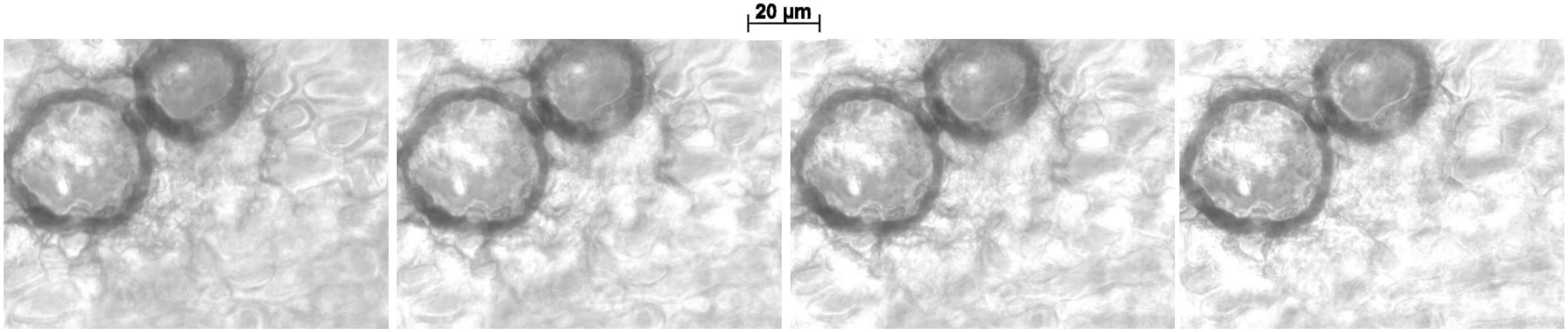


Figure 89. Ostwald ripening for 0.05% stabilized ice cream at 10 min (Run 2).

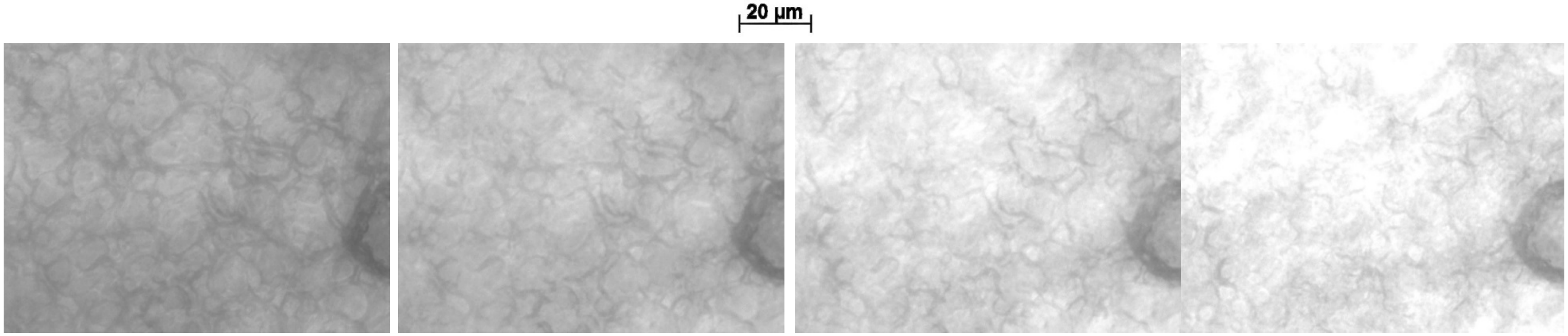


Figure 90. Ostwald ripening for 0.05% stabilized ice cream at 20 min (Run 2).

C. 0.10% stabilized ice cream

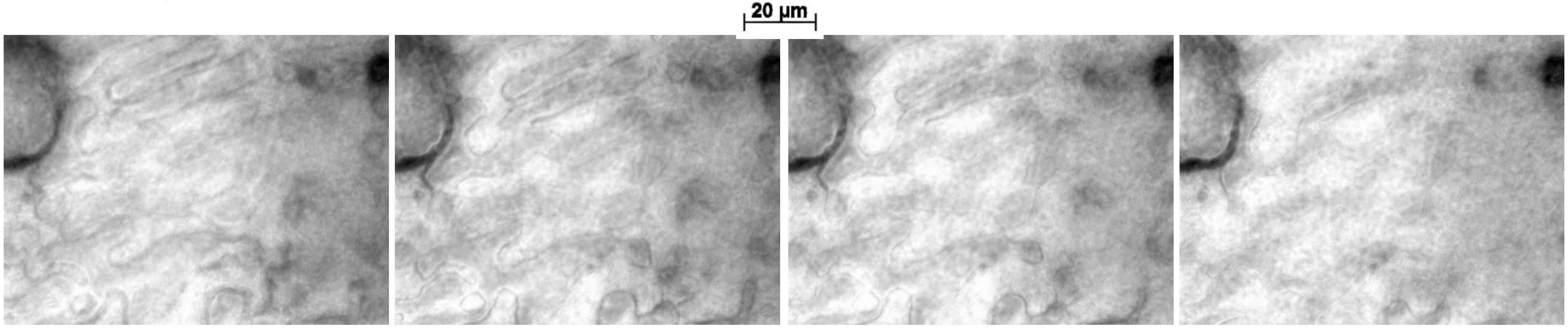


Figure 91. Ostwald ripening for 0.10% stabilized ice cream at 0 min (Run 1).

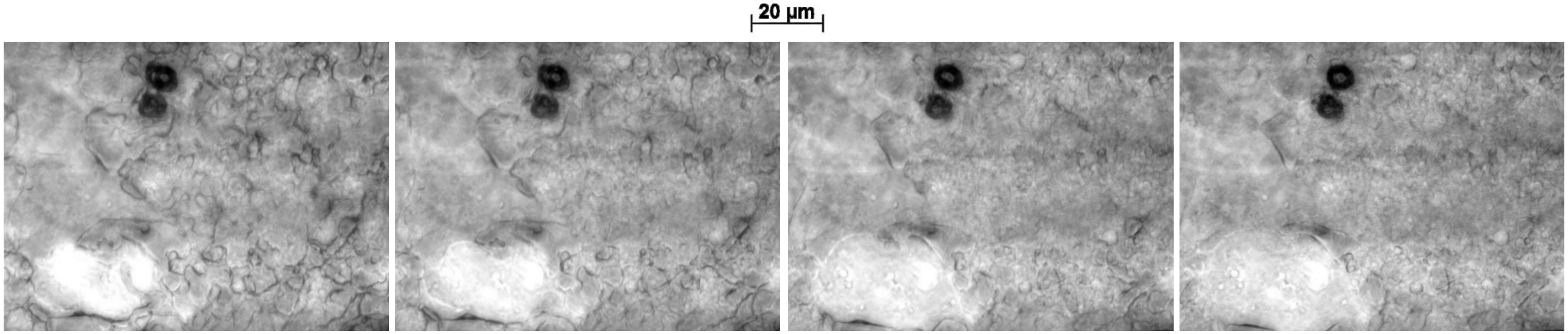


Figure 92. Ostwald ripening for 0.10% stabilized ice cream at 10 min (Run 1).

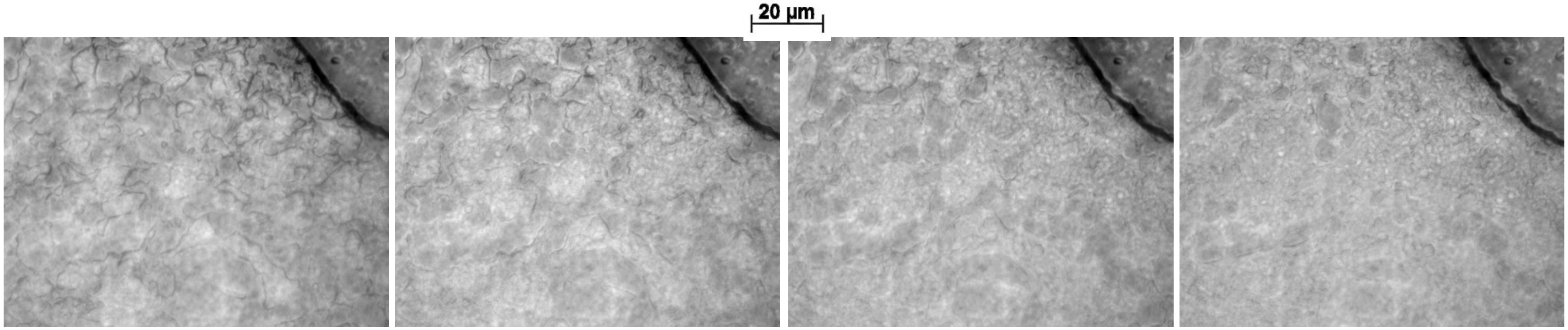


Figure 93. Ostwald ripening for 0.10% stabilized ice cream at 20 min (Run 1).

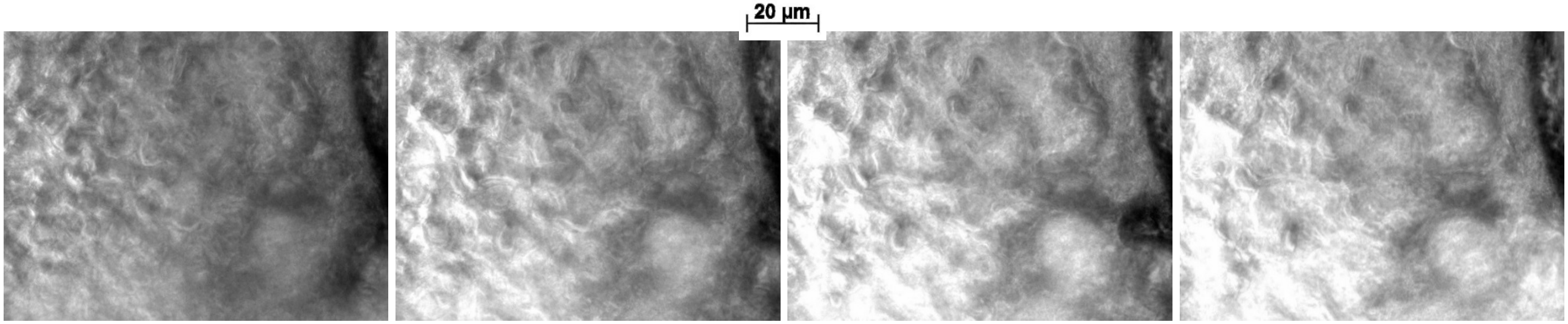


Figure 94. Ostwald ripening for 0.10% stabilized ice cream at 10 min (Run 2).

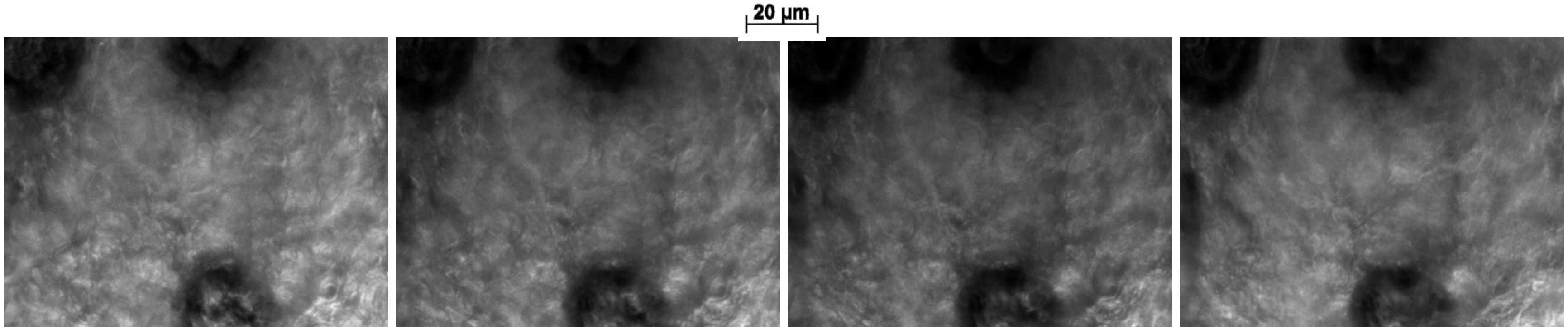


Figure 95. Ostwald ripening for 0.10% stabilized ice cream at 20 min (Run 2).

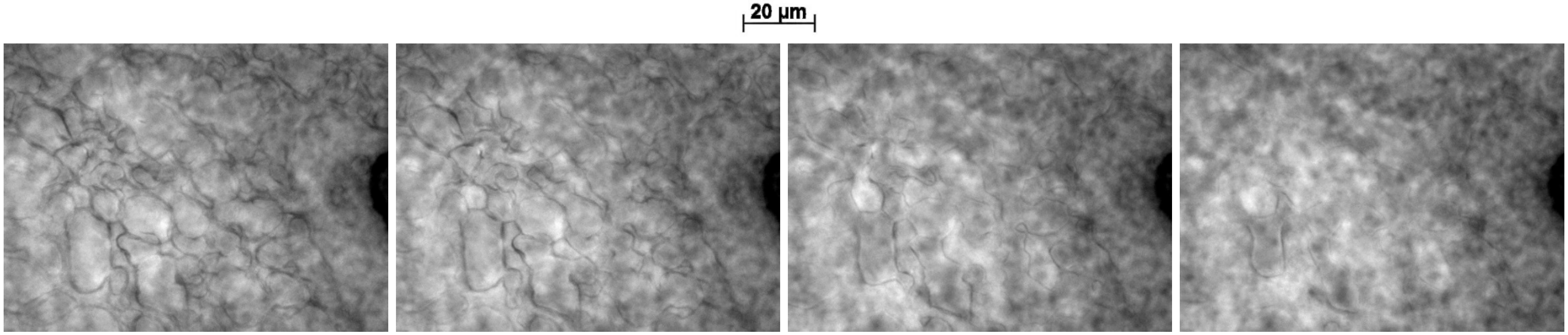


Figure 96. Ostwald ripening for 0.10% stabilized ice cream at 0 min (Run 3).

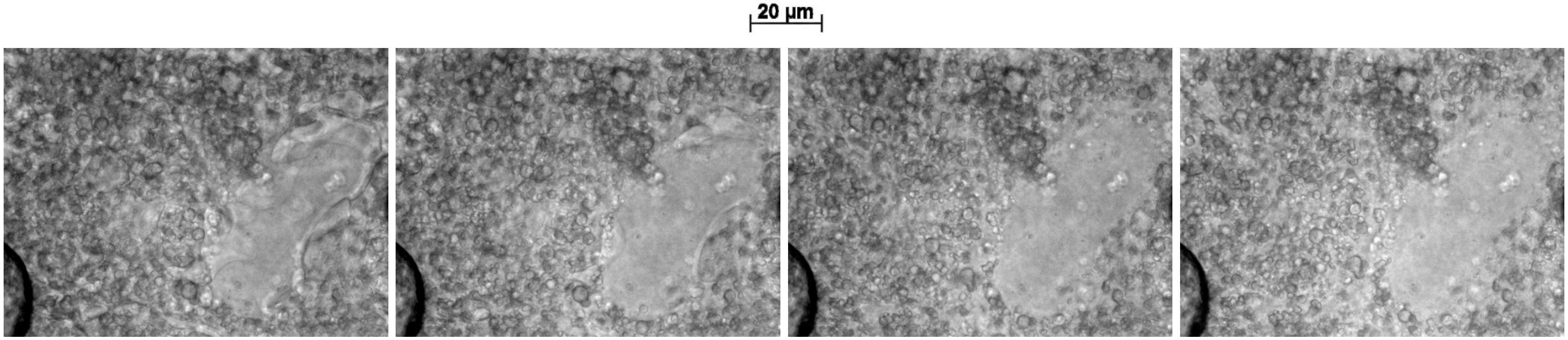


Figure 97. Ostwald ripening for 0.10% stabilized ice cream at 10 min (Run 3).

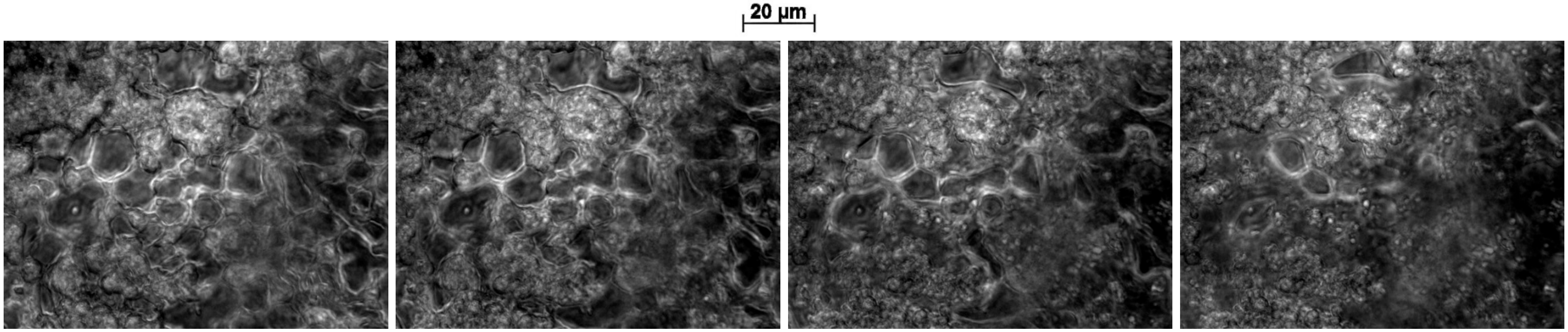


Figure 98. Ostwald ripening for 0.10% stabilized ice cream at 20 min (Run 3).

D. 0.15% stabilized ice cream

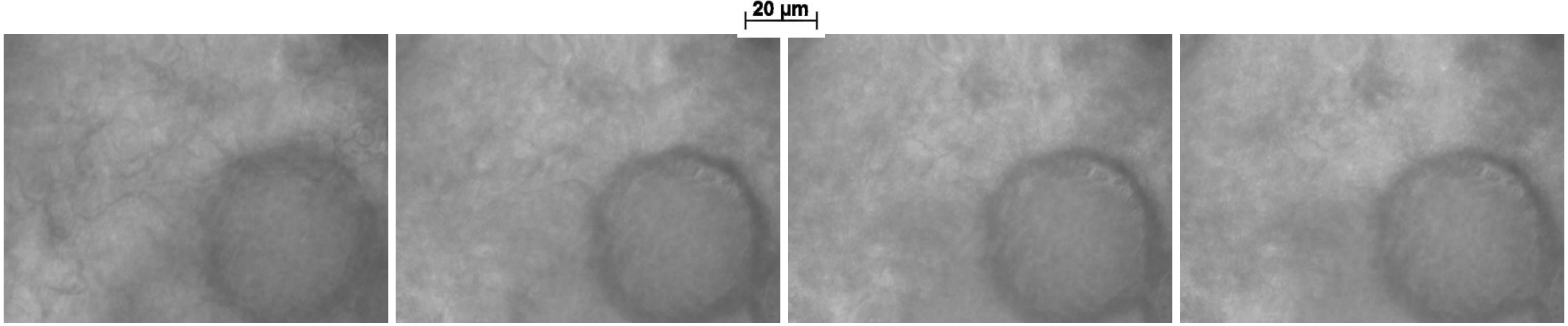


Figure 99. Ostwald ripening for 0.15% stabilized ice cream at 0 min (Run 1).

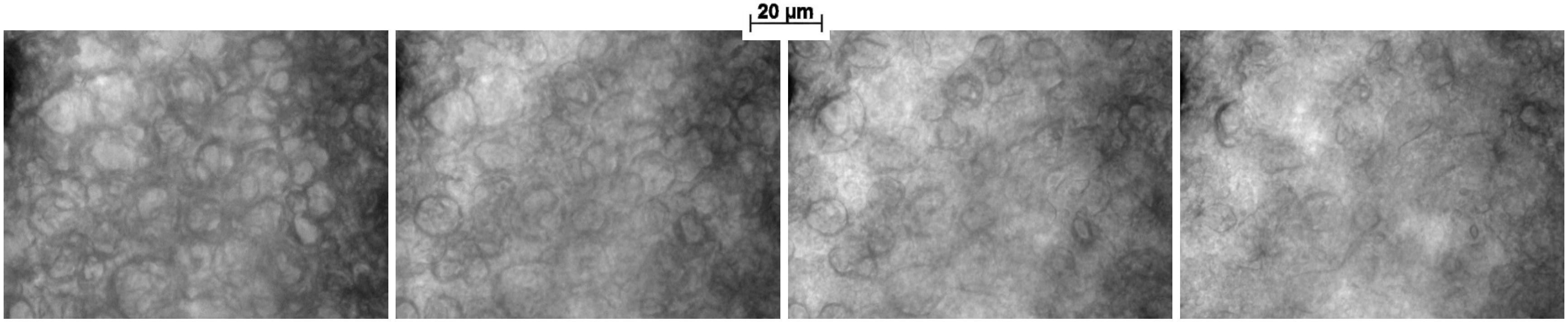


Figure 100. Ostwald ripening for 0.15% stabilized ice cream at 10 min (Run 1).

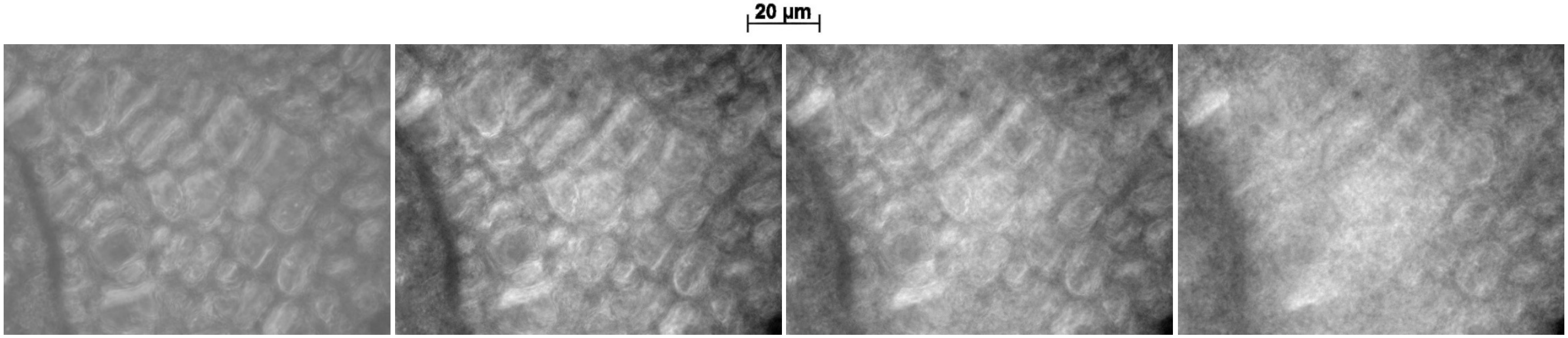


Figure 101. Ostwald ripening for 0.15% stabilized ice cream at 20 min (Run 1).

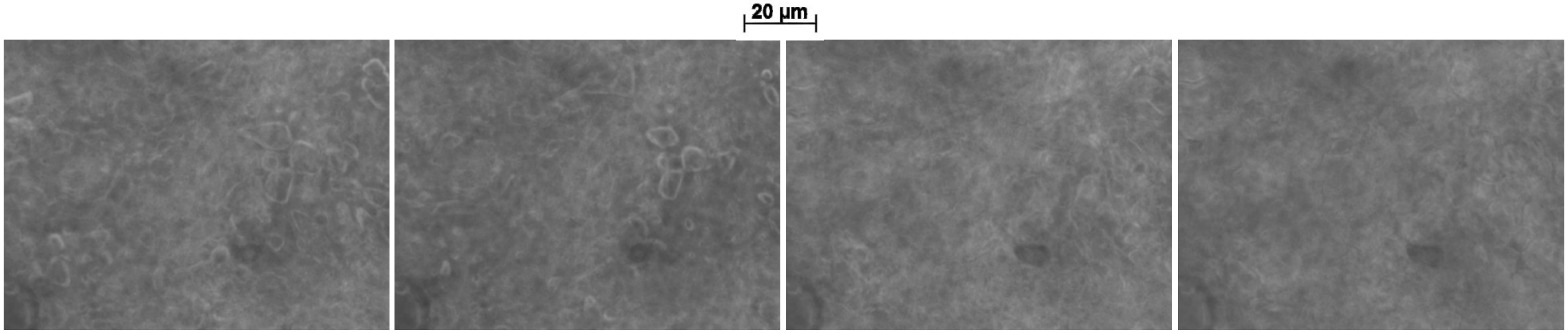


Figure 102. Ostwald ripening for 0.15% stabilized ice cream at 0 min (Run 2).

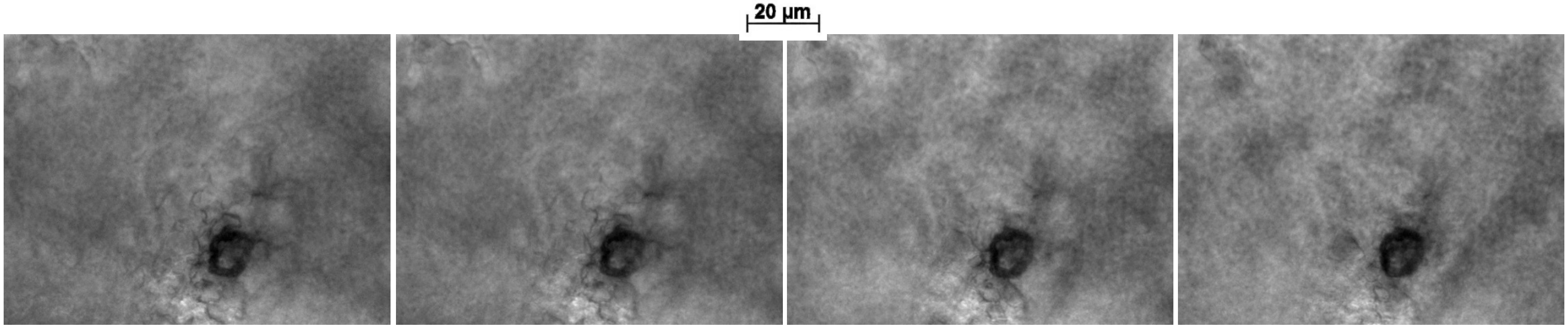


Figure 103. Ostwald ripening for 0.15% stabilized ice cream at 10 min (Run 2).

8.5 VISCOSITY CALCULATION

Applying the modified Power Law model, the n and K values were determined.

$$\ln(\eta) = (n-1)\ln(K) + (n-1)\ln(\dot{\gamma}) \tag{12}$$

Below is a sample calculation for unstabilized ice cream samples. The average recorded values for viscosity and the sear rate generated a graph, where the linear fit line had the following equation.

$$y = -0.5815x + 6.6536$$

Therefore,

$$n - 1 = -0.5815$$

$$\Rightarrow n = 0.4185 \ \approx 0.4$$

Also,

$$(n-1)\ln(K) = 6.6536$$

$$\ln(K) = \frac{6.6536}{n-1} = \frac{6.6536}{-0.5815} = -11.44$$

$$\Rightarrow K = 1.0 \times 10^{-5}$$

8.6 HARDNESS CALCULATION

The deformation at each time point was calculated by multiplying time with the set strain rate, which was 0.00166 m/s. The unit of deformation was then converted from meter to millimeter. An example of deformation was shown below using the data at time point 4.00 seconds in run XXX of ice cream 0min.

$$Deformation = 4.00s * 0.00166\frac{m}{s} * 1000\frac{mm}{m} = 6.64mm$$

The same method was repeated with all the data of sorbet and ice cream. The force was then graphed as a function of deformation as shown in the graphs below.

8.7 CRYSTALLINITY CALCULATION

The crystallinity of ice cream without stabilizers was calculated as shown below.

$$Crystallinity = \frac{\left(\frac{80.11\frac{J}{g}}{0.43}\right)}{294.11\frac{J}{g}} * 100 = 64\%$$

The same calculation was carried out for ice cream with different amount of stabilizers.

8.8 CALCULATION SPREADSHEETS

8.8.1 WEIGHTED AVERAGE CRYSTAL SIZE

A. SORBET

Table 14. Weighted average crystal size of sorbet.

Time (min)	Weighted Average Crystal Size (µm)								
	Run	M_I	N_I	M_I^2	1/M_I	w_I	wt. avg size	M_N	STD
0	Run 2	18.4	217	337.02	0.05	0.47	27.9	22.9	10.7
	Run 3	17.6	95	310.65	0.06	0.20			
	Run 4	46.9	62	2196.71	0.02	0.34			
10	Run 3	22.7	52	517.49	0.04	0.16	28.8	28.5	2.9
	Run 4	30.0	206	900.76	0.03	0.84			
20	Run 3	26.5	62	701.00	0.04	0.23	34.3	33.7	4.6
	Run 4	36.7	151	1344.95	0.03	0.77			
30	Run 1	40.2	188	1613.20	0.02	0.73	35.0	31.7	10.2
	Run 3	25.3	54	641.79	0.04	0.13			
	Run 4	17.0	85	287.50	0.06	0.14			
40	Run 4	20.3	175	411.61	0.05	1.00	20.3	20.3	5.2
50	Run 4	21.2	188	448.67	0.05	1.00	21.2	21.2	4.9

B. ICE CREAM

B.1 0.00% stabilized ice cream

Table 15. Weighted average crystal size for 0.00% stabilized ice cream.

Time (min)	Weighted Average Crystal Size (µm)								
	Run	M_i	N_i	M_i^2	1/M_i	w_i	wt. avg size	M_N	STD
0	Run 1	15.2	236	231.04	0.07	1	15.2	15.2	4.4
10	Run 1	19.5	67	380.25	0.05	1	19.5	19.5	4.9
20	Run 1	23.6	405	556.96	0.04	1	23.6	23.6	6.2

B.2 0.05% stabilized ice cream

Table 16. Weighted average crystal size for 0.05% stabilized ice cream.

Time (min)	Weighted Average Crystal Size (µm)								
	Run	M_i	N_i	M_i^2	1/M_i	w_i	wt. avg size	M_N	STD
0	Run 1	23.2	172	538.24	0.04	0.70	20.1	18.8	5.1
	Run 2	13.0	132	169.00	0.08	0.30			
10	Run 2	22.8	353	519.84	0.04	1.00	22.8	22.8	6.6
20	Run 2	23.0	420	529.00	0.04	1.00	23.0	23.0	6.9

B.3 0.10% stabilized ice cream

Table 17. Weighted average crystal size for 0.10% stabilized ice cream.

Time (min)	Weighted Average Crystal Size (µm)								
	Run	M_i	N_i	M_i^2	1/M_i	w_i	wt. avg size	M_N	STD
0	Run 1	25.4	217	645.16	0.04	0.34	23.4	23.3	1.4
	Run 3	22.4	482	501.76	0.04	0.66			
10	Run 1	22.6	162	510.76	0.04	0.43	22.7	22.5	2.0
	Run 2	19.9	115	396.01	0.05	0.27			
	Run 3	25.3	100	640.09	0.04	0.30			
20	Run 1	26.3	101	691.69	0.04	0.21	25.6	25.4	2.1
	Run 2	21.6	116	466.56	0.05	0.20			
	Run 3	26.7	275	712.89	0.04	0.59			

B.4 0.15% stabilized ice cream

Table 18. Weighted average crystal size for 0.15% stabilized ice cream.

Time (min)	Weighted Average Crystal Size (µm)								
	Run	M_i	N_i	M_i^2	1/M_i	w_i	wt. avg size	M_N	STD
0	Run 1	37.3	36	1391.29	0.03	0.26	25.7	24.3	5.9
	Run 2	21.6	177	466.56	0.05	0.74			
10	Run 1	28.7	263	823.69	0.03	0.55	27.1	27.0	1.8
	Run 2	25.1	243	630.01	0.04	0.45			
20	Run 1	27.3	180	745.29	0.04	0.76	27.5	27.5	0.3
	Run 2	28.0	54	784.00	0.04	0.24			

8.8.2 VISCOSITY MEASUREMENTS

A. SORBET

Table 19. Viscosity measurements for sorbet.

T (°C)	Shear rate		Viscosity (mPa·s)	Avg Viscosity (mPa·s)	STD	Avg STD
	RPM	1/s				
19.1	50	375	44.3	41.6	0.1	0.5
19.5			23.0		1.0	
19.1			38.2		0.0	
18.6			61.0		1.0	
18.6	100	750	28.6	23.3	0.5	0.9
18.9			18.9		0.1	
18.6			22.4		2.0	
18.4	150	1125	23.8	21.4	1.0	0.7
19.3			15.0		2.0	
19.3			16.0		0.5	
18.4			25.8		0.1	
18.4			26.5		0.1	

B. ICE CREAM

B.1 0.00% stabilized ice cream

Table 20. Viscosity measurements for 0.00% stabilized ice cream.

T (°C)	Shear rate		Viscosity (mPa·s)	Avg Viscosity (mPa·s)	STD	Avg STD
	RPM	1/s				
24.4	50	375	16.0	22.0	5.0	5.0
23.5			22.0		5.0	
22.6			28.0		5.0	
25.0	100	750	20.0	22.6	5.0	5.0
21.0			22.8		5.0	
21.2			25.0		5.0	
23.1	150	1125	9.3	10.7	2.0	2.0
22.7			10.6		2.0	
23.2			12.2		2.0	

B.2 0.05% stabilized ice cream

Table 21. Viscosity measurements for 0.05% stabilized ice cream.

T (°C)	Shear rate		Viscosity (mPa·s)	Avg Viscosity (mPa·s)	STD	Avg STD
	RPM	1/s				
20.5	50	375	58.7	52.2	10.0	13.3
20.1			50.0		20.0	
19.8			48.0		10.0	
19.3	100	750	25.0	25.3	3.0	3.0
19.3			28.0		3.0	
19.0			23.0		3.0	
18.0	150	1125	18.0	20.0	1.0	1.0
18.1			22.0		1.0	
18.0			20.0		1.0	

B.3 0.10% stabilized ice cream

Table 22. Viscosity measurements for 0.10% stabilized ice cream.

T (°C)	Shear rate		Viscosity (mPa·s)	Avg Viscosity (mPa·s)	STD	Avg STD
	RPM	1/s				
19.8	50	375	60.7	68.9	10.0	10.0
19.8			47.0		10.0	
19.2			88.0		10.0	
19.2			80.0		10.0	
19.0	100	750	28.1	42.7	0.5	5.3
19.2			33.2		1.0	
18.4			55.0		10.0	
18.9			40.0		5.0	
19.5	150	1125	18.8	23.3	0.5	0.5
18.9			27.4		0.5	
19.5			19.5		0.5	
19.4			27.4		0.5	

B.4 0.15% stabilized ice cream

Table 23. Viscosity measurements for 0.15% stabilized ice cream.

T (°C)	Shear rate		Viscosity (mPa·s)	Avg Viscosity (mPa·s)	STD	Avg STD
	RPM	1/s				
21.0	50	75	120.0	108.3	10.0	6.0
19.5			125.0		5.0	
18.7			80.0		3.0	
18.9	100	750	42.2	46.5	8.0	3.5
18.7			43.0		2.0	
18.2			50.0		5.0	
18.2	150	1125	40.0	32.0	2.0	2.4
17.7			38.0		2.0	
18.2			17.0		3.0	
17.8			32.2		2.0	
17.8			33.0		3.0	

8.9 DSC MEASUREMENT

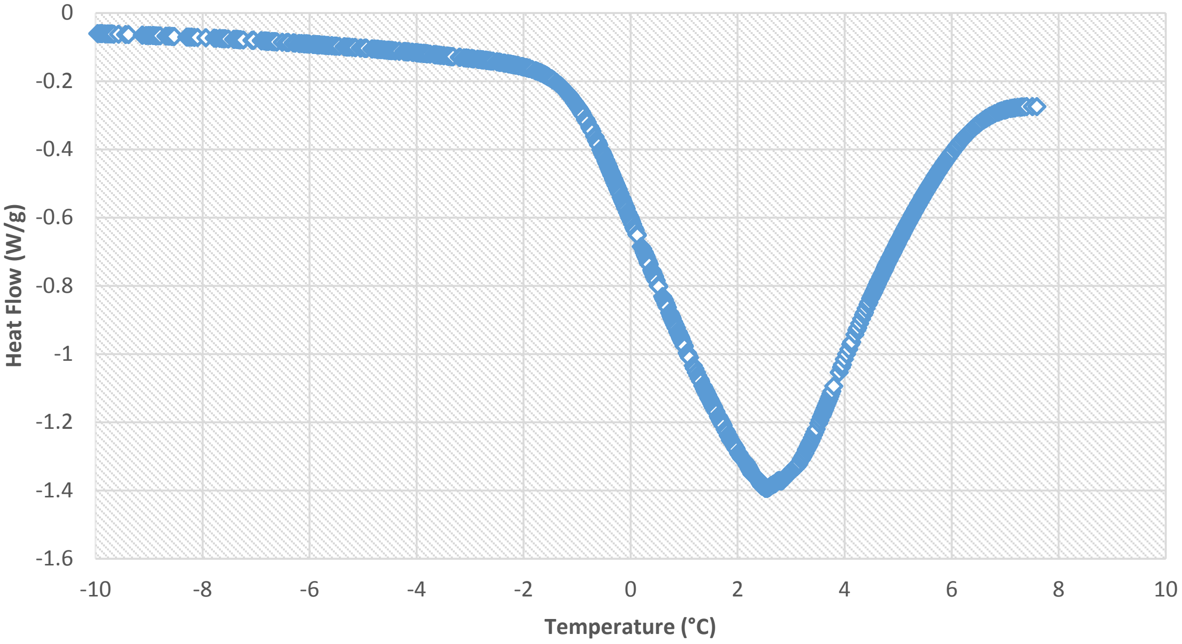


Figure 104. DSC measurement of water.

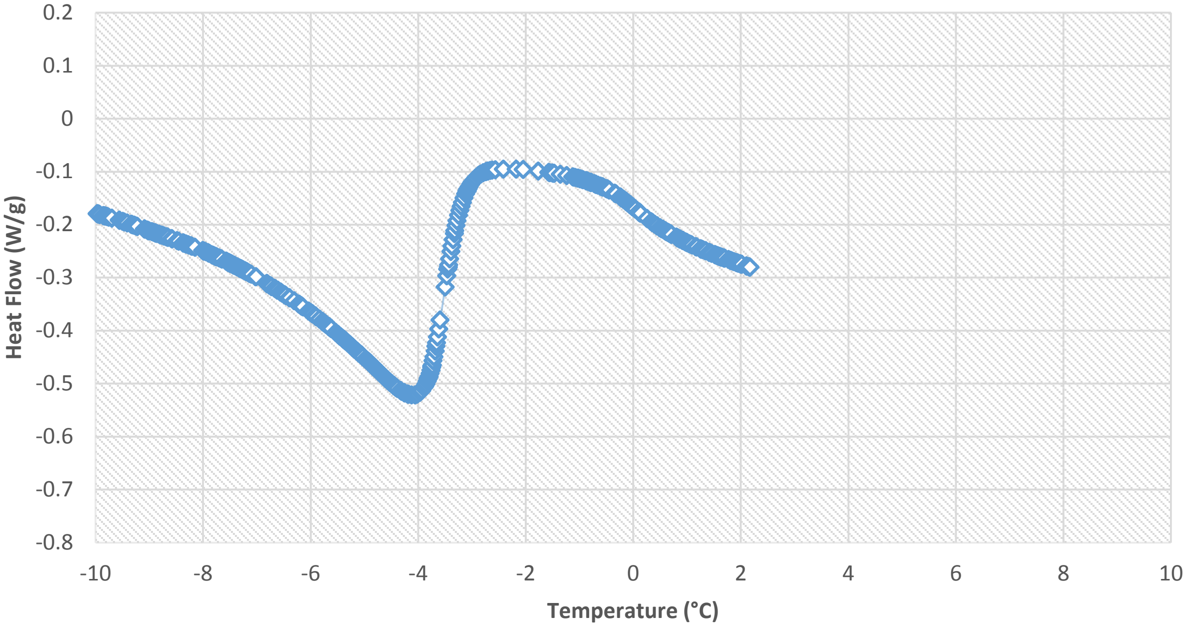


Figure 105. DSC measurement of Häagen-Dazs mango sorbet.

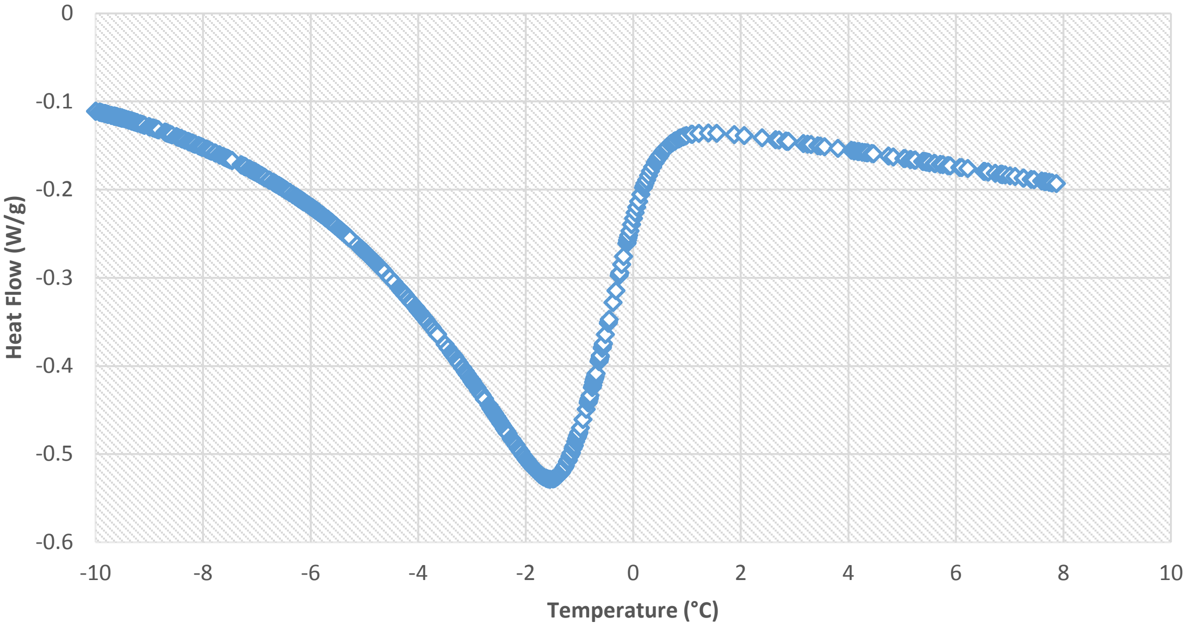


Figure 106. DSC measurement of 0.00% stabilized ice cream.

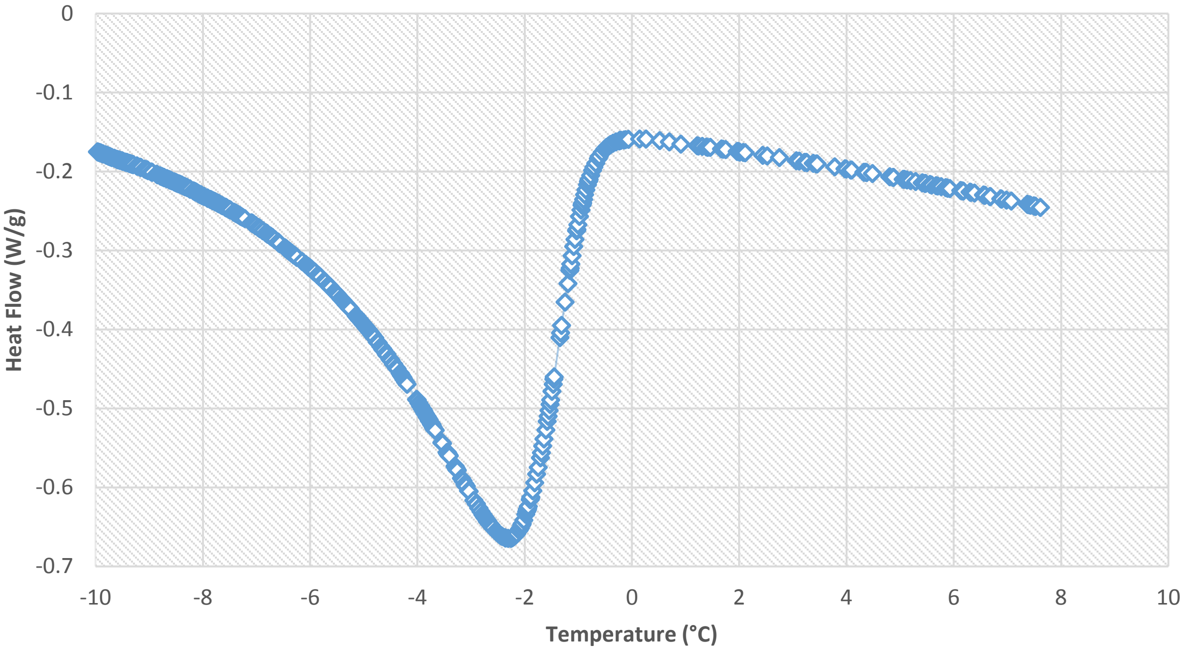


Figure 107. DSC measurement of 0.05% stabilized ice cream.

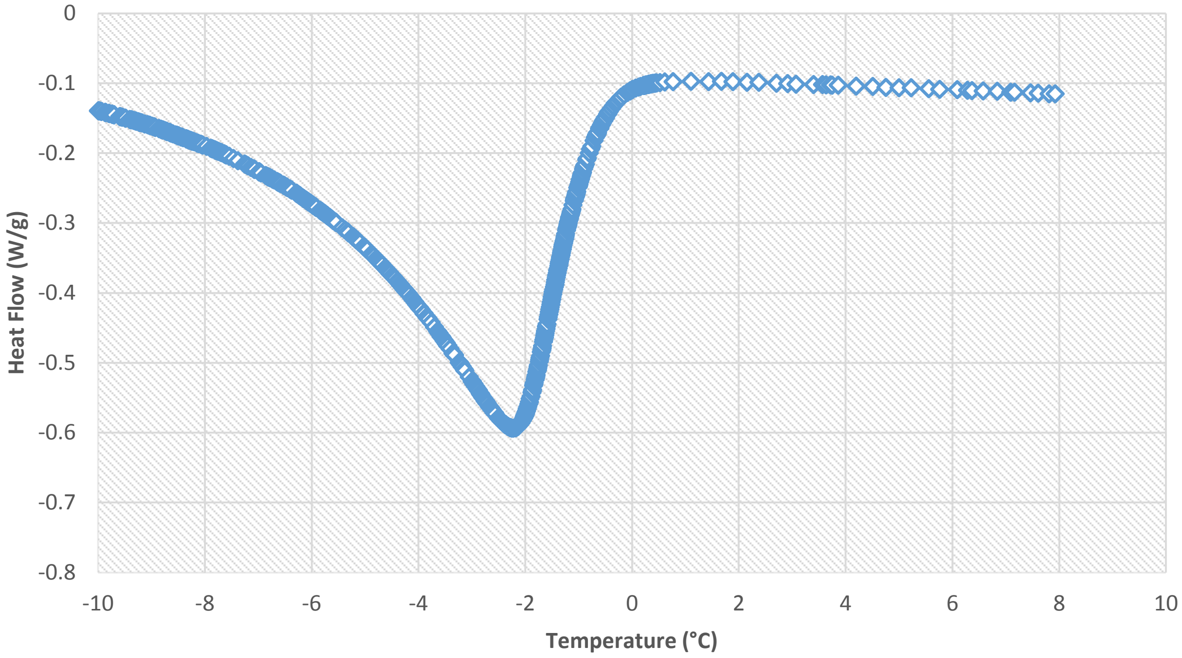


Figure 108. DSC measurement of 0.10% stabilized ice cream.

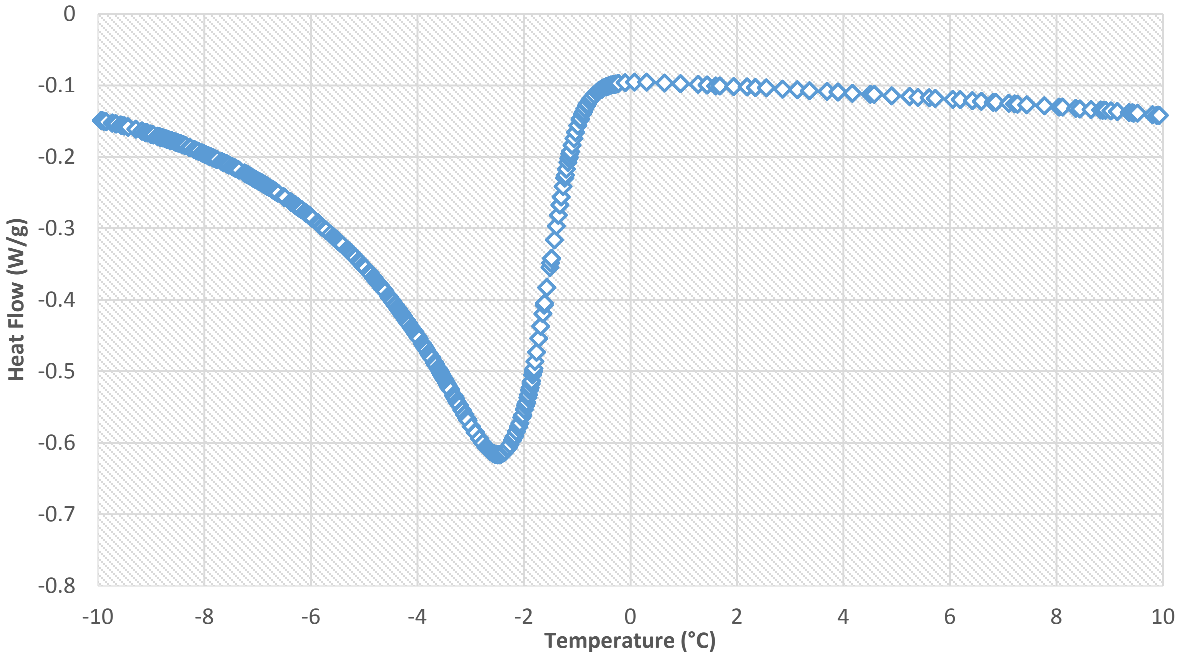


Figure 109. DSC measurement of 0.15% stabilized ice cream.
