Control of Physical Changes in Food Products

21

Kiyoshi Kawai and Tomoaki Hagiwara

Abstract

Food is a multicomponent system that mainly comprises protein, carbohydrate, fat, and water. During food processing and preservation, various physical changes (e.g., melting, crystallization, glass transition) occur in food products, affecting their quality. This chapter specifically examines the effect of physical changes on the quality of dry and frozen food products. Dry food products are commonly in an amorphous state. Therefore, glass transition occurs during their dehydration–rehydration processing. To control their texture and physical stability, it is important to elucidate the effects of water contents on the glass transition temperature of dry food products. Frozen foods consist of ice crystals and freeze-concentrated matrix. The formation of ice crystal and the dynamics of ice crystal evolution affect food quality. Therefore control of ice crystals is important for high-quality frozen food. Moreover, because freeze-concentrated matrix consists of solute that are plasticized by the unfrozen water and is in an amorphous state, it can undergo glass transition by freeze concentration. The physical state of freeze-concentrated matrix also strongly affects the stability of food quality during frozen storage.

Keywords

Glass transition · Water plasticizing · Ice crystallization · Dry food · Frozen food

Abbreviations

AFP	Antifreeze protein
DSC	Differential scanning calorimetry
MD	Maltodextrin
T_g	Glass transition temperature
T_g'	Glass transition temperature of the maximally freeze-concentrated phase
TRA	Thermal rheological analysis
W_c	Critical water content

K. Kawai (✉)
Graduate School of Biosphere Science, Hiroshima University, Higashi-Hiroshima, Hiroshima, Japan
e-mail: kawai@hiroshima-u.ac.jp

T. Hagiwara
Graduate School of Marine Science and Technology, Tokyo University of Marine Science Technology, Tokyo, Japan

21.1 Introduction

Food is a multicomponent system that mainly comprises protein, carbohydrate, fat, and water. During food processing and preservation, various

M. Iwaya-Inoue et al. (eds.), *Survival Strategies in Extreme Cold and Desiccation*, Advances in Experimental Medicine and Biology 1081, https://doi.org/10.1007/978-981-13-1244-1_21

physical changes (e.g., melting, crystallization, glass transition) occur in food products, affecting their quality. This chapter specifically examines the effects of physical changes on the quality of dry and frozen food products. In the first part, effect of water content on the glass transition temperature (T_g) of dry food products (dry fruits and cookie) and trial to predicting T_g is presented for understanding physical changes of dry food products induced by water sorption. In the second part, physical changes of frozen food products during cooling and frozen storage, such as ice crystallization, freeze concentration, eutectic separation, glass transition, recrystallization of ice crystal, and sublimation of ice, and their effects on quality of frozen food are reviewed.

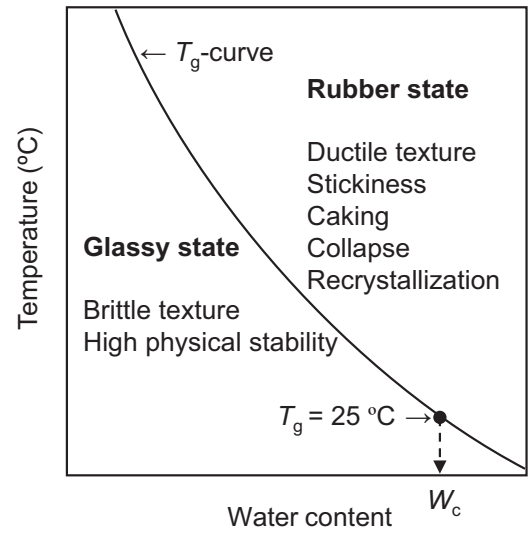


Fig. 21.1 Effect of water content on the T_g (T_g curve) of dry food products. The water content at which T_g is 25 °C is described as the critical water content (W_c)

21.2 Glass Transition of Dry Food Products

21.2.1 Role of Glass Transition in Dry Food Products

Dry food products are commonly in an amorphous state. Therefore, they undergo a glass to rubber transition (glass transition) during dehydration–rehydration processing. This transition involves a physical change between a solid-like (glassy) state and a liquid-like (rubbery) state and causes a drastic change in rheological properties. The temperature at which glass transition occurs is known as the glass transition temperature (T_g). Glass transition can also occur with no change in temperature if the water content changes because T_g of hydrophilic amorphous solids decreases with increased water contents. The water content at which T_g is 25 °C is described as the critical water content (W_c). The glass transition behavior can be described as a T_g curve (effect of water content on T_g), as presented in Fig. 21.1. In the area under the T_g curve, the food product is in a glassy state. Glassy food products have a hard or brittle texture because of their high elasticity (Payne and Labuza 2005a, b). In addition, glassy food products are expected to have greater physical stability than rubber ones because of their low molecular mobility. In the area above the T_g curve, the food products are in a rubber state. Rubbery food products, which have a soft or ductile texture, undergo various physical changes (e.g., stickiness, caking, collapse, sugar crystallization) because of their high molecular mobility (Roos 1995; Jaya and Das 2004; Cano-Chauca et al. 2005; Palzer 2005; Harnkarnsujarit and Charoenrein 2011a, b; Zou et al. 2013). To control their texture and physical stability, it is important to ascertain the T_g curve of dry food products.

21.2.2 Glass Transition of Dry Fruits

Dry fruits include large amounts of low-molecular-weight carbohydrates (e.g., sucrose, fructose, glucose). Because these carbohydrates have a low T_g, dry fruits readily undergo a glass transition because of water sorption.

The T_g of dry fruits is commonly evaluated using differential scanning calorimetry (DSC). Glass transition can be detected as an endothermic shift in a DSC thermogram. However, glass transition observed in the first scanning shows an endothermic peak because of the enthalpy relaxation effect depending on the thermal history of glassy samples (Kawai et al. 2005). Enthalpy

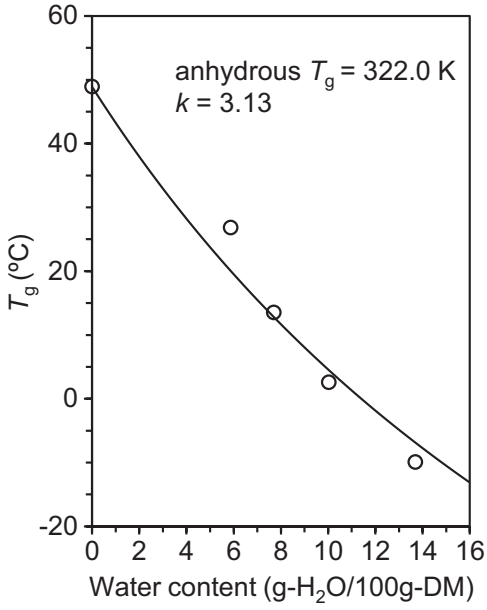


Fig. 21.2 Effect of water content on the T_g of dry mango pulp. The T_g was evaluated using DSC. The solid line was given by the Gordon–Taylor equation with two parameters (anhydrous T_g and k). The anhydrous T_g was evaluated experimentally and k was determined as a fitting parameter

relaxation is a process wherein the excess enthalpy of glass in a non-equilibrium thermodynamic state decreases spontaneously toward its equilibrium value. The T_g value is known to be affected to various degrees by the enthalpy relaxation effect (Haque et al. 2006). To cancel the thermal history of glassy samples on T_g, DSC measurement is taken again after the first scanning. Therefore, T_g can be determined from the onset point of the shift in the second scanning.

Effect of water content on the T_g of dry mango pulp is shown in Fig. 21.2. The T_g decreased with increased water content because of water plasticizing effect. This behavior can be summarized as a T_g curve, as depicted in Fig. 21.2. The solid line represents fitting of the Gordon–Taylor equation (Eq. 21.1) to the T_g data.

$$T_g = \frac{W_s T_{gs} + kW_w T_{gw}}{W_s + kW_w} \quad (21.1)$$

Therein, W_s and W_w, respectively, represent the weight fractions of mango pulp and water. T_{gs} and T_{gw} are T_g for anhydrous mango pulp and water, respectively, whereas k is a constant. T_{gs} was evaluated experimentally. T_{g2} was set to 136 K, as reported in the literature (Johari et al. 1987; Sastry 1999). When k was determined as a fitting parameter, the T_g curve presented in Fig. 21.2 was obtained. The k represents the sensitivity to water plasticizing: higher k is associated with greater T_g depression caused by water sorption. From the T_g curve, W_c can be evaluated.

For low-molecular-weight carbohydrates including polyol, a linear relation is known to exist between anhydrous T_g (°C) and k (Roos 1995) as

$$k = 0.0293 \times \text{anhydrous} T_g + 3.61 \quad (21.2)$$

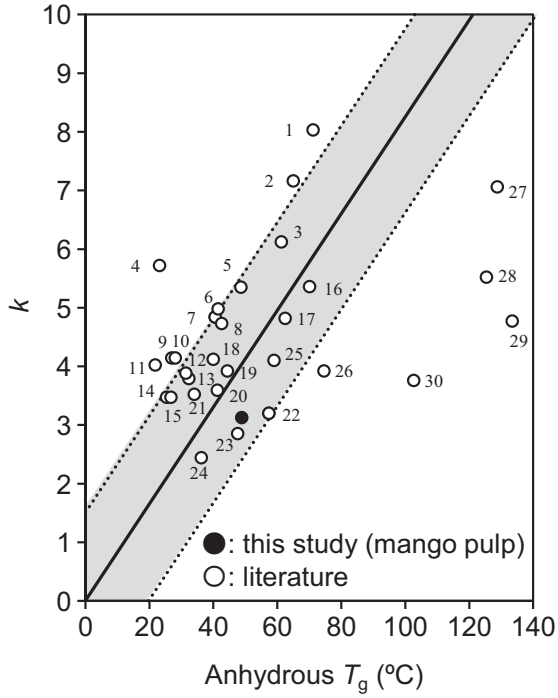
The major constituent of dry fruits is low-molecular-weight carbohydrates. Therefore, similar behavior would be expected in dry fruits. The relation between anhydrous T_g and k for dry fruits of various types (Bai et al. 2001; Fabra et al. 2011; Kasapis et al. 2000; Khalloufi et al. 2000; Kurozawa et al. 2012; Moraga et al. 2004, 2006, 2011; Mosquera et al. 2010, 2012; Oikonomopoulou & Krokida 2012; Silva et al. 2006; Sobral et al. 2001; Sonthipermpoon et al. 2006; Syamaladevi et al. 2009; Telis 2006; Telis & Martínez-Navarrete 2009; Vásquez et al. 2013; Wang et al. 2008; Zotarelli et al. 2017) is presented in Fig. 21.3. Although some outliers (e.g., camu camu, persimmon, plum) were observed, there was a roughly linear relation.

$$k = 0.0825 \times \text{anhydrous} T_g + 0.005 \pm 1.5749 \quad (21.3)$$

As described above, a T_g curve can be described by the Gordon–Taylor equation with two parameters (anhydrous T_g and k). W_c can be evaluated from the T_g curve. Consequently, Eq. 21.3 is expected to be useful for the prediction of T_g depression and physical changes of dry fruits induced by water sorption.

21.2.3 Physical Modification of Dry Fruits Based on T_g

As described above, dry fruits undergo physical deterioration of various types at temperatures higher than T_g. To improve their physical stability,



1. Kiwifruit1 (homogenized tissue) (Moraga et al., 2006)
2. Kiwifruit1 (entire tissue) (Moraga et al., 2006)
3. Banana (Moraga et al., 2011)
4. Chinese gooseberry (Wang et al., 2008)
5. Banana flake (Sonthipermpoon et al., 2006)
6. Kiwifruit 2 (homogenized tissue) (Moraga et al., 2006)
7. Kiwifruit 2 (entire tissue) (Moraga et al., 2006)
8. Raspberry (Syamaladevi et al., 2009)
9. Strawberry (homogenized tissue) (Moraga et al., 2004)
10. Strawberry (entire tissue) (Moraga et al., 2004)
11. Blueberry (Khalloufi et al., 2000)
12. Strawberry (Oikonomopoulou and Krokida, 2012)
13. Mango with maltodextrin (Zotarelli et al., 2017)
14. Apple (Moraga et al., 2011)
15. Mango (Zotarelli et al., 2017)
16. Borojó (Mosquera et al., 2010)
17. Noni (Fabra et al., 2011)
18. Blackberry (Khalloufi et al., 2000)
19. Camu-Camu (Silva et al., 2006)
20. Apple (Bai et al., 2001)
21. Strawberry (Khalloufi et al., 2000)
22. Date (Kasapis et al., 2000)
23. Raspberry (Khalloufi et al., 2000)
24. Blueberry (Vásquez et al., 2013)
25. Strawberry (Mosquera et al., 2012)
26. Grapefruit (Telis and Martínez-Navarrete, 2009)
27. Papaya (Kurozawa et al., 2012)
28. Camu-Camu with maltodextrin (Silva et al., 2006)
29. Persimmon (Sobral et al., 2001)
30. Plum (Telis, 2006)

Fig. 21.3 Relation between anhydrous T_g and k for various types of dry fruits. The solid line is a mean linear relationship. The upper and lower dotted lines are the variation of the mean linear relationship. Most of the data exist in the gray zone. The applied ranges of anhydrous T_g and k were 21–75 °C and 2.0–8.0, respectively

it is important to elevate the T_g of dry fruits by additives with high-T_g materials. Maltodextrin (MD), which has a much higher T_g (100–243 °C) than low-molecular-weight carbohydrates (Goula and Adamopoulos 2008), has been used as the physical modifier of dry fruits. For example, some related reports on it are being used in camu camu (Silva et al. 2006), tomato pulp (Goula and Adamopoulos 2008), grapefruit juice powder (Telis and Martínez-Navarrete 2009), borojó powder (Mosquera et al. 2010), orange juice powder (Goula and Adamopoulos 2010), strawberry (Mosquera et al. 2012), and mango powder (Zotarelli et al. 2017). In an earlier study conducted by the authors (Fongin et al. 2017), the effect of MD addition on the glass transition properties of dry mango pulp was investigated. It was demonstrated that the anhydrous T_g increased with an increase in MD content (Fig. 21.4). A systematic study showed that an abrupt anhydrous T_g change occurred between 60% and 70% MD. Similar observations were also obtained for the T_g change for glucose–MD and maltose–MD mixtures (Kawai and Hagura 2012). These results suggest that amorphous mixtures have heterogeneous molecular dynamics. MD is plasticized by the mango pulp above 70% MD content. Consequently, the anhydrous T_g decreases continually with increasing mango pulp content. In the region, glass transition of the mango pulp–MD mixture will occur cooperatively. Part of the mango pulp is excluded from the mango pulp–MD domain when the MD content decreases to less than 60%. Then, not only a mango pulp–MD domain but also a mango pulp-rich domain (lower anhydrous T_g) is formed in the amorphous system. Consequently, an abrupt anhydrous T_g change can be observed at MD contents of 60–70%.

The k value of dry mango pulp also increased with an increase in MD content. The relation between anhydrous T_g and k obeys Eq. 21.3 below MD content of 60%. By the further addition of MD, the relation between anhydrous T_g

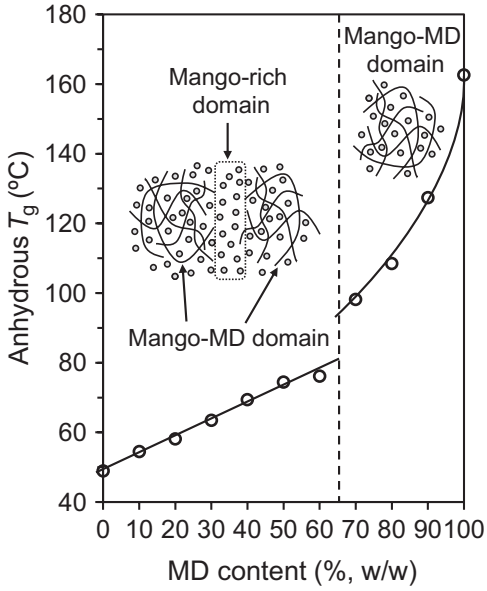


Fig. 21.4 Effect of maltodextrin (MD) addition on the anhydrous T_g of mango pulp. An abrupt anhydrous T_g change occurred between 60% and 70% MD. The suggested turning point is indicated by dotted line. Inserted drawing is a model of heterogeneous molecular dynamics in the amorphous system

and k deviates from Eq. 21.3 (for dry fruits) and approaches Eq. 21.2 (for low-molecular-weight carbohydrates). This can be related to the suggestion described above: the mango pulp-rich domain is lost from the amorphous mixture system at MD contents between 60% and 70%.

21.2.4 Glass Transition Properties of Dry Bakery Products

The T_g of amorphous materials has commonly been evaluated using DSC. However, when a more complex multicomponent system (e.g., a cookie) is subjected to DSC measurement, a continuous thermal response is observed. Also, the endothermic shift associated with the glass transition is overlapped. In addition, because starch-based food intrinsically shows a small and broad endothermic shift, it is difficult to evaluate the T_g from the DSC thermogram. In such cases, thermomechanical approaches such as thermomechanical compression test (TMCT), thermal mechanical analysis (TMA), and dynamic thermal mechanical analysis (DMTA) are useful. For example, T_g values of barley (van Donkelaar et al. 2015), rice (Thuc et al. 2010), dairy powder (Hogan et al. 2010), peas (Pelgrom et al. 2013), chocolate wafers (Payne and Labuza 2005b), and abalone (Sablania et al. 2004) have been found using thermomechanical approaches. An earlier study conducted by the authors (Kawai et al. 2014) established thermal rheological analysis (TRA), which is almost equivalent to TMCT and TMA. The TRA curve shows a clear force drop associated with the glass transition: mechanical T_g can be determined from the onset point. It is confirmed that TRA is an effective tool to evaluate T_g of bakery products including cookies. It is noteworthy that T_g determined by thermomechanical approaches does not always agree with that determined by DSC (Sandoval et al. 2009). Thermal T_g observed by DSC has a clear physical meaning, representing the temperature at which the viscosity is approximately 10^{12} Pa•s (Angell et al. 1994). Mechanical T_g is more sensitive to experimental conditions such as mechanical force, heating rate, and sample quantity (Lacík et al. 2000; Ross et al. 2002; Boonyai et al. 2007).

Cookie dough mainly comprises wheat flour, sugar, butter, and egg. Three types of sugar composition (sucrose alone, sucrose containing 40% trehalose, and sucrose containing 40% sorbitol on a dry weight basis) were used and baked for cookie production. Effect of water content on the mechanical T_g of the handmade cookie samples is presented in Fig. 21.5. The mechanical T_g of the cookie samples decreased with an increase in water content because of water plasticizing effect, similar to the case for dry fruits. The onset point would be independent of water content if the force drop observed in the TRA curve resulting from the melting of fat. The fact that the force-drop point decreased with an increase in water content reveals that the rheological response resulted from glass transition of the cookie samples and not simply by the melting of fat. The water content of cookies is approximately 3–4% under the initial conditions. Consequently, it was noted that normal cookies (sucrose alone) were in a glassy state at 25 °C,

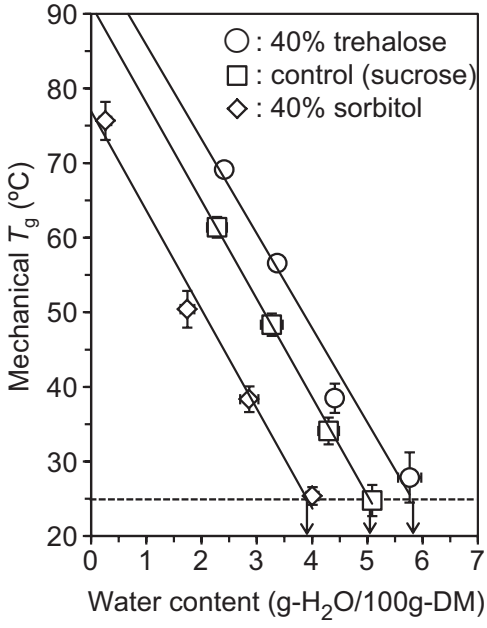


Fig. 21.5 Effect of water content on the mechanical T_g of cookie samples with varying sugar compositions. The mechanical T_g was evaluated using TRA

which explains why they had a brittle texture. When the water content of normal cookies became higher than W_c (5.04 g-H_2O/100 g-DM), they transitioned into a rubber state. Therefore, the brittle texture changed to a ductile one. Trehalose-added cookies had higher mechanical T_g and W_c than normal cookies because trehalose has higher anhydrous T_g (114 °C) than sucrose (62 °C). Consequently, it was concluded that trehalose can improve the physical stability of cookies; trehalose led to the brittle–ductile texture change occurring at higher water content than in normal cookies. By contrast, sorbitol-added cookies had lower mechanical T_g and W_c than normal cookies had because sorbitol has lower T_g (−9 °C) than sucrose. Considering these findings, the sorbitol-added cookies showed ductile texture, even at low water content. This texture is also important to control the cookie texture.

It is noteworthy that anhydrous mechanical T_g for cookies increased with an increase in the T_g for the sugar composition used for cookie preparation. When the anhydrous mechanical T_g for cookies (extrapolated value) was shown against anhydrous T_g for sugar composition (experimental value obtained by DSC), a linear relation (anhydrous mechanical T_g for cookie = 0.3245 × anhydrous T_g for sugar composition +71.62) was identified, which indicates that the mechanical T_g of cookies can be characterized by the T_g of sugar composition. Cookies comprise a continuous glassy sugar or toffee-like matrix containing embedded starch granules, an undeveloped gluten network, and fat (Slade and Levine 1994; Chevallier et al. 2002). Consequently, the physical properties of cookies depend strongly on the sugar composition. Numerous publications describe the T_g of carbohydrate materials and their mixtures. They are expected to be useful for predicting the T_g of cookies.

21.3 Physical Changes of Frozen Food Products During Cooling and Frozen Storage

21.3.1 Ice Crystallization in Frozen Food Products During Cooling

During cooling of food, crystallization of water component occurs after supercooling and nucleation. The size of ice crystal in frozen food strongly affects its quality. Rapid freezing gives smaller ice crystals and even distribution of ice crystals in food. The rate of ice nuclei formation is larger at lower temperatures. Ice crystal growth is most accelerated around the equilibrium ice melting temperature, a zone of maximum ice crystal formation (0 to −5 °C). Therefore more nuclei occur, and ice crystal growth is suppressed when a food is passed quickly through a maximum ice crystal production zone by rapid cooling. Rapid freezing is desirable for most foods. Slow freezing produces larger ice crystals, inhomogeneous locations of ice crystals, shrunken appearance of the microstructure, and usually lower quality than rapid freezing. For cryopreservation of living cells and microorganism, slow freezing might sometimes be preferred (Franks 1985). Rapid freezing usually causes intracellular ice crystal formation, which is lethal for cells. Slow freezing

initiates the formation of nuclei outside cell and extracellular ice crystallization occurs. Furthermore, cells are dehydrated during the process of extracellular ice crystallization. Extracellular crystallization and dehydration of cells suppress intracellular crystallization. Practically speaking, an aid of cryoprotectant such as dimethyl sulfoxide (DMSO), glycerol, and trehalose is needed for successful cryopreservation of living cells and microorganisms. Cryoprotectants permeate into a cell or dehydrate a cell by osmotic pressure action. Consequently, water contents in the cell are reduced, which suppresses intracellular crystallization (Franks 1985).

21.3.2 Freeze Concentration

Upon cooling food products below 0 °C, ice formation and separation of water from food solids occur. Consequently, solute concentration of unfrozen part increases as ice contents increase with declining temperatures. This phenomenon is called "freeze concentration." Generally, a rate of chemical reaction decreases at lower temperatures. However, the chemical or biochemical reaction rate increases sometimes because of lowered temperatures when the effect of increase of reactant by freeze concentration overcomes that from lowered temperatures (Fennema et al. 1973; Franks 1985). The freeze concentration engenders a change of pH or electrolyte concentration in food, which can cause protein denaturation (Fennema et al. 1973; Franks 1985).

Freeze concentration has been used for the concentration of liquid foods such as fruit juices (Deshpande et al. 1982; Bayindirli et al. 1993; Miyawaki et al. 2016), vegetable juices (Miyawaki et al. 2005), and dairy products (Hartel and Espinel 1993). Among the methods of concentrating liquid food, freeze concentration presents several benefits: low energy requirements, low process temperature preventing undesirable chemical and biochemical changes, and minimal loss of flavors and aromas (Ramteke et al. 1993; Liu et al. 1997).

21.3.3 Eutectic Separation

Lowering the temperature continuously, the concentration of freeze-concentrated phase reaches its solubility at last. At this point, the concentration of solute cannot become any higher without increasing the temperature (Franks 1985). When more ice is formed, the amount of dissolved solute is too high and solute crystals start to form simultaneously. This phenomenon is called "eutectic separation." The temperature at which eutectic separation occurs is known as the eutectic point. The eutectic point of sodium chloride is −21.1 °C. Practical eutectic separation probably occurs only rarely in most frozen foods because of the complex nature of food materials (Roos 1995). However, it is well known that lactose in ice cream is often crystallized during frozen storage by supersaturation. It does not crystallize immediately after freezing because of kinetic constraints, but it crystallizes after a certain period of storage. Subsequently, the crystals grow (Roos 1995). When lactose crystals grow so large that they can be detected in the mouth, the smooth texture of ice cream is transformed into a sandy texture: an unacceptable product (Marshall and Arbuckle 2000).

21.3.4 Glass Transition by Freeze Concentration

It is quite often true that the solute does not crystallize at the eutectic point from aqueous solution system within a practically realistic time scale. Consequently, freeze concentration proceeds continuously by lowering the temperature. Finally, the freeze-concentrated phase turns into a glassy state at a specific temperature (T_g'). Ice crystallization ceases at T_g' because the high viscosity of the freeze-concentrated matrix suppresses diffusion of water molecules to the surface of existing ice crystal (Franks 1985; Roos 1995). Frozen food below T_g' is a mixture of the glassy amorphous substance and ice crystals. It is generally acknowledged that the deterioration of frozen food during storage is minimized by

maintaining it below T_g' (Franks 1985; Agustini et al. 2001). It is noteworthy that exposure of a freeze-drying material to temperatures higher than T_g' causes melting of ice crystals and softening of the freeze-concentrated matrix (Roos 1995). Because the freeze-concentrated matrix cannot support its own weight, collapse, reduced water removal rate, and inferior product quality occur (Roos 1995).

21.3.5 Ice Recrystallization During Frozen Storage

Ice crystal size and shape are unstable during frozen storage even if the temperature is constant. They change continuously through the process of "recrystallization," which includes any change in number, size, shape, orientation, or perfection of crystals following the completion of initial solidification (Fennema et al. 1973). Recrystallization proceeds as a result of minimization of surface free energy of the entire crystal phase (Fennema et al. 1973; Hartel 1998). Recrystallization of ice crystals during storage and distribution is a major cause of deterioration in frozen foods, especially frozen desserts. Generally, the recrystallization of ice crystals in frozen foods is characterized as an increase in the mean size of ice crystals (Fennema et al. 1973; Hartel 2001) (Fig. 21.6).

Three recrystallization mechanisms are likely to occur during the conventional storage of frozen food: migratory, isomass, and accretion (Fennema et al. 1973; Hartel 2001). Migratory recrystallization refers to the trend for larger crystals in a polycrystalline system to grow in size at the expense of smaller crystals. Smaller crystals cannot bind their surface water molecules as tightly as larger ones because of the higher curvature and higher surface free energy. Therefore, the water molecules on the surface of smaller crystals tend to transfer to the surface of larger ones through the freeze-concentrated

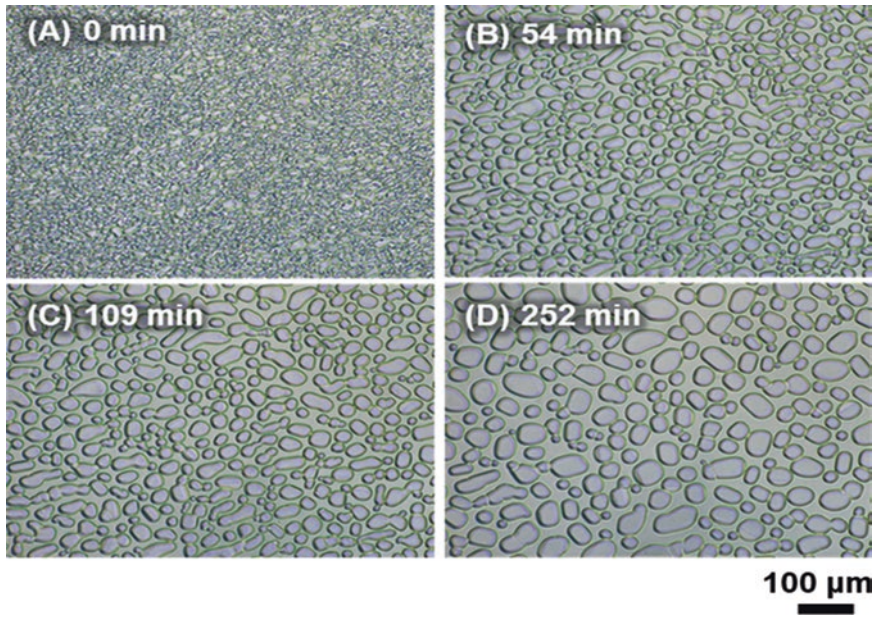


Fig. 21.6 Example of ice recrystallization during storage. Sample, 25% glucose; storage temperature, −10 °C; storage time (**a**) 0 min, (**b**), 54 min, (**c**) 109 min, (**d**) 252 min; observation procedure, 2 μl sample solution enclosed between two coverslips (diameter, 12 mm) was placed on the sample stage to be frozen at −22 °C. After 10 min, the temperature was elevated to the observation temperature (−10 °C) at a rate of 1.5 °C/min. Finally, after the observation temperature was reached, ice crystal images were periodically photographed (Hagiwara et al. 2006)

matrix, engendering the growth of larger crystals and disappearance of smaller ones. A similar process called isomass recrystallization can occur in a single crystal. Consider a single separated crystal with a rough surface. The part of the surface with higher curvature cannot bind surface water molecules as tightly as a smoother surface. As a result, the rougher surface becomes smoother. Accretion recrystallization is the process by which two crystals that are in mutual contact grow together into one larger crystal. Because the contact point has apparently high curvature and because it is not as stable as the rest, neck formation occurs by transportation of water molecules to this region, which engenders growth into one crystal.

When temperature fluctuations occur during storage, the recrystallization process is enhanced by melt–refreeze recrystallization, which is more important for ice cream texture/shelf life in practical situations than during isothermal processes (Hartel 2001).

To describe a change of ice crystal size by isothermal recrystallization, the following two equations have been used.

$$R^3 = R_0^{\,3} + kt \tag{21.4}$$

$$R^2 = R_0^{\,2} + kt \tag{21.5}$$

Therein, R stands for the averaged size of ice crystals, R_0 signifies the averaged size of ice crystals at time $t = 0$, and k denotes the isothermal recrystallization rate constant. The recrystallization process in ice cream and its model solutions can be described well by Eq. 21.4 (Sutton et al. 1996; Hagiwara et al. 2006; Klinmalai et al. 2017). Equation 21.5 was applied for ice recrystallization in frozen beef (Bevilacqua and Zaritzky 1982).

Recrystallization of ice crystals in frozen foods has been studied extensively. The group of Zaritzky et al. studied the recrystallization of frozen beef and its model system (Bevilacqua and Zaritzky 1982; Martino and Zaritzky 1988, 1989). The effects of storage temperature, temperature fluctuation, sweeteners, and stabilizers on the recrystallization rate of ice crystals in ice cream have also been reported (Donhowe and Hartel 1996a, b; Hagiwara and Hartel 1996; Miller-Livney and Hartel 1997).

Table 21.1 Sample sugar solutions. Values of ice content and concentration of freeze-concentrated matrix were calculated by using literature values of freezing point depression versus solute concentration (Young and Jones 1949; Young et al. 1952; Young 1957; Lide 2003)

Sample	Storage temperature(°C)	Freeze-concentrated matrix conc. (%)	Ice content (%)
21.8% maltose	−4.4	40.0	45.4
22.45% sucrose	−4.6	41.1	45.4
18.5% glucose	−5.8	34.0	45.5
25.0% sucrose	−5.8	45.8	45.5
22.45% fructose	−8.0	41.1	45.4
28.6% sucrose	−8.0	52.4	45.4
25.0% fructose	−10.0	45.8	45.5
25.0% glucose	−10.0	45.9	45.4

The ice contents of all samples were set almost equal to omit the detailed discussion about effect of ice content on recrystallization rate (Hagiwara et al. 2006)

To elucidate recrystallization phenomena, it is necessary to comprehend not only the correlation between production conditions and recrystallization rate constant but also the molecular-level mechanisms accounting for different recrystallization rates. A better understanding of the molecular mechanisms of recrystallization is expected to facilitate the systematic prediction and control of recrystallization behavior for various frozen foods. Recently it has been recognized that the concept of water mobility is useful for predicting and controlling the recrystallization rate in frozen foods (Ablett et al. 2002; Hagiwara et al. 2006, 2009; Klinmalai et al. 2017). Reportedly, recrystallization rates in a series of frozen saccharide solutions (Table 21.1) increased concomitantly with increasing the diffusion coefficients of water component in the freeze-concentrated matrix. A direct relation was found between the recrystallization rate and the diffusion coefficient (Hagiwara et al. 2006, 2009) (Fig. 21.7). This

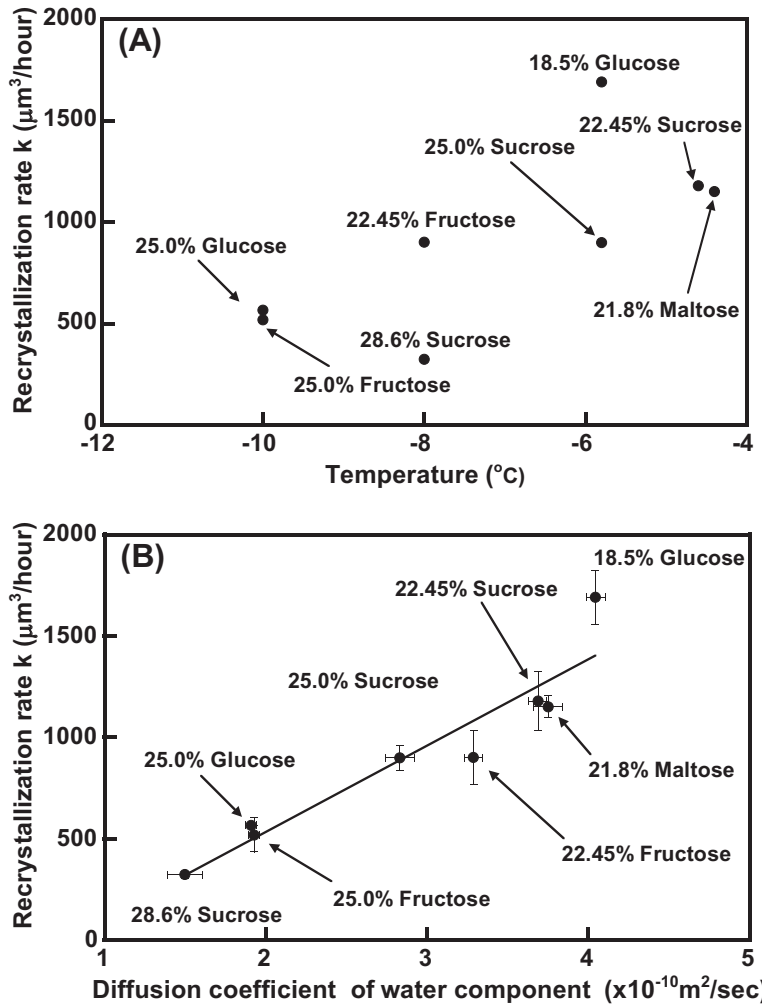


Fig. 21.7 Plots of recrystallization rate constant K of ice crystals in various frozen saccharide solutions as a function of (**a**) temperature and (**b**) diffusion coefficient of water component in a freeze-concentrated matrix. Sample saccharide solutions are listed in Table 21.1. The recrystallization rate constant K of ice crystals was obtained by using Eq. 21.4 (Hagiwara et al. 2006). The diffusion coefficient of water component was measured by pulse field gradient stimulated gradient echo proton NMR method (Hagiwara et al. 2006)

relation indicates that the self-diffusion coefficient of water component in freeze-concentrated matrix is a useful parameter for predicting and controlling recrystallization. The ^{1}H spin–spin relaxation time T_2 of water components in freeze-concentrated matrix also shows good correlation with the recrystallization rate constant (Ablett et al. 2002; Klinmalai et al. 2017).

21.3.6 Effects of Glass Transition on Recrystallization of Ice Crystals

Based on the concept of water mobility in freeze-concentrated matrix, the recrystallization of ice crystals is expected to be strongly suppressed below T_g' because the molecular mobility is strongly restricted. Hagiwara et al. (2005) investigated the recrystallization of ice crystals in a 30% sucrose solution at temperatures of −21 to −50 °C, including temperatures around T_g' (−32 °C). As the storage temperature decreased, a rapid decline in the recrystallization rate was observed between −29 and −35 °C (Fig. 21.8). This result is consistent with the concept of the glass transition of the freeze-concentrated matrix. It is noteworthy that even at −50 °C, at which the freeze-concentrated matrix is regarded as being in glassy state, an increase in the mean crystal size was observed within 20 h storage. This observation suggests that, over a realistic storage period, deterioration by recrystallization might occur, even in the glassy state. In general, it is

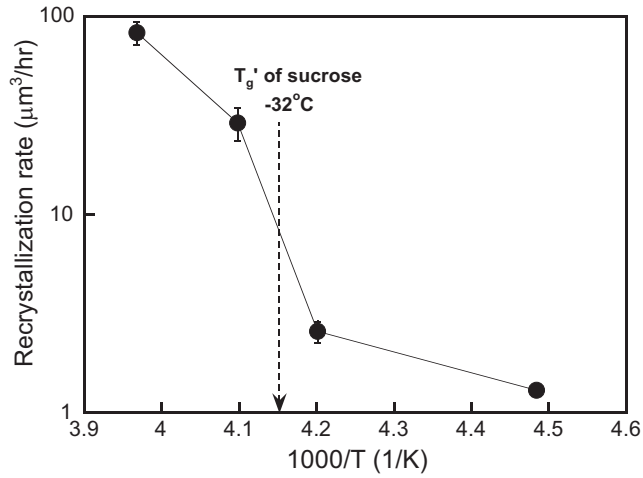


Fig. 21.8 Arrhenius plot of recrystallization rate of ice crystals in frozen 30% sucrose solutions

believed that food in a glassy state is very stable because its molecular motion is restricted severely. However, in the field of polymer science, it is well-recognized that molecular movement leading to macroscopic structural relaxation over a practical period remains below the glass transition temperature because of the non-equilibrium nature of glassy substances (Matsuoka 1992; Yoshida 1995; Tiemblo et al. 2002). Molecular mobility in glassy food and food component carbohydrates with low moisture content has also been investigated recently (Hancock et al. 1995; Urbani et al. 1997; Kim et al. 2003; Hashimoto et al. 2004; Kawai et al. 2005). Regarding frozen food systems, molecular mobility in the freeze-concentrated phase of trehalose (Pyne et al. 2003) and sucrose solutions (Inoue and Suzuki 2005) below T_g' was investigated on the concept of enthalpy relaxation. Molecular motion in a freeze-concentrated solute matrix might be sufficient to cause ice recrystallization over a realistic storage period, even in a glassy state.

21.3.7 Recrystallization of Ice Crystals in the Presence of Antifreeze Protein (AFP)

Recently, many antifreeze proteins (AFPs) have been extracted from a variety of sources (Davies and Hew 1990; Graether et al. 2000; Griffith and Yaish 2004; Regand and Goff 2006; Kawahara et al. 2009). They are now anticipated as additives for suppressing ice recrystallization process. AFPs suppress ice crystal growth by an adsorption–inhibition mechanism (Raymond and DeVries 1977). They inhibit thermodynamically favored ice crystal growth by their adsorption to specific planes of ice crystals (Raymond et al. 1989).

To put AFP into practical use as a recrystallization suppressor, evaluation of their suppression ability is fundamentally important. A typical AFP extracted from polar fish, AFP type I, actually suppresses the recrystallization of ice crystals efficiently, with quite a low concentration (Fig. 21.9) (Hagiwara et al. 2011). The recrystallization rate constant of 33 wt% sucrose solution containing 1 μg/ml AFP type I was about 13% of that of sample without AFP (Table 21.2). No marked reduction of recrystallization rate was observed for samples containing 0.1 μg/ml or 0.01 μg/ml AFP type I.

21.3.8 Sublimation of Ice in Frozen Food Products

When frozen foods are stored without appropriate moisture-proof package, the food surface is dehydrated. Consequently the surface has an opaque appearance called "freezer burn" (Fennema et al. 1973). Freezer burn results from the sublimation of ice on the surface of frozen foods when the water vapor pressure of the ice is higher than that in the environmental air

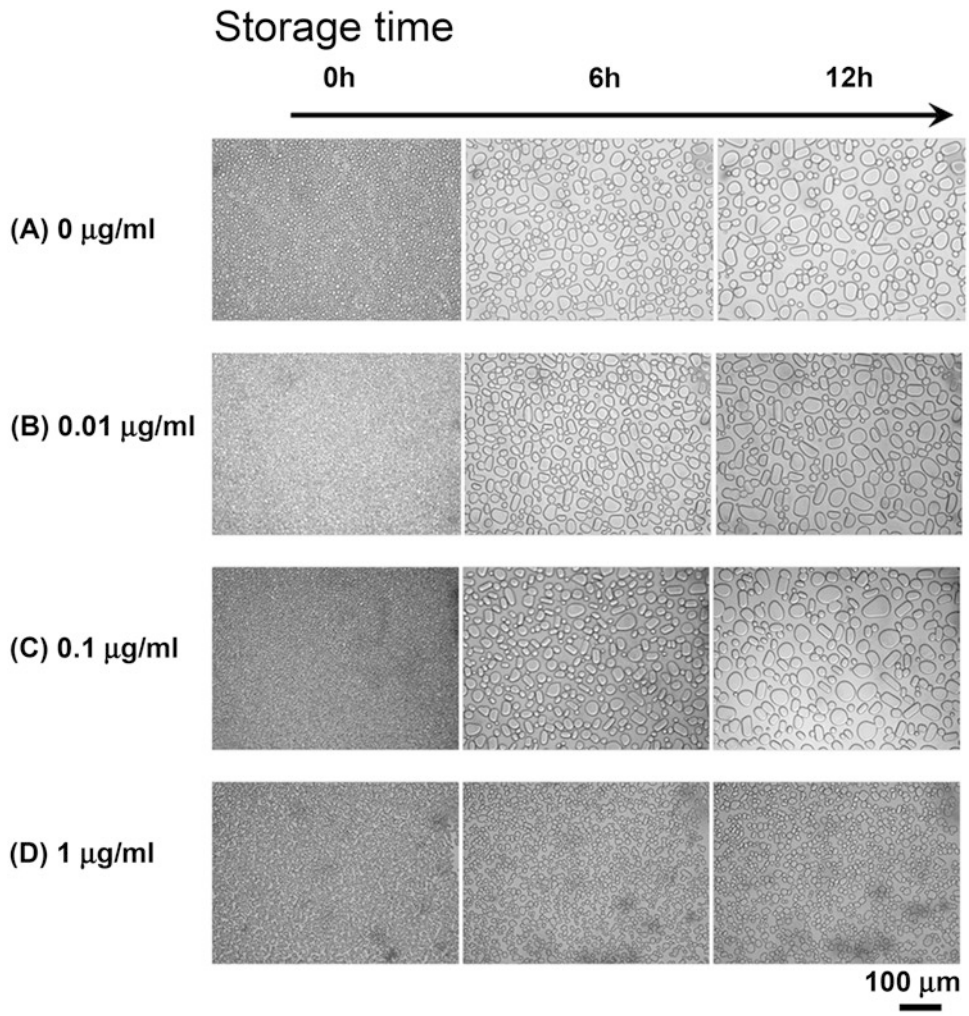


Fig. 21.9 Effects of AFP type I addition on recrystallization of ice crystals in 33% sucrose solution at −10 °C. The concentrations of AFP type I; (**a**) 0 μg/ml, (**b**) 0.01 μg/ml, (**c**) 0.1 μg/ml, (**d**) 1 μg/ml

Table 21.2 Summary of recrystallization rate constants for the samples with different AFP type I concentrations

	0 μg/ml	0.01 μg/ml	0.1 μg/ml	1 μg/ml
Recrystallization rate constant k ($\mu m^3/h$)	186 ± 54	200 ± 58	173 ± 25	24 ± 8

(Fennema et al. 1973). The temperatures of specific parts of the freezer shelf, such as the heat exchanger, are lowest: lower than the stored frozen foods. Therefore, the situation described above normally occurs in most cases. Vapor from the frozen food surface adheres to the surface of the lower temperature part in the shelf of freezer, which is familiar to us as "frost." The sublimation of ice enhances many deteriorative processes such as lipid oxidation, color change, protein denaturation, odorous emissions, and the decline of nutritional value. Therefore, suppression of ice sublimation is necessary for the long-term preservation of frozen foods.

21.4 Conclusion

As reviewed above, melting, crystallization, and glass transition occur in the food products during food processing and preservation and affect their quality. This chapter will help to control and predict the quality of dry and frozen food products. In addition, it is important to understand the adaptation mechanisms of organism in extreme cold and desiccation as seen in the other chapters.

Acknowledgments K. Kawai gratefully acknowledges financial support from JSPS KAKENHI: Grant-in-Aid for Young Scientists B (24780129) and Grant-in-Aid for Scientific Research C (15K07453). T. Hagiwara acknowledges funding from the Iwatani Naoji Foundation.

References

Ablett S, Clarke CJ, Izzard MJ, Martin DR (2002) Relationship between ice recrystallisation rates and the glass transition in frozen sugar solutions. J Sci Food Agr 82:1855–1859

Agustini TW, Suzuki T, Hagiwara T, Ishizaki S, Tanaka M, Takai R (2001) Change of K value and water state of yellowfin tuna (*Thunnus albacares*) meat stored in wide temperature range (20°C to −84°C). Fish Sci 67:306–313

Angell CA, Bressel RD, Green JL, Kanno H, Oguni M, Sare EJ (1994) Liquid fragility and the glass transition in water and aqueous solutions. J Food Eng 22:115–142

Bai Y, Rahman MS, Perera CO, Smith B, Melton LD (2001) State diagram of apple slices: glass transition and freezing curves. Food Res Int 34:89–95

Bayindirli L, Özilgen M, Ungan S (1993) Mathematical analysis of freeze concentration of apple juice. J Food Eng 19:95–l07

Bevilacqua AE, Zaritzky NE (1982) Ice recrystallization in frozen beef. J Food Sci 47:1410–1414

Boonyai P, Howes T, Bhandari B (2007) Instrumentation and testing of a thermal mechanical compression test for glass–rubber transition analysis of food powders. J Food Eng 78:1333–1342

Cano-Chauca M, Stringheta PC, Ramos AM, Cal-Vidal J (2005) Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. Innov Food Sci Emerg Technol 6:420–428

Chevallier S, Valle GD, Colonna P, Broyart B, Trystram G (2002) Structural and chemical modifications of short dough during baking. J Cereal Sci 35:1–10

Davies PL, Hew CL (1990) Biochemistry of fish antifreeze proteins. FASEB J 4:2460–2468

Deshpande SS, Bolin HR, Salunkhe DK (1982) Freeze concentration of fruit juices. Food Technol May:68–82

Donhowe DP, Hartel RW (1996a) Recrystallization of ice in ice cream during controlled accelerated storage. Int Dairy J 6:1191–1208

Donhowe DP, Hartel RW (1996b) Recrystallization of ice during bulk storage of ice cream. Int Dairy J 6:1209–1221

Fabra MJ, Márquez E, Castro D, Chiralt A (2011) Effect of maltodextrins in the water-content – water activity – glass transition relationships of noni (*Morinda citrifolia L.*) pulp powder. J Food Eng 103:47–51

Fennema OR, Powrie WD, Marth EH (1973) Low-temperature preservation of foods and living matter. Marcel Dekker, New York

Fongin S, Kawai K, Harnkarnsujarit N, Hagura Y (2017) Effects of water and maltodextrin on the glass transition temperature of freeze-dried mango pulp and an empirical model to predict plasticizing effect of water on dried fruits. J Food Eng 210:91–97

Franks F (1985) Biophysics and biochemistry at low temperatures. Cambridge University Press, Cambridge

Goula AM, Adamopoulos KG (2008) Effect of maltodextrin addition during spray drying of tomato pulp in dehumidified air: I. Drying kinetics and product recovery. Dry Technol 26:714–725

Goula AM, Adamopoulos KG (2010) A new technique for spray drying orange juice concentrate. Innov Food Sci Emerg 11:342–351

Graether SP, Kuiper MJ, Gagné SM, Walker VK, Jia Z, Sykes BD, Davies PL (2000) β-Helix structure and ice-binding properties of a hyperactive antifreeze protein from an insect. Nature 406:325–328

Griffith M, Yaish MWF (2004) Antifreeze proteins in overwintering plants: a tale of two activities. Trends Plant Sci 9:399–405

Hagiwara T, Hartel RW (1996) Effect of sweetener, stabilizer, and storage temperature on ice recrystallization in ice cream. J Dairy Sci 79:735–744

Hagiwara T, Mao J, Suzuki T, Takai R (2005) Ice recrystallization in sucrose solutions stored at temperatures of −21°C to −50°C. Food Sci Technol Res 11:407–411

Hagiwara T, Hartel RW, Matsukawa S (2006) Relationship between recrystallization rate of ice crystals in sugar solutions and water mobility in freeze-concentrated matrix. Food Biophys 1:74–82

Hagiwara T, Sakiyama T, Watanabe H (2009) Estimation of water diffusion coefficients in freeze-concentrated matrices of sugar solutions using molecular dynamics. Food Biophys 4:340–346

Hagiwara T, Ohmoto E, Tokizawa K, Sakiyama T (2011) Recrystallization behavior of ice crystals in sucrose solution in the presence of AFP Type I. In 11th International Congress on Engineering and Food (ICEF11), Athens, 2011, http://www.icef11.org/main.php?fullpaper&categ=AFT

Hancock BC, Shamblin SL, Zografi G (1995) Molecular mobility of amorphous pharmaceutical solids below

their glass transition temperatures. Pharm Res 12:799–806
Haque MK, Kawai K, Suzuki T (2006) Glass transition and enthalpy relaxation of amorphous lactose glass. Carbohydr Res 341:1884–1889
Harnkarnsujarit N, Charoenrein S (2011a) Effect of water activity on sugar crystallization and β-carotene stability of freeze-dried mango powder. J Food Eng 105:592–598
Harnkarnsujarit N, Charoenrein S (2011b) Influence of collapsed structure on stability of β-carotene in freeze-dried mangoes. Food Res Int 44:3188–3194
Hartel RW (1998) Mechanisms and kinetics of recrystallization in ice cream. In: Reid DS (ed) The Properties of Water in Foods: ISOPOW 6. Blackie Academic & Professional, London, pp 287–319
Hartel RW (2001) Crystallization in foods. Aspen Publisher, Gaithersburg
Hartel RW, Espinel LA (1993) Freeze concentration of skim milk. J Food Eng 20:101–120
Hashimoto T, Hagiwara T, Suzuki T, Takai R (2004) Study of the enthalpy relaxation of Katsuobushi (dried glassy fish meat) by differential scanning calorimetry and effect of physical aging upon its water sorption ability. Jpn J Food Eng 5:11–19
Hogan SA, Famelart MH, O'Callaghan DJ, Schuck P (2010) A novel technique for determining glass–rubber transition in dairy powders. J Food Eng 99:76–82
Inoue C, Suzuki T (2005) Enthalpy relaxation of freeze concentrated sucrose-water glass. Cryobiology 52:83–89
Jaya S, Das H (2004) Effect of maltodextrin, glycerol monostearate and tricalcium phosphate on vacuum dried mango powder properties. J Food Eng 63:125–134
Johari GP, Hallbrucker A, Mayer E (1987) The glass–liquid transition of hyperquenched water. Nature 330:552–553
Kasapis S, Rahman MS, Guizani N, Al-Aamri M (2000) State diagram of temperature vs. date solids obtained from the mature fruit. J Agric Food Chem 48:3779–3784
Kawahara H, Fujii A, Inoue M, Kitao S, Fukuoka J, Obata H (2009) Antifreeze activity of cold acclimated Japanese radish and purification of antifreeze peptide. CryoLetters 30:119–131
Kawai K, Hagura Y (2012) Discontinuous and heterogeneous glass transition behavior of carbohydrate polymer–plasticizer systems. Carbohydr Polym 89:836–841
Kawai K, Hagiwara T, Takai R, Suzuki T (2005) Comparative investigation by two type analytical approaches on enthalpy relaxation for glassy glucose, sucrose, maltose and trehalose. Pharm Res 22:490–495
Kawai K, Toh M, Hagura Y (2014) Effect of sugar composition on the water sorption and softening properties of cookie. Food Chem 145:772–776
Khalloufi S, El-Maslouhi Y, Ratti C (2000) Mathematical model for prediction of glass transition temperature of fruit powders. J Food Sci 65:842–848
Kim YJ, Hagiwara T, Kawai K, Suzuki T, Takai R (2003) Kinetic process of enthalpy relaxation of glassy starch and effect of physical aging upon its water vapor permeability property. Carbohydr Polym 53:289–296
Klinmalai P, Shibata M, Hagiwara T (2017) Recrystallization of ice crystals in trehalose solution at isothermal condition. Food Biophys 12:404–411
Kurozawa LE, Hubinger MD, Park KJ (2012) Glass transition phenomenon on shrinkage of papaya during convective drying. J Food Eng 108:43–50
Lacık I, Krupa I, Stach M, Kučma A, Jurčiová J, Chodák I (2000) Thermal lag and its practical consequence in the dynamic mechanical analysis of polymers. Polym Test 19:755–771
Lide DR (2003) CRC handbook of chemistry, physics, 84th edn. CRC Press, Boca Raton
Liu L, Miyawaki O, Nakamura K (1997) Progressive freeze-concentration of model liquid food. Food Sci Technol Int Tokyo 3:348–352
Marshall RT, Arbuckle WS (2000) Ice cream. Aspen Publisher, Gaithersburg
Martino MN, Zaritzky NE (1988) Ice crystal size modifications during frozen beef storage. J Food Sci 53:1631–1637 1649
Martino MN, Zaritzky NE (1989) Ice recrystallization in a model system and in frozen muscle tissue. Cryobiology 26:138–148
Matsuoka S (1992) Relaxation phenomena in polymers. Carl Hanser Verlag, Munich
Miller-Livney T, Hartel RW (1997) Ice recrystallization in ice cream: interactions between sweeteners and stabilizers. J Dairy Sci 80:447–456
Miyawaki O, Liu L, Shirai Y, Sakashita S, Kagitani K (2005) Tubular ice system for scale-up of progressive freeze-concentration. J Food Eng 69:113–107
Miyawaki O, Omote C, Gunathilake M, Ishisaki K, Miwa S, Tagami A, Kitano S (2016) Integrated system of progressive freeze-concentration combined with partial ice-melting for yield improvement. J Food Eng 184:38–43
Moraga G, Martınez-Navarrete N, Chiralt A (2004) Water sorption isotherms and glass transition in strawberries: influence of pretreatment. J Food Eng 62:315–321
Moraga G, Martínez-Navarrete N, Chiralt A (2006) Water sorption isotherms and phase transitions in kiwifruit. J Food Eng 72:147–156
Moraga G, Talens P, Moraga MJ, Martínez-Navarrete N (2011) Implication of water activity and glass transition on the mechanical and optical properties of freeze-dried apple and banana slices. J Food Eng 106:212–219
Mosquera LH, Moraga G, Martínez-Navarrete N (2010) Effect of maltodextrin on the stability of freeze-dried borojó (*Borojoa patinoi* Cuatrec.) powder. J Food Eng 97:72–78
Mosquera LH, Moraga G, Martínez-Navarrete N (2012) Critical water activity and critical water content of freeze-dried strawberry powder as affected by maltodextrin and arabic gum. Food Res Int 47:201–206

Oikonomopoulou VP, Krokida MK (2012) Structural properties of dried potatoes, mushrooms, and strawberries as a function of freeze-drying pressure. Dry Technol 30:351–361

Palzer S (2005) The effect of glass transition on the desired and undesired agglomeration of amorphous food powders. Chem Eng Sci 60:3959–3968

Payne CR, Labuza TP (2005a) The brittle–ductile transition of an amorphous food system. Dry Technol 23:871–886

Payne CR, Labuza TP (2005b) Correlating perceived crispness intensity to physical changes in an amorphous snack food. Dry Technol 23:887–905

Pelgrom PJM, Schutyser MAI, Boom RM (2013) Thermomechanical morphology of peas and its relation to fracture behavior. Food Bioprocess Technol 6:3317–3325

Pyne A, Surana R, Suryanarayanan R (2003) Enthalpic relaxation in frozen aqueous trehalose solutions. Thermochim Acta 405:225–234

Ramteke RS, Singh NL, Rekha MN, Eipeson WE (1993) Methods for concentration of fruit juices: a critical evaluation. J Food Sci Technol 30:391–402

Raymond JA, DeVries AL (1977) Adsorption inhibition as a mechanism of freezing resistance in polar fishes. Proc Natl Acad Sci U S A 74:2589–2593

Raymond JA, Wilson P, DeVries AL (1989) Inhibition of growth of nonbasal planes in ice by fish antifreezes. Proc Natl Acad Sci U S A 86:881–885

Regand A, Goff HD (2006) Ice recrystallization inhibition in ice cream as affected by ice structuring proteins from winter wheat grass. J Dairy Sci 89:49–57

Roos YH (1995) Phase transition in foods. Academic, San Diego

Ross KA, Campanella OH, Okos MR (2002) The effect of porosity on glass transition measurement. Int J Food Proc 5:611–628

Sablania SS, Kasapis S, Rahmana MS, Al-Jabria A, Al-Habsi N (2004) Sorption isotherms and the state diagram for evaluating stability criteria of abalone. Food Res Int 37:915–924

Sandoval A, Nuñez M, Müller AJ, Valle GD, Lourdin D (2009) Glass transition temperatures of a ready to eat breakfast cereal formulation and its main components determined by DSC and DMTA. Carbohydr Polym 76:528–534

Sastry S (1999) Supercooled water: going strong or falling apart? Nature 398:467–469

Silva MA, Sobral PJA, Kieckbusch TG (2006) State diagrams of freeze-dried camu-camu (*Myrciaria dubia* (HBK) McVaugh) pulp with and without maltodextrin addition. J Food Eng 77:426–432

Slade L, Levine H (1994) Water and the glass transition – dependence of the glass transition on composition and chemical structure: special implications for flour functionality in cookie baking. J Food Eng 22:143–188

Sobral PJA, Telis VRN, Habitante AMQB, Sereno A (2001) Phase diagram for freeze-dried persimmon. Thermochim Acta 376:83–89

Sonthipermpoon W, Suwonsichon T, Wittaya-areekul S, Wuttijumnong P (2006) Effect of maltodextrin on glass transition temperature and water activity of production banana flake. Kasetsart J (Nat Sci) 40:708–715

Sutton RL, Lips A, Piccirillo G, Sztehlo A (1996) Kinetics of ice recrystallization in aqueous fructose solutions. J Food Sci 61:741–745

Syamaladevi RM, Sablani SS, Tang J, Powers J, Swanson BG (2009) State diagram and water adsorption isotherm of raspberry (*Rubus idaeus*). J Food Eng 91:460–467

Telis VRN (2006) Sorption isotherm, glass transitions and state diagram for freeze-dried plum skin and pulp. Food Sci Technol Int 12:181–187

Telis VRN, Martínez-Navarrete N (2009) Collapse and color changes in grapefruit juice powder as affected by water activity, glass transition, and addition of carbohydrate polymers. Food Biophys 4:83–93

Thuc TT, Fukai S, Truong V, Bhandari B (2010) Measurement of glass-rubber transition temperature of rice by thermal mechanical compression test (TMCT). Int J Food Prop 13:176–183

Tiemblo P, Guzman J, Riande E, Mijangos C, Reinecke H (2002) Effect of physical aging on the gas transport properties of PVC and PVC modified with pyridine groups. Polymer 42:4817–4823

Urbani R, Sussich F, Prejac S, Cesàro A (1997) Enthalpy relaxation and glass transition behaviour of sucrose by static and dynamic DSC. Thermochim Acta 304–305:359–367

van Donkelaar LH, Martinez JT, Frijters H, Noordman TR, Boom RM, van der Goot AJ (2015) Glass transitions of barley starch and protein in the endosperm and isolated from. Food Res Int 72:241–246

Vásquez C, Díaz-Calderón P, Enrione J, Matiacevich S (2013) State diagram, sorption isotherm and color of blueberries as a function of water content. Thermochim Acta 570:8–15

Wang H, Zhang S, Chen G (2008) Glass transition and state diagram for fresh and freeze-dried Chinese gooseberry. J Food Eng 84:307–312

Yoshida H (1995) Relaxation between enthalpy relaxation and dynamic mechanical relaxation of engineering plastics. Thermochim Acta 266:119–127

Young FE (1957) D-glucose–water phase diagram. J Phys Chem 61:616–619

Young FE, Jones FT (1949) Sucrose hydrates. J Phys Chem 53:1334–1350

Young FE, Jones FT, Lewis HJ (1952) D-fructose–water phase diagram. J Phys Chem 56:1093–1096

Zotarelli MF, da Silva VM, Durigon A, Hubinger MD, Laurindo JB (2017) Production of mango powder by spray drying and cast-tape drying. Powder Technol 305:447–454

Zou K, Teng J, Huang L, Dai X, Wei B (2013) Effect of osmotic pretreatment on quality of mango chips by explosion puffing drying. Food Sci Technol 51:253–259