Chapter 18
Glass Transitions: Opportunities and Challenges

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18.1 Introduction

Glass transition is a well-known transformation of the solid-fluid states of noncrystalline solids and liquids. In food systems the glass transition is often a property of carbohydrates and proteins, as observed in numerous food materials (White and Cakebread 1966; Slade and Levine 1995). Glass transition results in various physicochemical and thermal phenomena associated with the solid–liquid transformation of a supercooled liquid. A number of noncrystalline polymers, as well as sugar melts, exhibit glass transition at approximately 100–150°C below their equilibrium melting temperature (Roos 1993). The glass transition of low water and frozen foods has been recognized as one of the most important factors affecting food properties, processing characteristics, and shelf life (Roos 1995a). Glass transition contributes to numerous engineering properties of foods, their structure and texture, and reaction kinetics. It is also useful in understanding sensory properties, including hardness, crispiness, softness, and flavor release (Slade and Levine 1995; Roos 1995a; Roudaut et al. 2004). Knowledge of molecular mobility and changes in mechanical and physical properties over the glass transition can be used to control the characteristics of food solids, for example, in drying, freeze-drying, freezing, and extrusion. An overview of the importance of the glass transition in food engineering, including selected food systems and processes, as well as challenges in using glass transition data in the control of food properties, food processing, and storage stability, will be highlighted in this review.

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18.1.1 Confectionary

The physical state of sugars is important in manufacturing and control of quality changes during storage of confectionery. Formation of noncrystalline solid sugar structures is the basic technology underpinning the manufacturing of hard sugar candies, which are often produced from sugar melts or concentrates by rapidly cooling the product after heating to above melting temperatures. High solids concentration and rapid cooling enhance the formation of solid, transparent, and brittle, glassy materials. White and Cakebread (1966) stated that food materials containing amorphous sugars, such as hard candies, were stable at temperatures below their glass transition. Cotton candy is another example of sugar glass technology. Cotton candy is made by melting crystalline sucrose, which is spun under rapid cooling and dehydration into an amorphous (glassy) solid. At temperatures exceeding the glass transition temperature, T_g, of sucrose, the spun structure collapses as a result of crystallization of the sugar. A hard lump of sucrose crystals imbedded in a partially glassy structure may form, making the shelf life of the product very short (Labuza and Labuza 2004).

18.1.2 Frozen Foods

Crystallization and recrystallization of amorphous food components are time-dependent phase transitions. Crystallization and recrystallization processes are affected by the physical state of food solids and may be controlled by the glass transition. One example is lactose crystallization in frozen desserts and ice cream. Such solute crystallization is a result of freeze concentration of the solutes and subsequent supersaturation. At sufficiently low temperatures the solutes, along with some unfrozen water, vitrify into the solid (glassy) state reducing diffusion and causing crystallization processes to cease. Crystallization and recrystallization processes, however, take place in frozen foods above the onset temperature of ice melting in the maximally freeze-concentrated solute matrix (Roos and Karel 1991b, d; Roos 1995a). As lactose is one the least soluble sugars, lactose crystallization often occurs in ice cream produced without stabilizers. Lactose crystallization causes an undesirable coarse and sandy mouthfeel, while ice recrystallization may be observed from large, coarse ice crystals and flaky ice structure.

Various authors (White and Cakebread 1966; Livney et al. 1995; Roos 1995a) have reported that rates of crystallization processes increase above the glass transition. At temperatures approaching the glass transition, crystallization and recrystallization rates reduce as a result of limited molecular mobility (Roudaut et al. 2004) when the material is transformed into the solid (glassy) state. At temperature below the glass transition, crystallization of food components as well as their recrystallization is unlikely because of the solid-like structure and absence of translational diffusion of molecules (Roos 1995a; Hartel 1996;

Roudaut et al. 2004). Recrystallization phenomena are typical of frozen foods, which often may be stored at fairly high temperatures or exposed to significant temperature fluctuations after manufacturing. Recrystallization of ice is a time-dependent process and generally characterized by an increase in the size of ice crystals with storage time (Roos 1995a; Hagiwara et al. 2005). Roos (1995a) pointed out that rates of ice formation and recrystallization could be controlled by using the temperature difference of the T_g (referred to as $T-T_g$) as the rate-defining factor. The recrystallization rate is strongly reduced below the glass transition of the freeze-concentrated, unfrozen system (Carrington et al. 1996). Thus, the glass transition temperatures, T_g, of the freeze-concentrated solutes and unfrozen water content at temperatures during frozen storage are the most important composition-dependent factors, which then can be used to control the extent of ice formation and ice recrystallization in frozen foods at any given storage temperature.

18.1.3 Cereal Foods

Starch is a mix of carbohydrate polymers and the main component of cereal foods. Starch is present also in legume seeds and tuber plants. The two starch components, amylose and amylopectin, may exist in crystalline, partially crystalline, and amorphous states (Slade and Levine 1991). In native starches, amylose may exist as a noncrystalline component but amylopectin often exhibits partial crystallinity (Roos 1995a). Water in amorphous parts of starch components acts as a plasticizer and decreases the T_g. Glass transition, melting temperatures, and water content are the most important parameters characterizing the state and physical properties of starch components over a wide temperature range in cereals processing and product storage.

Phase transitions associated with gelatinization and loss of native structure in granular starches can define and explain differences in the physical properties of starches and their behavior in food products (Lund 1989). Levine and Slade (1990) pointed out that starch gelatinization is a nonequilibrium melting process that occurs during the heating of starch in the presence of water. Retrogradation of starch is a temperature-, water-content-, and time-dependent crystallization phenomenon and occurs after cooling of gelatinized starch. The rate of retrogradation depends on the presence and ratio of amylopectin and amylose, and the molecular weight of these starch components (Roos 1995a; Jouppila and Roos 1997). After cooling of gelatinized starch, amylose crystallization occurs rapidly, while crystallization of amylopectin may occur during storage of gelatinized starch and cereal foods (Roos 1995a; Ronda and Roos 2008).

Several studies (Le Meste et al. 1992; Jouppila and Roos 1997; Ronda and Roos 2008) indicated that the textural characteristics of cereal foods at different temperatures and water contents could be explained in terms of temperature with respect to T_g. Starch retrogradation, including a basic crystallization process of gelatinized starch components, can be detected by DSC from observed physical

change in a starch gel or paste, and by X-ray diffraction methods (Roos 2007a). Glass transition can control texture- and stability-related phenomena such as gelatinization and retrogradation, which may proceed over the temperature range $T_g < T < T_m$ (Biliaderis 1992; Yoshimura et al. 1996). Crystallization in gelatinized starch (or starch retrogradation) and the loss of water during storage were found to contribute to aging and bread staling above the glass transition (Roos et al. 1996; Champion et al. 2000; Ronda and Roos 2008). Moreover, crispness, which is affected by water content and glass transition, is an essential factor in achieving acceptable quality among numerous cereal and snack foods (Roudaut et al. 2002). Many cereal-based foods, such as breakfast cereals, wafers, and biscuits, have a crispy or crunchy texture when consumed at low water contents (below 10% water); however, crispness may be lost as the water content increases due to water sorption and subsequent water plasticization of amorphous structures (Nicholls et al. 1995; Roos et al. 1998; Hochstetter et al. 2006). A critical water activity (a_w) at which crispness is lost was found to be specific according to each material. A change resulting in loss of crispness often occurred around 0.35–0.50 a_w (Roos 1993; Roos et al. 1996). When the critical water content or water activity is exceeded, the T_g of the material occurs below the ambient temperature (Roos 1993).

18.1.4 Food Powders and Dehydrated Foods

Food powders containing amorphous carbohydrates, such as lactose in dairy powders, may show changes in physical properties, for example, crystallization, clumping, stickiness, and caking during processing, handling, and storage (Levine and Slade 1986). Stickiness and caking phenomena are related to the collapse phenomena occurring in amorphous solids, and often result from increased temperature or exposure of powders to high-humidity conditions.

Caking of powders may be considered as a collapse phenomenon, which occurs when particle surfaces in contact form permanent aggregates and harden causing a loss of free-flowing properties in powder particles. Boonyai et al. (2004) explained the difference between stickiness and caking of food powders. They stated that stickiness is an instantaneous process but caking occurs over a time period. The common cause of stickiness is plasticization of particle surfaces, which allows a sufficient decrease of surface viscosity for the formation of liquid bridges between particles (Downton et al. 1982; Roos 1995a). These phenomena in powders, with amorphous components contributing to stickiness, can be characterized as time-dependent surface flow properties that are controlled by properties of the amorphous components and their flow at temperatures above the glass transition (Roos 1995a). Several researchers (Roos and Karel 1991a, b; Chuy and Labuza 1994; Roos 1995a; Bhandari and Howes 1999) have illustrated possible relationships among stickiness, caking, and glass transition. The food polymer science approach has increased understanding of the state of food materials and its use to control or prevent undesirable physical changes, including powder stability (Bhandari and

Howes 1999). Amorphous solids exist in a supercooled liquid (rubbery state) above the glass transition at which plasticization-dependent viscosity decreases occur rapidly. Glass transition enhances molecular mobility and flow, leading to stickiness and crystallization problems in low-water and frozen foods (Roudaut et al. 2004). Therefore, glass transition is an important and useful concept in observation of parameters, such as temperature and water content for the control or reduction of liquid-like properties of powder components during processing and storage.

Collapse during freeze-drying and collapse of freeze-dried matrices may adversely affect material properties during dehydration and storage, respectively. Collapse is a result of viscous flow of amorphous materials or their components, causing loss of structure, reduction of pore size, and shrinkage. Such collapse is associated with undesirable appearance and loss of texture, and volatile substances (Karel and Flink 1973; Levi and Karel 1995). It occurs above glass transition, the rate of which depends on temperature and water content. Levi and Karel (1995) found that rates of collapse were strongly dependent on the temperature above the glass transition. Increasing water content depressed the T_g and increased the $T–T_g$ at the observed temperature. The flow and rate of collapse above T_g were functions of temperature difference ($T–T_g$), which could be modeled by the Williams-Landel-Ferry (WLF) relationship (Roos 1995a). This suggested that the T_g was an applicable parameter for the prediction and control of collapse during freeze-drying and storage of amorphous foods.

18.2 Glass Transition: Opportunities

An increase in molecular mobility above the glass transition enhances flow of amorphous structures and results in time-dependent physical changes (Roos and Karel 1991a; Bhandari et al. 1997; Bhandari and Howes 1999). This occurs above a critical temperature, or plasticization level, which often refers to the glass transition temperature, T_g, or water activity and water content, respectively (Roos 2007b). Glassy states may form in numerous food processes involving cooling of highly supercooled liquids or removal of water by dehydration or freezing (Fig. 18.1). Glass formation or vitrification of food solids may occur in various glassy, non-equilibrium (solid glassy state) solid structures. These may have different physical appearances, such as freeze-dried or spray dried structures, and also may exhibit varying thermodynamic states (Roos 2008).

18.2.1 Freezing and Freeze-Drying

Ice crystallization and collapse of structure in partially frozen systems are controlled by the molecular mobility of food components in freeze-concentrated, unfrozen water-solute systems (Levi and Karel 1995; Roos 1995a). These changes are time-dependent and reduce in rate as the maximally freeze-concentrated state is

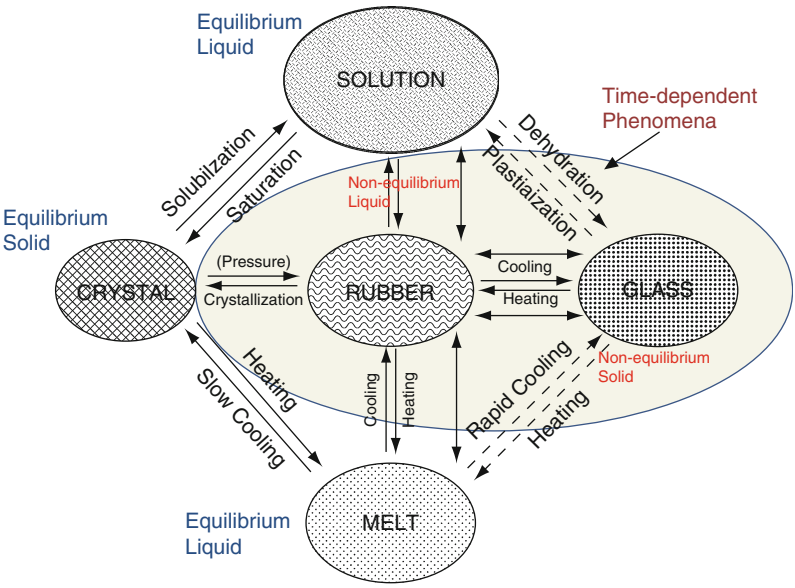

Fig. 18.1 Changes in physical state of amorphous materials around glass transition and time-dependent characteristics (Data are from Roos and Karel 1991a)

approached. The glassy structures of the unfrozen water-solids phases that are formed in maximally freeze-concentrated systems support the structure against flow and collapse, but the structure does not allow further ice formation (Roos and Karel 1991d; Roos 2007a). Freezing and frozen storage conditions, however, affect the size of ice crystals, which could probably be further manipulated by the control of freeze-concentration and ice formation.

Ice formation in foods results in a freeze-concentration of solids and a gradually decreasing freezing temperature as the solute concentration of the unfrozen phase increases. The freeze-concentrated, amorphous unfrozen phase contains unfrozen water and solids; it provides a continuous phase for the dispersed ice crystals and possibly lipids or other nondissolved solid components (Roos 1995a). The glass transition temperature of the maximally freeze-concentrated unfrozen phase (T_g') is independent of the solute concentration prior to freezing and often corresponds with a solute concentration (C_g') of 80% (w/w) (Roos et al. 1996). At temperatures below the T_g' the amorphous unfrozen phase is vitrified and exists as a glassy solid (Roos and Karel 1991d), whereas ice dissolution at temperatures above the onset temperature of ice melting, T_m', decreases the viscosity of the unfrozen phase, which shows viscous flow under gravity. Hence, frozen systems at temperatures above the T_m' cannot support the solid structure (Fig. 18.2) and show collapse or shrinkage (Bhandari and Howes 1999; Le Meste et al. 2002; Alves-Filho and Roos 2006). Stability of frozen foods can be accomplished by manipulation of food composition to increase the T_m' or by using storage temperatures lower than the T_m' (Hartel 1996). However, compositional changes in food formulations are not always possible.

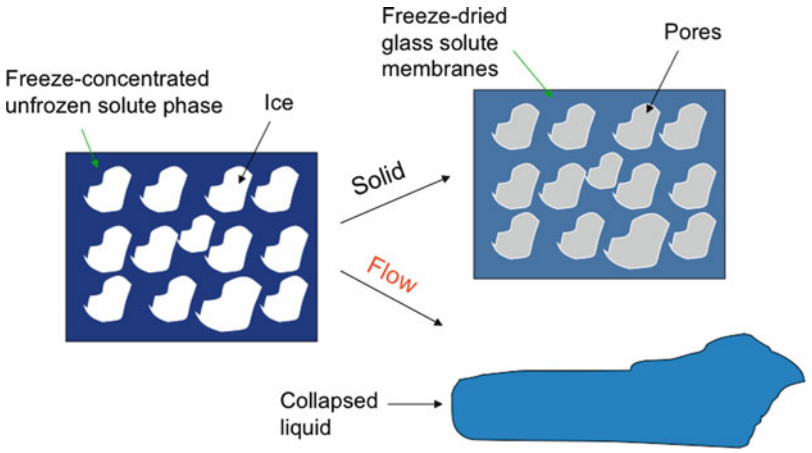

Fig. 18.2 Viscous flow of freeze-concentrated liquid phase in freeze-drying

The control of ice crystal growth in frozen foods and ice cream has been postulated by the T_m' control (Goff et al. 1993). They suggested that polysaccharides provided resistance to thermal deformation and increased subzero viscosity above the T_m'. Hence, ice crystal size and the rate of growth of ice crystals in frozen foods and ice cream containing polysaccharides were smaller than in frozen foods and ice cream without added polysaccharides. Ice formation ceases as a result of kinetic limitations for crystal growth below T_g'; some frozen foods are stable against deteriorative changes because of the glassy state of the unfrozen phase (Levine and Slade 1986; Roos and Karel 1991d). However, some reactions, such as oxidation of sensitive components may accelerate as a result of maximum freeze-concentration of foods. Studies of frozen food stability are relatively few and therefore it requires substantial further attention by researchers. It appears, however, that the control of the glass transition of the unfrozen phase and ice melting is fundamental to freezing and frozen storage as well as freeze-drying.

18.2.2 Spray Drying

Particle stickiness and subsequent deposition of semi-dried particles on dryer surfaces is regarded as one of the most typical problems in spray drying. During drying of sugar-rich foods, such as fruit juices, honey, and some starch derivatives (glucose syrup/maltodextrins with higher dextrose equivalent values), their structures may remain as syrup-like liquids; such particles stick on the drier surfaces leading to lower product yields and operating problems (Bhandari et al. 1997). In industrial applications, sticky-point temperature curves may be generated and used to develop optimal drying operations to minimize stickiness problems.

Stickiness is a time-dependent phenomenon that is related to structural transformations and flow of amorphous solids around the glass transition (Roos and Karel 1991c; Roos 1995a). Measured T_g values have correlated well with sticky-point measurements and the glass transition concept has provided a better fundamental understanding and predictability of stickiness (Roos et al. 1996; Adhikari et al. 2001, 2005). Application of glass transition data is extremely useful in the design of dehydration equipment to minimize the stickiness of sugar-rich food solids (Truong et al. 2005a, 2005b). Truong et al. (2005a, b) suggested that the glass transition approach could be used to reduce stickiness because the difference between the outlet air temperature and the T_g of the solids of the final product ($T-T_g$) was a measurable, stickiness controlling property of the particles in the spray-drying process. The T_g was influenced by solids composition, which affects the physical changes in foods (Ozkan et al. 2002; Fitzpatrick et al. 2007a, b; Nijidam and Langrish 2006; Haque and Roos 2006). Amorphous low-molecular weight substances such as fructose and glucose have a low T_g. High-molecular weight components, such as polysaccharides and proteins, increase the T_g of mixtures containing sugars (Roos and Karel 1991c; Haque and Roos 2004; Shrestha et al. 2007); they also affect the powder characteristics during spray drying as shown in (Fig. 18.3) (Haque and Roos 2006).

Maltodextrins are widely used as food components to reduce stickiness in sugar-rich foods because of their T_g and viscosity increasing property in mixtures with sugars (Bhandari et al. 1997). Addition of low dextrose equivalent (DE) maltodextrins decreases stickiness and caking during drying and storage (Adhikari et al. 2004; Langrish et al. 2007), and provides an excellent opportunity to improve processing and storage characteristics. The effect on mixture properties can be predicted using T_g data. The stickiness behavior can be characterized by various techniques (Lazar et al. 1956; Downton et al. 1982; Chuy and Labuza 1994; Hennigs et al. 2001; Ozkan et al. 2002). The sticky points of powders were found

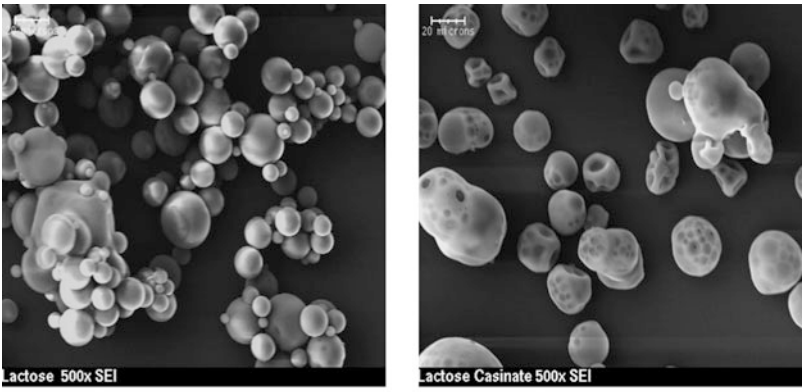

Fig. 18.3 Composition affects glass transition and dehydration characteristics using scanning electron microscopy (SEM) (Further data can be found in Haque and Roos 2006)

to be associated with glass transition temperatures at 10–20°C above the T_g (Roos and Karel 1991b; Roos 1995a; Hennigs et al. 2001; Ozmen and Langrish 2002; Adhikari et al. 2005). This indicated that the glass transition is a useful parameter to control dehydration and powder characteristics, including stickiness, caking, and agglomeration during drying processes and product storage.

18.2.3 Extrusion

Extrusion has become a well-established and widely used food processing method. Extrusion processes often involve conversion of solid ingredients to a viscous but homogeneous mixture followed by formation of dense, solid, or expanded highly porous structures. Biodegradable packaging and edible films may also be manufactured using extrusion processes. The use of extrusion in food applications is often based on empirical knowledge of solids behavior and structure formation. However, the materials science understanding of foods and knowledge of their phase and state transitions are fundamental in the control of extrusion processes and material behavior in structure formation and storage (Slade and Levine 1991, 1995; Roos 1995a). This development also is an opportunity to improve extrusion processes and product quality, particularly in the development of novel extrusion applications.

The formation of the structure of several extruded foods and low-moisture foods, such as snack foods and breakfast cereals, is influenced by temperature and water content. The glass transition can be used to control their plasticization, gelatinization, and the glass formation. In plasticization, increasing the temperature or the water content results in a decrease of the T_g. Water plasticization also controls modulus and tensile strength of extruded films produced by extrusion (Garcia et al. 2004; Roos 1995a; Hochstetter et al. 2006). One of the desired characteristics of extruded snacks and breakfast cereals is a crispy texture. At the expansion of plasticized foods, starchy solids are rapidly dehydrated and the solids vitrify, i.e., the structure of the food solids becomes a glass, forming thin membranes with brittle and crispy characteristics. Details on plasticization and structure formation in extrusion provide new opportunities for controlling the process and the texture and deterioration of extruded products since water plasticization and oxygen permeability can be manipulated during storage (Roos 1995a; Roos et al. 1996; Hochstetter et al. 2006). For example, Garcia et al. (2004) used glass transition data to control the thermal and water plasticization of extruded meat products and to achieve improved water permeability properties of films.

18.2.4 Encapsulation

Encapsulation processes are used to entrap food ingredients, enzymes, cells, or other components in structure-forming, encapsulant materials. Applications of

encapsulation have been increased in the food industry, since this process often aims at improved protection from heat and loss, or otherwise stabilizes sensitive components in food processing and storage. Dispersed droplets and particles in encapsulant matrices show reduced reaction rates and are often protected from surrounding reactants as a result of decreased diffusion through the glassy structure below the glass transition (Roos 1995a). Both temperature and water plasticization of encapsulant matrices may increase structural changes and release of encapsulated substances. Above the glass transition, the amorphous materials exhibit viscous flow and structures of food materials often change, which can result in collapse and release of encapsulated components.

The formulation of encapsulant matrices and control of glass formation may be used to improve encapsulation and stability of food products. For example, highly polymeric compounds such as proteins and hydrocolloids have high glass transition temperatures. These high molecular weight miscible compounds with miscible lower molecular weight components increase the glass transition temperature of the mixture and stabilize the glassy state against higher temperatures and water contents (Roos 2008). There is, however, very little information about the miscibility of carbohydrate polymers and proteins in food systems, as well as on how the use of various processes affects glass formation. Food structures also have heterogeneities that can greatly affect encapsulation, so their role in stability and shelf-life control needs to be investigated further.

18.3 Glass Transition: Challenges

Changes in physicochemical and physical properties of foods are likely to occur around glass transition, the point at which amorphous solids convert to liquids and exhibit viscous flow. The glass transition results in enhanced molecular mobility, which is associated with decreasing relaxation times and a lower viscosity. There have been numerous studies of enthalpy relaxations around the glass transition (Haque et al. 2006). These relaxations are examples of time-dependent glass formation and present challenges in the understanding of glassy structures formed in food processing.

Food processes, such as freezing and freeze-drying, spray drying or extrusion, may produce structures specific to the product composition, process, and processing parameters. These factors, together with thermal and water effects in storage, contribute to the properties and quality of food systems at the time of consumption. Understanding the state of glassy food materials and their time-dependent characteristics may require rigorous experimental studies, as such research would clarify the role of glassy states in the control of reaction rates and stabilization of highly sensitive food systems.

It is generally agreed that endothermic enthalpy relaxations increase with increasing aging time and temperature below the glass transition (Haque et al. 2006). Relaxations may also indicate exothermic enthalphy changes as translational

mobility of molecules appears around the glass transition (Roos 1995a, 2008). These relaxations show qualitative and quantitative information on the enthalpy state of molecules within a glass. As translational mobility of molecules appears around the glass transition materials may either require (endothermal relaxation) or release (exothermal relaxation) heat as they respond to the increasing temperature. Molecular mobility and the time-dependent nature of the glass transition can also be observed from mechanical and dielectric properties of materials (Champion et al. 2000; Le Meste et al. 2002; Roudaut et al. 2004; Roos 2008). Both dielectric and dynamic mechanical properties show the α-relaxation around the glass transition.

The α-relaxation can be observed using dielectric analysis (DEA) or dynamic-mechanical analysis (DMA) (Laaksonen and Labuza 2001; Laaksonen and Roos 2001; Royall et al. 2005; Hochstetter et al. 2006; Roos 2008). The α-relaxation temperatures obtained are frequency-dependent, indicating the nonequilibrium and time-dependent nature of the system. These relaxations may be used to describe mechanical properties of food materials, such as stickiness and caking of amorphous powders. Silalai et al. (2009a) found that the α-relaxation of dairy powders shifted to higher temperatures with increasing frequencies of DEA and DMA measurements (Fig. 18.4). The frequency-dependence of the α-relaxation followed the Arrhenius relationship (Talja and Roos 2001), and a frequency corresponding to the glass transition temperature could be identified. The glass transition measured by DSC and the α-relaxation temperatures (T_α) determined by DMA and DEA correlated closely with the sticky-point temperatures obtained using an empirical measurement (Silalai et al. 2009b).

Solids composition also affects structural formation and the quality of foods during processing and storage. For example, powders containing high amounts of lactose exhibited high adhesion of powder particles with increasing temperature and water content as a result of surface plasticization. Surface plasticization caused

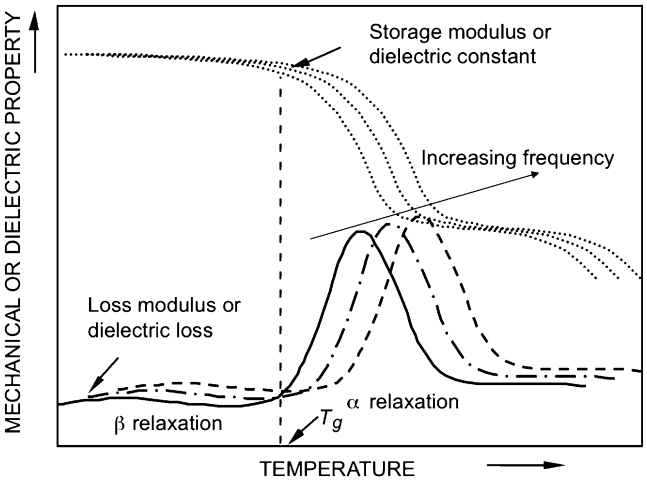

Fig. 18.4 Time-dependent characteristics and relaxations of the amorphous state

a decrease in sticky-point temperatures (Silalai et al. 2009b). Although many researchers (Roos and Karel 1991b; Chuy and Labuza 1994; Roos 2002) have demonstrated that stickiness and caking of dairy powders are related to glass transition, the time-dependent flow and contact time measurements still remain as challenging areas in glass transition research. However, composition, plasticization, and temperature are the main causes leading to a sufficient decrease in surface viscosity and higher adhesion and cohesion of powder particles. It was also shown by Downton et al. (1982) that powders were free-flowing particles at temperatures below glass transition; they became plasticized at above these temperatures, at decreasing viscosity in the range 10^7 to 10^9 Pa s.

Crystallization of amorphous components, particularly sugars in low-water and frozen foods, and starch components in gelatinized starch-containing foods, is often the most dramatic change in food systems. Numerous examples are available on lactose crystallization in dairy powders (Jouppila et al. 1997) and ice cream (Hartel 1996), as well as on starch retrogradation, including amylopectin crystallization (Jouppila et al. 1997). Crystallization is affected by water content and other components in low-water and frozen foods. Haque and Roos (2004) found that the T_g of spray-dried lactose–protein mixtures increased as a result of added protein components. The rate of crystallization of amorphous lactose was also reduced in spray-dried lactose–protein mixtures (Fig. 18.5). The data suggested that various proteins may affect lactose crystallization properties differently; studies of crystallization with salts showed that salts may further complicate crystallization (Omar and Roos 2007). These findings with information on water plasticization and component miscibility are fundamental in describing the spray-drying characteristics and product stability of sugar-containing food solids. The practical applications of these data are numerous but may require a systematic materials science approach in product formulation and equipment design.

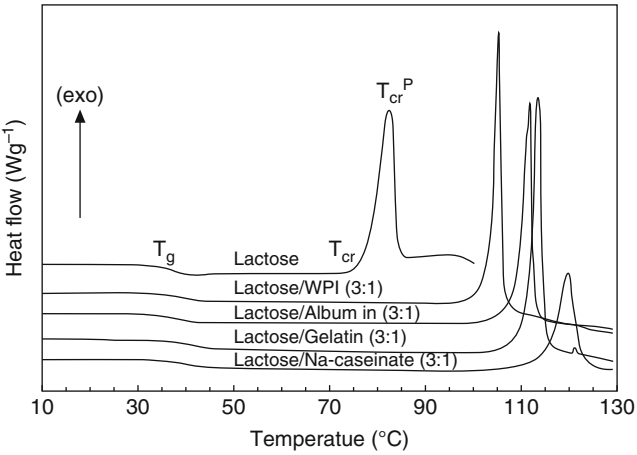

Fig. 18.5 Glass transition and crystallization temperatures of amorphous lactose in the presence of various proteins (From Haque and Roos 2004)

The effects of food components in mixtures on dielectric and mechanical properties around the glass transition have been reported in several studies (Kalichevsky et al. 1993; Nilolaidis and Labuza 1996; Talja and Roos 2001; Laaksonen and Labuza 2001; Laaksonen et al. 2002; Laaksonen and Roos 2001, 2003; Hashimoto et al. 2003). According to Silalai et al. (2009a, 2009b), dairy powders with increased protein content exhibited higher T_g values as measured by DSC. This was in agreement with increased T_α values as determined by DEA and DMA. There were also other changes in mechanical and dielectric relaxations. Dielectric and mechanical properties of powders with high lactose contents changed considerably around the glass transition as compared to powders with high protein contents (Figs. 18.6 and 18.7).

In frozen and freeze-drying systems, solids composition affects the glass transition of the maximally freeze-concentrated unfrozen phase, T_g', and onset temperature of ice melting, T_m' (Roos and Karel 1991d; Goff et al. 1993). The α-relaxations of frozen systems were also affected by composition and frequency, as observed from dielectric and dynamic-mechanical relaxations (Laaksonen and Roos 2001; Laaksonen et al. 2002). These data are of significant importance in the control of freezing and freeze-drying properties of food and other biological materials. The challenges in the control of freezing properties, frozen food stability, as well as freeze-drying can be addressed by understanding the state and phase transitions of freeze-concentrated systems. For example, polymeric materials in mixtures containing sugar lower the T_g' but increase the T_m'. This increases the broadness of the transition

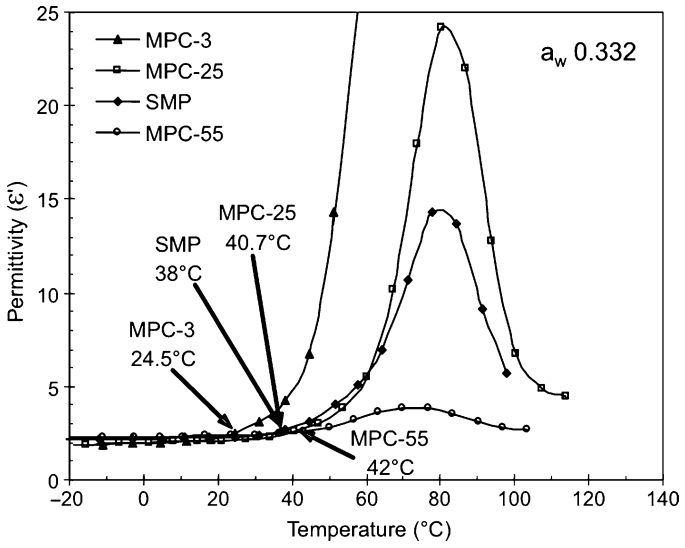

Fig. 18.6 Dielectric thermal analysis (*DEA*) thermograms showing the effect of carbohydrate–protein composition on dielectric relaxations of nonfat milk solids at water activity of 0.332. The carbohydrate–protein ratios for MPC-3, MPC-25, SMP, and MPC-55 were 15:74, 27:59, 40:48, and 56:32 (% of total solids, w/w), respectively

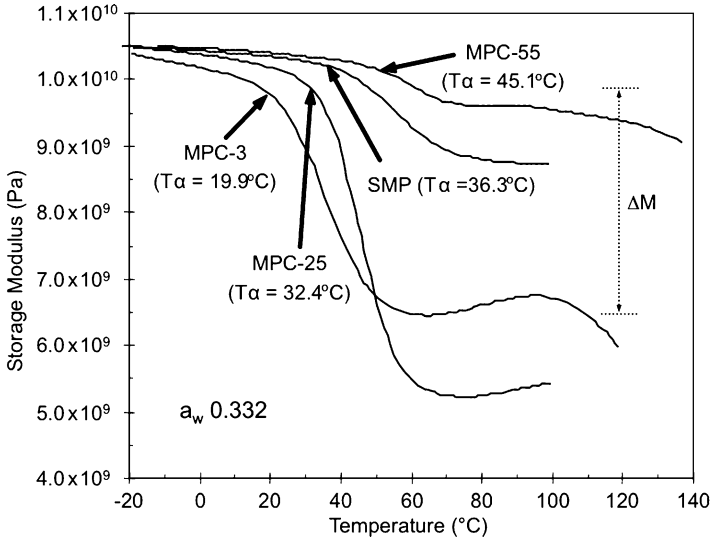

Fig. 18.7 Dynamic mechanical analysis (*DMA*) thermograms showing the effect of carbohydrate–protein composition on dielectric relaxations of nonfat milk solids at water activity of 0.332. The carbohydrate–protein ratios for MPC-3, MPC-25, SMP, and MPC-55 were 15:74, 27:59, 40:48, and 56:32 (% of total solids, w/w), respectively

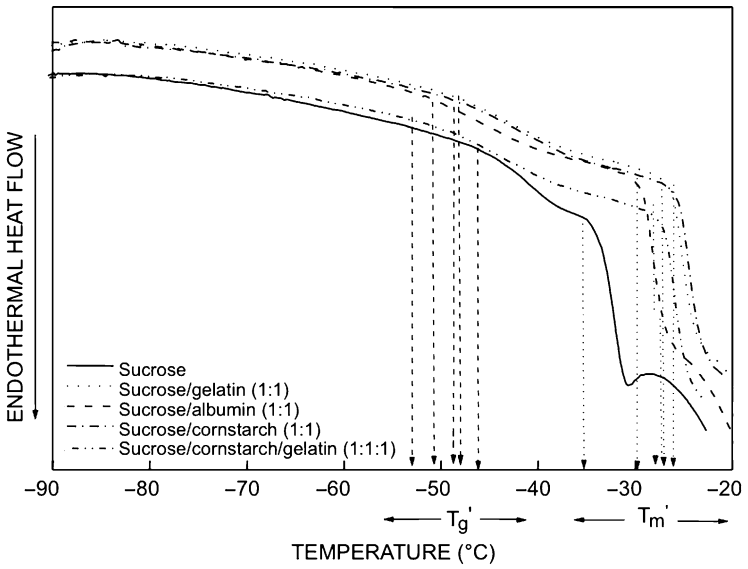

Fig. 18.8 Differential scanning calorimetry (*DSC*) thermograms showing glass transition and ice melting in sucrose and protein–starch systems (Data are from Singh and Roos 2005)

temperature range and suggests that ice formation is affected by the composition and diffusional characteristics of the unfrozen matrix. It seems that polymeric compounds, such as gelatin and corn starch, as shown in (Fig. 18.8), inhibit ice formation resulting in a higher unfrozen water content with corresponding lowering of the T_g' and increase of the T_m' (onset of melting occurred at a higher temperature corresponding to a lower ice content and higher melting temperature) (Singh and Roos 2005). Although it appears that compositional changes affect food properties in freeze-concentrated systems, their complex structure makes experiments and collection of low temperature data complicated. However, further analysis of heterogeneities and time-dependent changes in composition and microstructure in frozen systems will be useful in the design of freezing processes and formulation of frozen foods with improved quality and stability.

18.4 Conclusion

Significant progress has been made in understanding the role of glass transitions in food materials during food processing and storage. Glass transitions in foods have been shown to affect the flow properties of concentrated systems and, therefore, challenges exist in processes such as dehydration, extrusion, and freezing. The glass transitions and water plasticization behavior of food solids may affect structural changes, crystallization processes, as well as deteriorative reactions, which often limit the shelf life of low-water and frozen foods. Novel thermal analytical systems and other techniques are crucial to further understanding the complex nature of food systems, as well as the translation of knowledge of glass transition properties to the benefit of processing equipment and food product design for meeting processing needs and establishing the highest quality standards.

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