Glass Transition Temperature and Its Relevance in Food Processing

Yrjö H. Roos

Department of Food and Nutritional Sciences, University College Cork, Ireland,
email: yrjo.roos@ucc.ie

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Abstract

Amorphous, noncrystalline solids are typical of low water content and frozen foods. Solids in these foods, e.g., confectionary, dehydrated foods, cereal foods, and frozen foods, often form nonequilibrium glass-like structures. The glassy state of the solids forms during food processing in a reversible glass transition. Vitrification can occur in numerous glassy states that exhibit various relaxations around the glass transition. The success of freeze drying, spray drying, and extrusion and the stability of dehydrated foods against flow, collapse, and crystallization is based on the control of the glassy state during the dehydration process and storage. Encapsulation processes often use glass-forming materials to entrap dispersed components or improve retention of volatiles. Plasticization of the noncrystalline structures by temperature or water reduce relaxation times exponentially above the glass transition, which results in rapid deterioration. Critical values for water activity and water content express the level of water plasticization leading to glass transition in food storage.

INTRODUCTION

An amorphous state of a material refers to its random, disordered molecular structure, i.e., no exact position for any of the constituent molecules at a given time can be defined. Amorphous states include gaseous and liquid states of materials, whereas the crystalline state is highly organized. Cooling of a liquid to well below its equilibrium melting temperature without crystallization retains the molecular disorder and may allow freezing of the molecules to their random positions and formation of a solid-like but disordered, noncrystalline glass. The solid-liquid transformation of the amorphous material is known as glass transition. Glass transition is one of the most important physicochemical characteristics of noncrystalline, amorphous solids. It governs functional characteristics and plasticization of synthetic polymers as well as inorganic glasses. Both the supercooled, amorphous liquid (rubbery, leathery, etc.) and glassy states are thermodynamically nonequilibrium states, and their properties are time-dependent (Kauzmann 1948, Debendetti & Stillinger 2001, Sperling 2006). The glass transition is reversible, and it occurs over a temperature range. Well below the glass transition, molecules are frozen in their positions, and their molecular motions are limited to rotations and vibrations, which results in the solid-like characteristics of the material (Sperling 2006). When a glass is heated to above the glass transition, molecules gain translational mobility and enter the supercooled, liquid-like state with a concomitant appearance of viscous flow (Sperling 2006). In cooling to below the glass transition, the amorphous material vitrifies to a solid-like, brittle, and transparent structure typical of the glassy state (Sperling 2006). These properties and significant differences of the solid- and liquid-like states of amorphous materials make the glass transition perhaps the most important state transition responsible for processing, stability, and quality characteristics of food materials (White & Cakebread 1966, Slade & Levine 1991, Roos 1995).

The importance of the glass transition to processing and stability control of foods and pharmaceuticals was recognized in the development of dehydration and freezing technologies. The development of milk powder and ice cream manufacturing showed challenges in the stabilization of amorphous lactose at high humidities and partially frozen food systems (Troy & Sharp 1930). These food materials have high solute concentrations, which are required for glass formation in foods and may be achieved by freezing of water to concentrate solutes in an unfrozen solute phase or by dehydration (White & Cakebread 1966). Simple sugar solutions and biological systems form freeze-concentrated solute systems during freezing (Luyet & Rasmussen 1968). The freeze-concentrated solute systems vitrify at solute specific temperatures (Luyet & Rasmussen 1968; Simatos & Turc 1975; Levine & Slade 1986, 1989). Transformations of solute structures in freeze-concentrated systems were also found to contribute to flavor retention (Flink & Karel 1970) and affect collapse in freeze drying (Bellows & King 1973; To & Flink 1978; Levine & Slade 1986, 1989). The formation of noncrystalline glassy structures of sugars in dehydration has been well documented (Roos & Karel 1991a, Roos 1995). Glass transition and plasticization data are also important in manufacturing of various cereal products and snacks by extrusion (Roos 1995) or setting parameters for edible films processing (Gontard et al. 1993).

Levine & Slade (1986, 1989) and Slade & Levine (1991, 1995) have emphasized the food polymer science approach in the physico-chemical characterization of food systems. They reviewed applications of polymer science to foods and reported how various food properties were affected by the glass transition and water plasticization (Slade & Levine 1995). The key processes requiring understanding of the amorphous state and glass transitions of food systems are those occurring at limited water contents (Roos 1995). Hence, these cover cereal systems and processing, food freezing and frozen foods, confectionary and candies, dehydration processes and dehydrated foods, extrusion, and extruded foods, among others. Probably the few processes in which the glass transition has less importance are those occurring at high water contents, including thermal processing (canning, pasteurization), membrane separations, and equilibrium processes (e.g., solvent extraction, distillation).

The present review considers glass transition and its relevance to food processing by introducing food material properties as amorphous substances, component interactions, and contributions of the glass transition to food processing and storage.

GLASS TRANSITION

Glass transition is a well-known change in the state of amorphous materials. It is a reversible transformation of the solid- and liquid-like states of supercooled liquids (**Figure 1**). Glass transition occurs over a temperature range in the cooling of a liquid-like material, resulting in solidification to a glassy substance (vitrification). In a heating process, glass transition results in increasing translational mobility of molecules and the concomitant appearance of liquid-like characteristics of the substance (**Figure 2**). Glass transition occurs at approximately 100°C to 150°C below

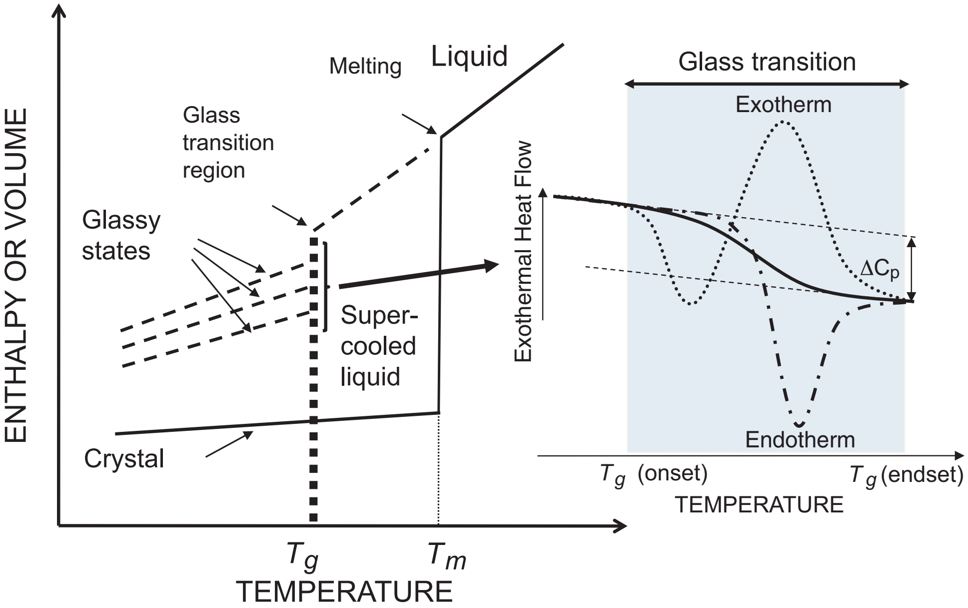

Figure 1

Enthalpy and volume of various states of materials. The liquid and crystalline states are equilibrium states. A supercooled liquid can retain the amorphous, disordered liquid-like structure. Molecules of such supercooled materials become frozen to form a solid glass structure below the glass transition temperature range. The glassy state of a material can show freezing of the molecules at various heat contents and volumes depending on the cooling process. The glass transition in a differential scanning calorimetry measurement appears as an endothermic step change corresponding to a heat capacity change, ΔC_p, over the glass transition temperature range. Enthalpy and volume relaxations are typical of glass transition measurements, as they indicate the appearance of translational mobility around the glass transition and the concomitant ability of the material to respond to increasing temperature. Hence, an endothermic or exothermic change with a corresponding volume change may appear, depending on the differences of the thermodynamic properties of the glassy and supercooled liquid-state at the glass transition.

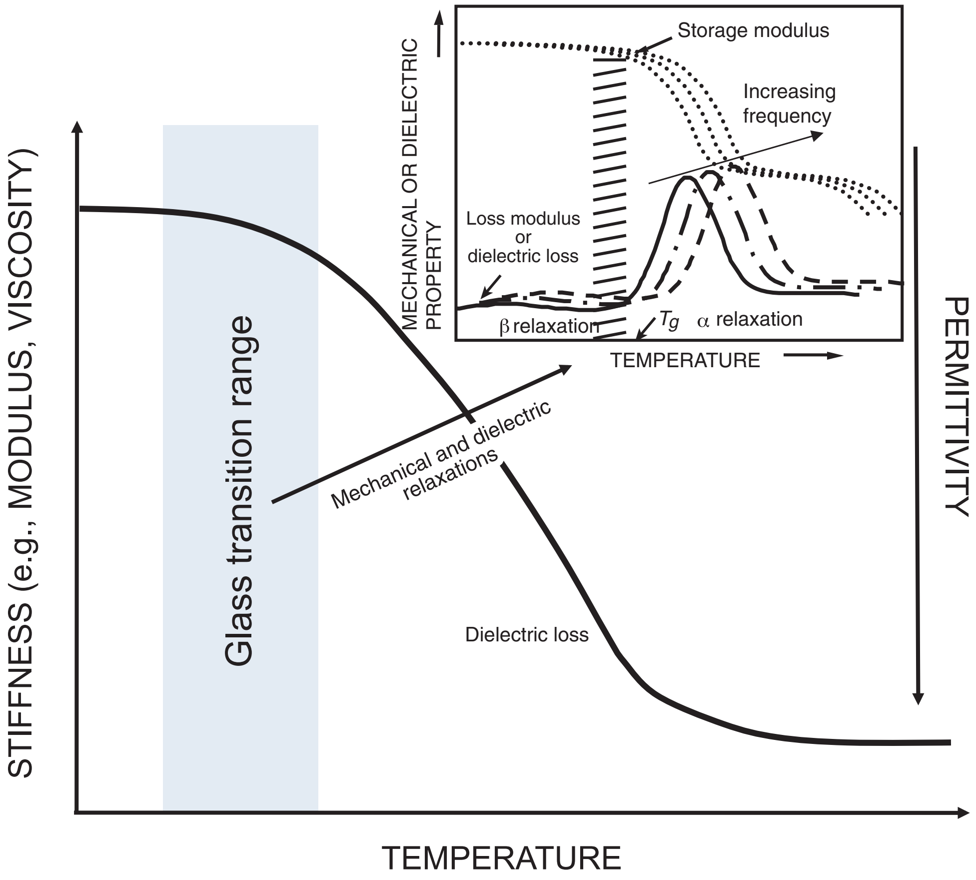

Figure 2

Changes in dielectric and mechanical properties of materials at and above the glass transition. The rapid increase in molecular mobility around the glass transition in heating of a material can be observed in an exponential decrease in modulus and viscosity (storage modulus). In dielectric measurements, this appears as an α-relaxation and rapidly increasing permittivity. The α-relaxation in both dynamic dielectric (thermal) (DEA/DETA) and dynamic mechanical (thermal) analysis (DMA/DMTA) can be identified from a peak in loss modulus. β-relaxations below the glass transition often suggest some changes in molecular mobility in the solid state.

the equilibrium melting temperature of a pure substance (Sperling 2006). In most studies, glass transitions are reported as results of measurements of thermodynamic changes during heating of a glassy system to above its glass transition. A differential scanning calorimetry (DSC) measurement as an example shows a change in heat capacity over the material specific glass transition (**Figure 1**). Other properties of materials changing dramatically around the glass transition include modulus and viscosity, volume and thermal expansion, and dielectric properties (**Figure 2**). The characteristic change in heat capacity is often used to observe the thermodynamic changes of materials around their glass transition. The glass transition is associated with a mechanical and dielectric α-relaxation (**Figure 2**). The methods used to detect the glass transition and associated relaxations were discussed by Roos (1995, 2008) and Sperling (2006).

Theories of Glass Transition

The glass transition exhibits no latent heat, and no temperature can be defined where the glassy and liquid-like states could coexist. Both the solid glassy and the supercooled liquid states, separated by the glass transition, are nonequilibrium states. This suggests that properties of amorphous materials may vary with time, and no stable glass can be obtained. The glassy state is often referred to as a metastable solid state, which also applies to glasses formed in food systems (Slade & Levine 1991). Rates of changes of amorphous materials are highly time-dependent and controlled by the ability of molecules within the material to respond to changes in their surroundings. The nonequilibrium state of amorphous materials has no characteristic order of molecular arrangement, which has caused difficulties in understanding their properties. Several theories of the glass transition have been used to explain the nature of the glass transition (Debendetti & Stillinger 2001, Sperling 2006).

The enthalpy of a material changes differently with temperature in the glassy and liquid-like states, showing that the glass transition is associated with a change in heat capacity (**Figure 1**). However, no single temperature in glass transition measurements can be identified for the change in heat capacity. Furthermore, the change occurs differently in slowly and rapidly cooled materials suggesting that the transition cannot be defined as an equilibrium change in state, and it has both dynamic (kinetic) and thermodynamic properties shown in **Figure 1**. These observations of the changes in thermodynamic properties (volume, enthalpy, entropy) and the kinetic nature of the glass formation have led to numerous explanations of the glass transition using thermodynamic and kinetic approaches (Debendetti & Stillinger 2001).

The free-volume theory. The free volume of polymers has been discussed by Slade & Levine (1991) and Sperling (2006). The free-volume theory of glass transition uses the concept of holes or places that are available for molecular movement (Eyring 1936, Sperling 2006). The expansion of the material occurs differently in the glassy and rubbery states, whereas the free volume is constant at the glass transition. It may be shown that the free volume at the glass transition is constant at 2.5% (Sperling 2006). A relationship of the free volume and viscosity may be used to show the applicability of the Williams-Landel-Ferry (WLF) relationship to fit viscosity data and relaxation times above the glass transition (Williams et al. 1955, Slade & Levine 1991, Roos 1995, Sperling 2006). The WLF (Williams et al. 1955) as well as the Vogel-Tammann-Fulcher (VTF) (Angell et al. 1994) relationships can be used to describe changes in relaxation times above the glass transition. The applicability of the WLF equation to relaxation times above the glass transition in food systems was emphasized by Slade & Levine (1991), and the VTF relationship is used in the description of the properties of fragile and strong glass formers (Angell et al. 1994, Angell 1995).

Kinetic theory. Debendetti & Stillinger (2001) discussed the thermodynamic and kinetic aspects of the glass transition. They stated in line with the Gibbs & DiMarzio (1958) theory of glass transition that the glass transition observed experimentally is a kinetically controlled manifestation of an underlying thermodynamic transition to an ideal glass with a unique configuration. The kinetic theory recognizes the time-dependent characteristics of the glass transition. It takes into account observations of free volume of the material, which changes around the glass transition and suggests that the glass transition occurs at a higher temperature when the frequency of the experiment decreases (Sperling 2006). This also results in the observed enthalpy relaxations shown in **Figure 1**.

Thermodynamic theory. The thermodynamic theory recognizes the glass transition as a second-order phase transition. This is based on the observed changes in heat capacity and thermal expansion coefficient that take place over the glass transition. Gibbs & DiMarzio (1958) suggested that although observed glass transitions are time-dependent, the real thermodynamic change in state occurs at infinitely long times.

Glass Transition and Relaxation Measurements

Glass transitions and relaxations of amorphous materials may be measured with calorimetric, dielectric, mechanical, and spectroscopic techniques. The glass transition appears as a change in enthalpy and volume in the measurement of thermodynamic properties, whereas the appearance of translational mobility of molecules around the glass transition results in a frequency-dependent alpha relaxation measured by the mechanical and dielectric techniques. The spectroscopic techniques provide information on chemical bonding and molecular mobility.

Thermal. Thermal and thermodynamic properties of amorphous materials can be measured using thermal analytical techniques such as DSC and dilatometry (Wunderlich 2005, Sperling 2006, Roos 2008). DSC is probably the most common method used to measure glass transitions in food and other systems. Glass transition in a DSC analysis appears as an endothermal step change in heat flow to a sample resulting from the increase in heat capacity when a material is heated to above its glass transition. The onset or midpoint temperature of the change in heat capacity is typically taken as the glass transition temperature, T_g (**Figure 1**). These values, however, vary, and the values need to be interpreted in applications of T_g data accordingly. The noncrystalline state can also exist in an infinite number of glassy structures formed in cooling or dehydration (glass formation) of the same solids (**Figure 1**). This means that varying relaxations with changes in heat content may accompany the DSC glass transition (Roos 1995, 2008; Wunderlich 2005), suggesting that the molecules of the material become mobile and respond to the change in state around the glass transition differently depending on the glass characteristics. Such relaxations are typical of DSC scans, and they may appear as endothermic or exothermic changes in heat content over the glass transition temperature range (Wunderlich 2005, Roos 2008). The endothermal changes around glass transition have often been associated with physical aging of glasses (Sperling 2006). These relaxations in food and pharmaceutical systems, however, may differ significantly from those of synthetic polymers. Relaxations and aging in food glasses may result from thermal annealing or changes in water content and composition during dehydration and storage (Roos 1995, Kim et al. 2003). Some of these relaxations have been studied systematically, for example, for amorphous lactose (Haque et al. 2006) and frozen systems (Inoue & Suzuki 2006) but their possible effects on food properties, such as food stability or rehydration and sensory characteristics, have not been established. Exposures of low water and frozen foods to varying temperatures and water contents are typical in normal food storage and distribution. These are likely to result in efficient annealing and affect thermal and water content history of food systems during their shelf life.

Mechanical. Amorphous materials show various relaxations when exposed to an external, oscillating small stress (**Figure 2**). Such relaxations can be followed using dynamical mechanical (thermal) analysis (DMA/DMTA) or mechanical spectroscopy (Sperling 2006, Roos 2008). The main relaxations associated with the glass transition is known as α-relaxation. The α-relaxation appears as a dramatic decrease in modulus observed from a rapid decrease in storage modulus and increase in loss modulus with increasing temperature. These changes are frequency-dependent and follow the nonequilibrium, time-dependent nature of the glassy and supercooled liquid forms of the amorphous material (Roos 2008). The DMA data of food and other systems have shown that the method is more sensitive to changes in material properties around the glass transition than DSC (Kalichevsky & Blanshard 1992, Roos 1995, Sperling 2006). However, sample preparation and dehydration of samples during heating are typical problems of the DMA analysis of food materials. Some studies have used membranes between samples (MacInnes 1993) or stainless steel sheet pockets (Silalai et al. 2009) to avoid loss of water. These systems also allow the use of the equipment to observe transitions of powders as well as the use of liquid samples in studies at freezing temperatures (MacInnes 1993, Laaksonen & Roos 2000, Silalai et al. 2009).

The glass transition involves the transformation of a solid to a supercooled liquid state. This allows the observation of the transition from a rapid change in flow properties and softening. These changes can be detected using various empirical methods that allow a dynamic change in temperature and concomitant change in a mechanical property. An example of such is a temperature-controlled cell attached to a texture analyzer developed by Boonyai et al. (2007) to allow measurements in flow properties over the glass transition temperature range.

Dielectric. Dielectric thermal analysis (DEA/DETA) provides analogous relaxation information to DMA data on dielectric relaxations in amorphous systems (**Figure 2**). The method is less frequently used in food studies, but it can be used in the characterization of liquid and powder samples over a wide range of temperatures, including those allowing studies of freeze-concentrated solute-water systems and foods (Laaksonen & Roos 2000). Laaksonen & Roos (2000) used DEA to observe glass transitions in frozen dough systems, and Talja & Roos (2001) measured properties of amorphous polyols. These data showed low-temperature gamma-relaxations, α-relaxation at the temperature corresponding to the glass transition of maximally freeze-concentrated solutes, and onset of ice melting. The results showed high correlation with DSC and DMA measurements. DEA has also been used by Silalai et al. (2009) to observe effects of carbohydrate and protein composition of dairy powders on their thermal and glass transition behavior.

Spectroscopic. Several spectroscopic techniques can be used to observe molecular mobility in amorphous materials. These include infra-red and Fourier transform infra-red (IR/FTIR), Raman, Electron Spin Resonance (ESR), and various NMR spectroscopies as discussed by Roos (1995). Raman spectroscopic studies of amorphous glucose have suggested that the glass transition results in weakening of the hydrogen bonding network (Söderholm et al. 2000). These techniques with FTIR and Raman microscopy give detailed information of glass-forming materials in food systems. The microscopic techniques may also be used to locate crystallinity or varying amorphous components in the food microstructure. One of the key findings of the spectroscopic methods in studies of glass transitions and food material properties has been that the glass transition has only a small effect on the mobility and diffusion of water molecules, and water molecules remain mobile in glassy food systems (LeMeste et al. 2002). You & Ludescher (2009) have applied fluorescence spectroscopy to derive molecular mobility in various glass-forming materials.

Glass Transition Temperatures of Food Solids

Glass transitions can be observed for most hydrophilic food components, i.e., nonfat food solids. These solids have strong interactions and hydrogen bonding with water (Flink & Karel 1970, Söderholm et al. 2000). Water is recognized as a strong plasticizer of foods solids (Slade & Levine 1991), i.e., they become softened by water and some other small molecular weight hydrophilic solvent components (Bhandari & Roos 2003). Common glass formers in foods are sugars and other carbohydrates that show a strong water content dependence on the glass transition temperature as a result of plasticization (Roos & Karel 1991c). Proteins as nonfat food solids also exist in noncrystalline forms and show glass transition and water plasticization behavior (Cocero & Kokini 1991). Most foods are mixtures of carbohydrates and proteins, but relatively few studies have reported glass formation and glass transition data for mixed carbohydrate-protein systems. It seems that carbohydrates and proteins show some miscibility (Taylor & Zografi 1998, Haque & Roos 2004), but they may also exist in separate phases (Sun & Davidson 1998). Although glass transition data are available for several complex foods, such as dairy powders (Jouppila et al. 1997), the level of miscibility of the glass-forming components remains unknown. Furthermore, food solids at varying storage conditions differ in water sorption and glass transition characteristics. This increases the complexity of the analysis of glass transitions in food solids. However, several studies on sugar-protein mixtures and dairy powders have suggested that the contribution of proteins to the glass transition is relatively small in comparison to that of sugars (Jouppila et al. 1997, Haque & Roos 2004).

Glass Transition and Water Plasticization

The glass transition temperatures of food components vary significantly from temperatures below room temperature for fructose and some polyols (Roos 1993a, Talja & Roos 2001) to decomposition temperatures of biopolymers, such as starch (Zeleznak & Hoseney 1987, Roos & Karel 1991d) and gluten proteins (Noel et al. 1995), as shown in **Figure 3**. Measured glass transition temperatures, T_g, decrease with increasing water content showing significant water plasticization

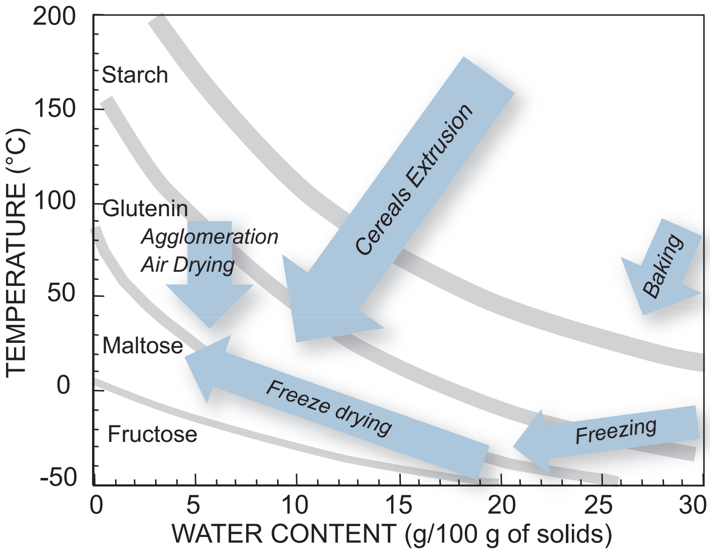

Figure 3

Glass transition temperatures of fructose, maltose, glutenin, and starch and their water plasticization shown by decreasing glass transition temperature with increasing water content. The glass transition temperature range often increases in broadness with increasing molecular weight as shown by the increasing thickness of the transition curves. Examples of processes and material properties controlled by water and temperature around the glass transition are shown in relevant temperature and water content areas. The food component data suggest that cereal materials can be plasticized and extruded to form glassy structures, whereas amorphous fructose cannot exist in the solid state (e.g., as powder) at typical ambient temperatures.

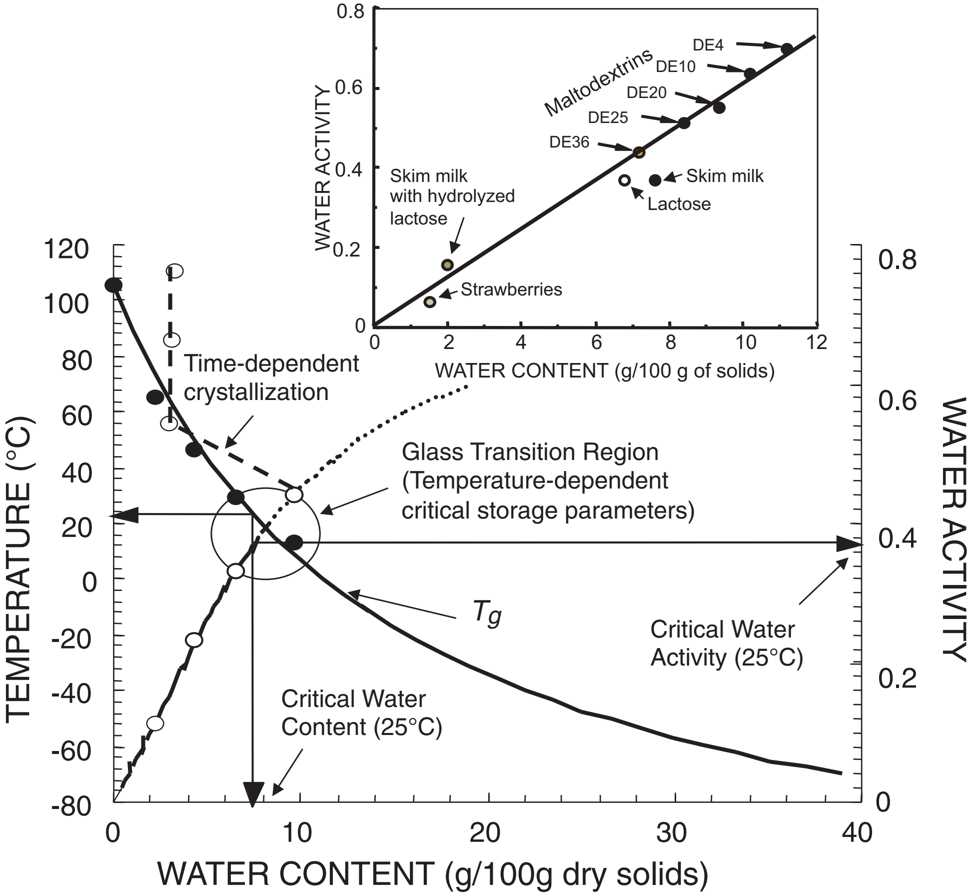

Figure 4

Glass transition and water sorption properties of amorphous lactose. The critical water content corresponds to critical water activity with the glass transition temperature, T_g, being the same as the water sorption temperature. Water contents exceeding the critical value result in flow and time-dependent lactose crystallization. The critical water activity and water content seem to have a linear relationship for maltodextrins decreasing with increasing dextrose equivalent (DE).

(Levine & Slade 1986, Roos 1986, Slade & Levine 1991, Roos & Karel 1991c). Several studies have used the Gordon-Taylor (Roos & Karel 1991a) or the Couchman-Karasz (Kalichevsky & Blanshard 1993) relationship to predict the water content dependence of glass transition temperatures. Roos (1987) reported that the glass transition temperature of strawberry solids decreased almost linearly with increasing water activity. The glass transition dependence on water content has been taken into account in the prediction of food stability at varying water activities and water contents. Roos (1993b) fitted the Gordon-Taylor and the Guggenheim-Anderson-de Boer (GAB) relationships to glass transition, water plasticization, and water sorption data. The GAB model is well known to fit to the water sorption data of food materials at various relative humidities (Roos 1995). It can be used to predict the relationship of water content and relative humidity at equilibrium at a constant temperature, i.e., the water sorption isotherm. The models could locate critical water activities and water contents for food components (**Figure 4**).

Frozen Food Systems

Frozen food systems represent a complex, temperature-dependent phase and state transition behavior. Freezing of water results in temperature-dependent, freeze concentration as ice crystals are separated from dissolved and other solids as dispersed ice in a continuous, unfrozen phase (Luyet & Rasmussen 1968). This unfrozen phase has a temperature and composition-dependent water plasticization behavior as the plasticizing unfrozen water content changes with temperature, and concomitant changes in the ice and unfrozen water contents take place (Roos & Karel 1991a). Numerous studies have been conducted to observe the freeze-concentration and vitrification behavior of sugar systems (Luyet & Rasmussen 1968, Bellows & King 1973, Levine & Slade 1986, Roos & Karel 1991a). Studies of frozen sugar solutions have reported two low-temperature endothermic transitions followed by the main ice-melting endotherm during rewarming of frozen solutions using differential scanning calorimetry (Luyet & Rasmussen 1968, Simatos & Turc 1975, Roos & Karel 1991a, Goff et al. 2003).

The vitrification of freeze-concentrated solutes and cryostabilization of frozen foods in the maximally freeze-concentrated state were emphasized by Levine & Slade (1986, 1989). The maximally freeze-concentrated state can be formed in the vicinity of the glass transition of the maximally freeze-concentrated solute phase. Glass formation in freeze-concentrated solutions and food systems occurs as a result of (*a*) the separation of ice in a dispersed solid phase, and (*b*) the decreased temperature and increased viscosity of the unfrozen phase. As the freeze-concentrated phase approaches a high solids content and high viscosity, the rate of crystallization of water is reduced. At some level of freeze-concentration and increasing viscosity, ice formation ceases. Roos & Karel (1991a) suggested that the viscosity at which ice formation ceased was 10^7 Pas. This occurred at T_m', which in a DSC heating scan was the temperature of the onset of ice melting (**Figure 4**). Roos & Karel (1991a) showed that (*a*) the ice formation in the freeze-concentrated sucrose solution was time-dependent, (*b*) the solute concentration in the maximally freeze-concentrated sucrose solution was 80%, and (*c*) the maximum ice formation was possible only at temperatures above the onset of the glass transition of the maximally freeze-concentrated solution, T_g' but below T_m', as shown schematically in **Figure 5**.

Although Levine & Slade (1989) considered the higher transition as the T_g', it seems that both the T_g' and T_m' transitions describe the complex glass transition associated with ice formation and melting. Roos & Karel (1991d) reported that higher molecular-weight food components, e.g., maltodextrins and starch, showed decreasing temperature difference for T_g' and T_m' with increasing molecular size and the transitions coincided for high molecular weight solutes (**Figure 5**). This also agreed with increasing T_g values with increasing molecular weight in general (Roos 1995, Sperling 2006) and the decreasing capability of high molecular-weight molecules to depress the ice-melting temperature as suggested by Raoult's law. Goff et al. (2003) suggested that the T_m' transition included solute inclusion within the ice phase. However, a pure crystalline ice phase appeared after maturation of the crystals. The highly time- and temperature-dependent nature of the maximum ice formation seems to be challenging in studies, such as that of Goff et al. (2003), using modulated temperature scanning of samples. It also seems to be difficult to observe small changes in unfrozen water associated with ice melting around T_m' as suggested by the data and conclusions of Sacha & Nail (2009). However, it seems obvious that ice melting is temperature-dependent above the T_m', and the onset of ice melting, although latent heat is involved, cannot be separated from a glass transition–type endothermic step in a heating scan or temperature modulation. The maximum freeze-concentration of sugar systems results in vitrification of the unfrozen solute phase. The glass transition occurs over a temperature range that for most materials seems not to be completed prior to the onset of ice melting. The onset of

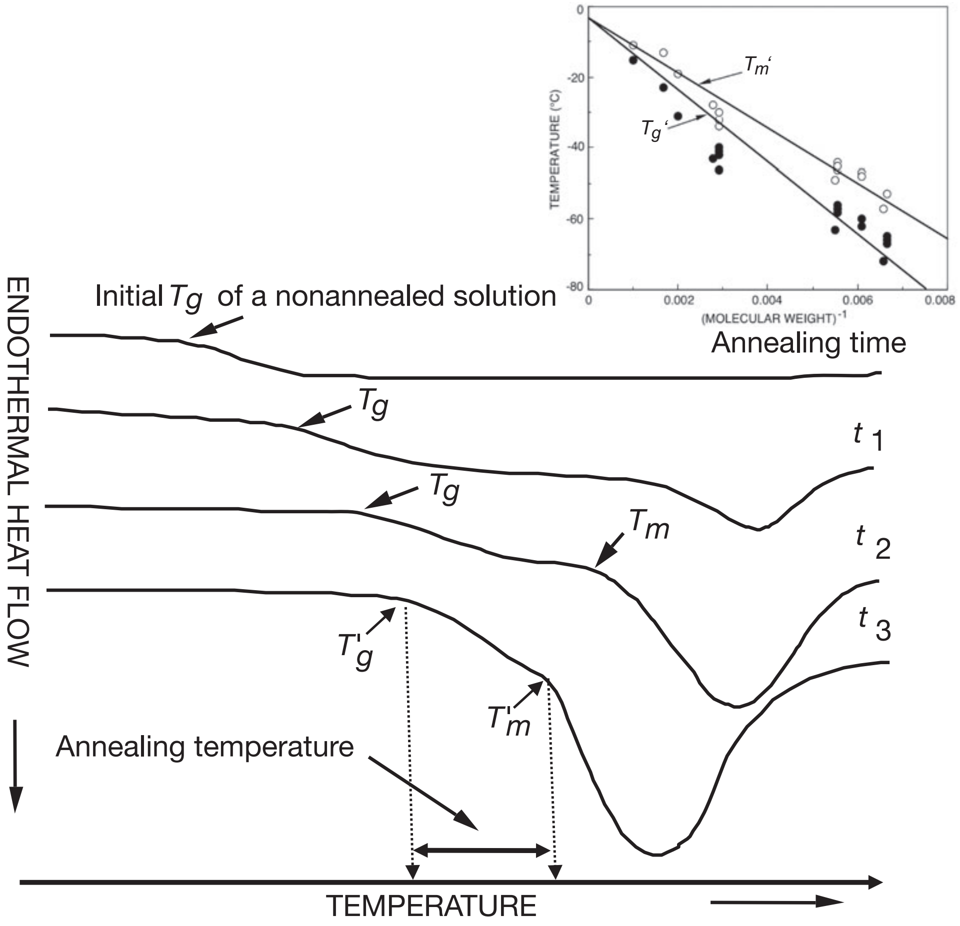

Figure 5

Ice formation in frozen, freeze-concentrated systems with no solute crystallization. The time-dependent ice formation is described using schematic differential scanning calorimetry curves for a solution with no ice formation in a rapidly cooled solution and an initial glass transition with onset at T_g in a heating scan. An isothermal holding (annealing) at a temperature between the onset of glass transition, T'_g, and onset of ice melting, T'_m, for the maximally freeze-concentrated solute plasticized by unfrozen water followed by cooling and reheating shows a higher glass transition as a result of time-dependent ice formation. Annealing time of t_3 resulting in maximum freeze-concentration gives a system with T'_g and T'_m as well as the lowest and largest ice-melting endotherm. The T'_g and T'_m increase with increasing molecular weight and coincide for maximally freeze-concentrated high molecular weight solutes as shown by data for monosaccharides, disaccharides, and maltodextrins (Roos 1995).

ice melting shows a significant change in the heat capacity (Roos & Karel 1991c) as a result of increasing enthalpy corresponding to ice dissolution and increased mobility (Reid et al. 2003) over a narrow temperature range that, however, cannot be taken as a glass transition (Roos & Karel 1991a). The ice dissolution takes place over a temperature range with a concomitant change in enthalpy that produces a similar, but larger, change in heat capacity to that observed at a glass transition.

State Diagrams

The understanding of glass transitions of food systems has allowed food material characterization and prediction of their behavior at high solids contents and in the frozen state at varying temperatures and water contents. State diagrams or supplemented phase diagrams (Slade & Levine 1991) provide useful maps for the observation of changes in glass transition as a function of water content or varying levels of freeze-concentration (Roos & Karel 1991b). State diagrams have been established for several sugars, polysaccharides, and proteins (Roos 1995, Icoz & Kokini 2008). The establishment of state diagrams for pure food components, such as sugars, is straightforward as glass transitions can be followed using DSC and other thermal analytical techniques. The glass transition is strongly dependent on water content, which often causes large differences in reported glass transition temperatures. This has been a particular problem for the anhydrous glass transition data. Pure sugars may also crystallize above their glass transition, and glass transition data at intermediate water contents may not be measured (Roos 1993a). The glass transition and ice-melting temperatures of maximally freeze-concentrated systems (**Figure 6**) are essential in the understanding of freezing and freeze drying. Thermal behavior of sugar systems, however, has

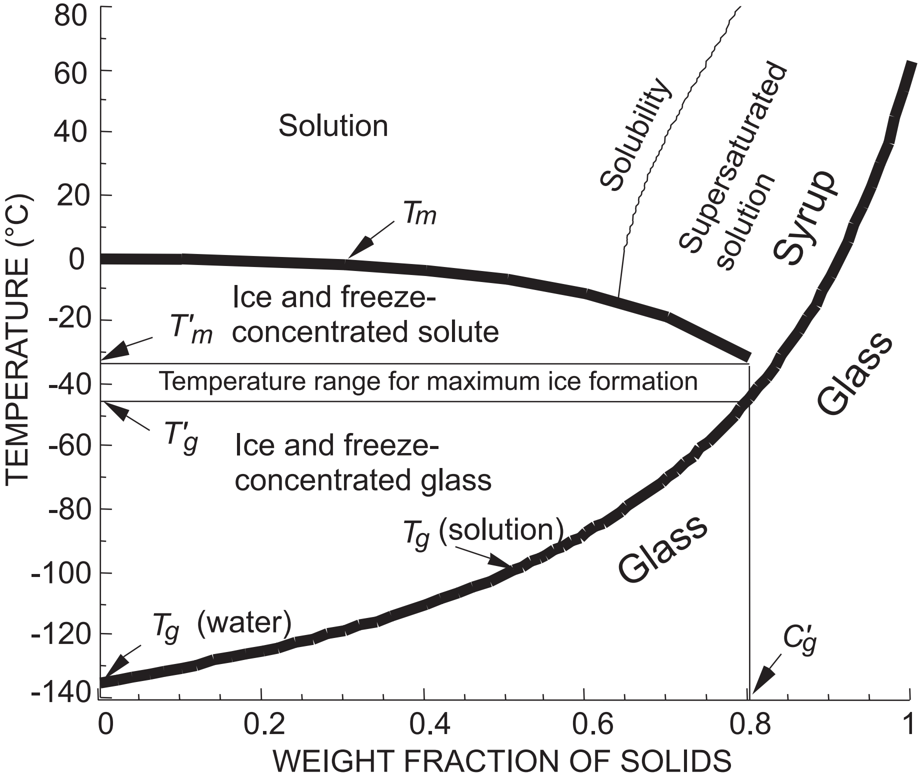

Figure 6

State diagram of sucrose. The state diagram shows the glass transition, T_g, dependence on water content, solubility, and ice formation. The T_m curve shows equilibrium melting temperature for ice and T'_g and T'_m indicate the onset glass transition and onset for ice-melting temperatures in a maximally freeze-concentrated solution. Data from Roos & Karel (1991a).

been interpreted differently in several studies (Levine & Slade 1986, 1989; Roos & Karel 1991a,e; Sacha & Nail 2009), but the nature and time-dependent characteristics of freeze-concentrated systems include concomitant changes in viscosity and ice content.

One of the most studied amorphous food components is sucrose (Roos & Karel 1991a, Ablett et al. 2002, Sacha & Nail 2009). Its state diagram (**Figure 6**) has been often used to show solubility, glass transition, and ice formation properties of food and pharmaceutical systems at various water contents and levels of water plasticization. The state diagram of sucrose can be considered as a model state diagram of fully amorphous components. Amorphous sucrose can be prepared by freeze drying, and the dehydrated material can be exposed to relative humidities up to 33% in water sorption studies without extensive sucrose crystallization (Roos & Karel 1991a). Sucrose can also be dissolved at high solids concentrations with no sucrose crystallization or ice formation to obtain glass transition data at low temperatures. The equilibrium ice-melting temperature data over a broad range of sucrose concentrations in water are also available (Roos 1995). Furthermore, the Gordon-Taylor (Gordon & Taylor 1952) and freezing temperature depression models (Roos 1995) are important in predicting the water content dependence of the glass transition and ice melting, respectively (Roos 1995, LeMeste et al. 2002).

Some studies have reported state diagrams for food systems, such as fruits and dairy powders. Glass transitions in these systems are often governed by their main carbohydrates. For example, the glass transition of milk powders followed closely that of lactose (Jouppila & Roos 1994). When lactose was hydrolyzed to its glucose and galactose components, a significantly lower glass transition and critical water activity and water content (**Figure 4**) were observed (Jouppila & Roos 1994, Roos 1995).

Glass Transitions of Food Materials

Several studies have reported glass transitions and state diagrams for food solids, such as strawberries (Roos 1987), dairy powders (Chuy & Labuza 1994, Jouppila & Roos 1994), crackers (Nikolaidis & Labuza 1996), zein (Madeka & Kokini 1996), apples (Sá et al. 1999, Bai et al. 2001), pineapple (Telis & Sobral 2001), tomato (Telis & Sobral 2002), kiwi fruit (Moraga et al. 2006), breakfast cereal and its components (Sandoval et al. 2009), and raspberries (Syamaladevi et al. 2009). In general, these studies have found that the glass transitions of food materials occur at temperatures well above 100°C for high molecular-weight systems such as cereal and high-protein foods, or at temperatures reflecting the sugar components of the materials. Food systems are significantly plasticized by water and the glass transition temperatures are depressed to below normal food storage temperatures at relatively low or intermediate water contents depending on the main hydrophilic components responsible for the observed glass transition temperatures. The main benefit in the understanding of the glass transition behavior of real food systems is in predicting its effects in dehydration and stability of foods at low water contents or in freezing and frozen state stability of foods (Levine & Slade 1989, Roos 1995, LeMeste et al. 2002), as illustrated in **Figure 3**.

GLASS TRANSITION AND FOOD PROCESSING

The formation of solid structures from supercooled liquids is known to take place when a material is cooled to well below its glass transition at a rate that is more rapid than the rate of nucleation and crystallization (e.g., Kauzmann 1948, Angell 1995, Sperling 2006). Roos & Karel (1991b), as shown in **Figure 7**, described glass formation in food processing as a phenomenon resulting from a rapid cooling of food solids or rapid removal of plasticizing water by dehydration or freezing. The metastability of the glassy state and plasticization above the glass transition were useful in

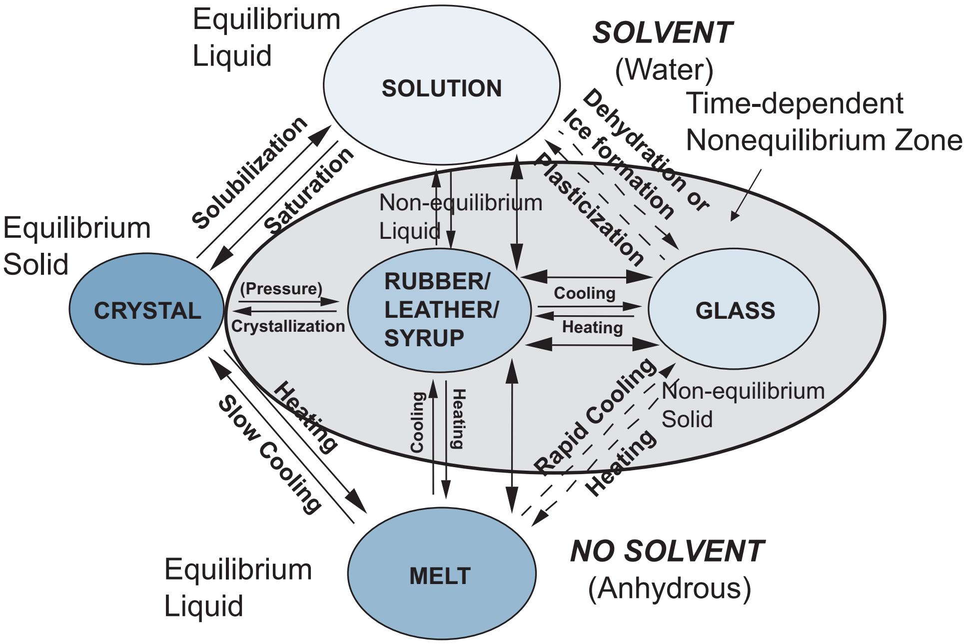

Figure 7

Relationships of equilibrium and nonequilibrium states of food systems in processing and storage. Rapid cooling or removal of water results in glass formation, which is applied, for example, in dehydration processes and manufacturing of confectionary with glassy sugars. The noncrystalline states are nonequilibrium states and exhibit time-dependent characteristics.

explaining food properties in relation to the glass transition (Slade & Levine 1991; Roos 1995, 2009).

Freezing

Freezing in the food industry is often carried out using equipment that decreases the food temperature to approximately −40°C followed by storage and distribution at temperatures at approximately −20°C. However, these temperatures are selected on the basis of available equipment and good practice rather than scientific evidence. It is often correctly assumed, however, that rapid freezing decreases ice crystal size and provides a better retention of food quality after frozen storage and thawing of frozen foods. The main changes of frozen foods during storage are chemical and biochemical reactions such as enzymatic changes and oxidation, affecting product quality as well as crystallization of solutes, e.g., lactose in ice cream and recrystallization of ice (Levine & Slade 1989, Roos 1995, Hartel 2001). Knowledge of the glass transition behavior of frozen food systems is important in understanding the freezing process and frozen state stability of foods.

The food polymer science approach introduced by Levine & Slade (1986) introduced the glass transition temperature of the maximally freeze-concentrated system, T_g', as the key parameter for the control of stability of frozen foods. Stability according to the cryostabilization concept introduced by Levine & Slade (1989) was achieved by frozen food storage at temperatures below the T_g'. At the maximally freeze-concentrated state, i.e., a maximum amount of water had crystallized and dispersed within an unfrozen water and hydrophilic solutes and solids phase as ice, diffusion of reactants and products was reduced as the freeze-concentrated solutes formed a glassy unfrozen solute matrix. However, at conditions above the T_g', reaction rates were likely to increase exponentially according to the WLF relationship (Levine & Slade 1989). According to Lim & Reid (1991), maltodextrins showed cryostabilization behavior and reduced rates of enzyme hydrolysis, protein aggregation, and nonenzymatic oxidation in frozen solutions. Significant retardation of the reactions was observed in the glassy, freeze-concentrated systems. The consideration of reaction rates in frozen systems requires knowledge of the T_g' and T_m' as well as the extent of freeze-concentration at temperatures above the T_m' (Roos 1995). The reaction rates in vitrified systems may not always be retarded by the glass transition as a result of structural heterogeneities as well as varying diffusional characteristics of food components and gases (LeMeste et al. 2002). Ablett et al. (2002) showed that recrystallization of ice in frozen sugar systems was affected by the mobility of water and solute molecules, and the rates were increasing exponentially with increasing temperature above the glass transitions of the maximally freeze-concentrated systems.

Most fruits and berries contain fructose, glucose, and sucrose as the main water soluble components. The thermal behavior of these sugars is well known (e.g., Luyet & Rasmussen 1968; Roos & Karel 1991a,e; Roos 1993a). Roos (1987) carried out a systematic study of glass transitions of strawberries. The T_g' derived from his data appeared at temperatures below −40°C, and ice melting had an onset at −42°C. These data showed that the ice melting in frozen fruits occurred at temperatures well below the common temperatures of frozen storage. Similar data have been reported for several other fruits (see state diagrams). Storage of fruit solids at normal frozen storage temperatures at approximately −20°C allows ice melting and recrystallization as the conditions do not support the formation of the maximally freeze-concentrated state required for the physical stability (Levine & Slade 1989, Hartel 2001, Ablett et al. 2002). The information on the freezing properties of fruit solids is probably most important to commercial freezing of fruits and berries as food ingredients and to the production and distribution of fruit juice concentrates.

Ice formation and melting in ice cream have been studied extensively because of the complexity of ice cream freezing and stabilization against recrystallization of ice and crystallization of lactose during ice cream storage. As shown in **Figure 8** by the lactose state diagram, lactose solubility in the freeze-concentrated ice cream is extremely poor and both lactose crystallization and recrystallization of ice are possible within the critical zone below T_m but above T_m' of lactose. Often the data measured for sucrose solutions have served as a model for ice cream freezing to understand the freezing and melting behavior of ice in ice cream–type products (Goff et al. 1993, Ablett et al. 2002). The glass transition of ice cream systems can be assumed to be mainly controlled by the main sugars used in ice cream formulation. However, our studies have suggested that the T_g' is lower in sugar-protein systems than for the sugar solutions (Singh & Roos 2005). Also the T_m' is at a higher temperature suggesting a broader temperature range for the glass transition and maximum ice formation. The main quality changes controlled by the glass transition in ice cream are recrystallization of ice and lactose crystallization. These changes occur at normal frozen storage temperatures as the maximum freeze-concentration required for ice cream stabilization requires storage at temperatures below −35°C, which is the onset temperature for ice melting in sucrose solutions (**Figure 6**). Roos & Karel (1992) showed that lactose crystallization at low water contents occurred time dependently at temperatures above the T_g. They also showed that crystallization of water in freezing ceased when the unfrozen solute phase viscosity exceeded 10^7 Pas (Roos & Karel 1991a). The novel ice cream products, such as Dippin' Dots, are stabilized using temperatures supporting the glassy state of the freeze-concentrated solutes in manufacturing, distribution, and storage of the product.

Cryostabilization and state transitions of frozen dough systems have been considered in several studies. The freezing of the dough requires knowledge of dough components and their effects

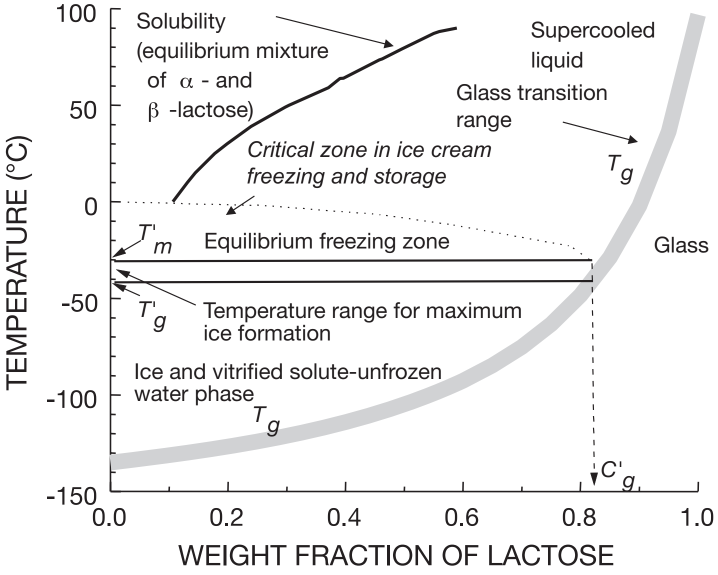

Figure 8

State diagram of lactose. Extrapolation of solubility data suggests that lactose solubility is exceeded in freeze-concentrated systems. Recrystallization of ice may occur at temperatures above the onset temperature of ice melting in the maximally freeze-concentrated system, T'_m. The glass transition temperature of the maximally freeze-concentrated state is shown by T'_g. The glass transition temperature, T_g, dependence on water content is shown by the T_g curve. At low water contents, the glass transition can be used to establish appropriate dehydration processes for dairy solids and to ensure their stability during storage.

on the melting properties of water in the frozen systems as well as of yeast viability. The main components affecting freezing properties of dough at lower temperatures are carbohydrates and salts. Although the T'_g of starch is relatively high at approximately −5°C (Roos & Karel 1991d), sugars and salts may decrease the T'_g to below −30°C (Räsänen et al. 1998, Laaksonen & Roos 2000, Ribotta & Le Bail 2007). It seems that although the cryostabilization concept uses the assumption of stability in the maximally freeze-concentrated state, yeast viability decreases during storage of dough in its maximally freeze-concentrated state, and a better survival of yeast can be achieved at lower levels of freeze-concentration at higher temperatures (Sieviläinen & Roos 1996, Yi & Kerr 2009).

The melting of bulk ice in protein systems takes place relatively close to 0°C (Roos 1995), but there have been very few studies of glass transitions in meat systems. DSC studies of meat systems have suggested that ice melting occurs at temperatures between −40 and −30°C (Roos 1986). Other protein systems studied include fish, such as tuna meat (Inoue & Ishikawa 1997). Studies on fish proteins have suggested very low glass transitions, such as −71°C to −68°C for tuna meat (Inoue & Ishikawa 1997). It may be assumed that meat products show ice recrystallization behavior above the T'_m, but rates of chemical changes, such as oxidation, require careful further studies to understand possible effects of the physicochemical properties of the freeze-concentrated phase on deterioration during frozen storage.

One of the most challenging areas of freezing and frozen storage is the freezing and thawing of biologically active materials. Many fundamental studies on the thermal behavior of carbohydrate systems were aimed at understanding their cryoprotective properties, glass formation, and effects on ice formation and melting. Pehkonen et al. (2008) found that probiotic bacteria cells were entrapped in freezing and suggested that the survival of the cells in a freezing process was enhanced in less than maximally freeze-concentrated systems. It seems that the survival of the bacteria is also affected by the sugar composition inside the cells at the time of freezing. Our studies have suggested that freezing to the maximally frozen state may be more detrimental to the stability of bacteria cells than storage at a higher temperature in a less freeze-concentrated state of the solids (Pehkonen et al. 2008).

Dehydration

Dehydration of food materials is often carried out by air drying, allowing free evaporation of water with decreasing volume and changes in food structure. At high levels of solids, air-dried foods may exist above the glass transition, e.g., dehydrated fruits, or as glassy solids, such as food powders produced by spray drying. Dehydration may also be carried out by freeze drying, which requires prefreezing and sublimation of ice to produce high-volume, glassy structures of food solids.

Air-drying processes. Dehydration is an efficient food preservation method that reduces the water content and water activity to levels that do not allow growth of microorganisms. Dehydrated foods may exhibit a semisolid or solid-like appearance. Examples of semisolid dehydrated foods include some fruits and vegetables, e.g., raisins. These often contain sugars and macromolecules as the main components, which do not always enter the glassy state at normal dehydration or storage conditions (**Figure 3**). For example, fruits with high fructose, glucose, and sucrose contents have glass transitions below room temperature as anhydrous or low water content materials (Roos 1987, 1993). Such viscous, semisolid appearance often results from air drying and is typical of numerous dried fruits (e.g., apples, apricots, dates, raisins). The glass formation and glassy structures are, however, fundamental properties of freeze-dried and spray-dried materials (Roos 2009).

Anglea et al. (1993) suggested that the quality of dehydrated foods could be improved by keeping the material temperature close to the glass transition to avoid structural and other quality changes during dehydration. Karanthanos et al. (1993), however, found that the collapse at high water contents was difficult to control, but volume changes were reduced at low water contents. Spray-drying processes involved atomization of liquids and rapid dehydration of the fine particles into glassy structures (Bhandari & Howes 1999, Roos 2002). The process requires solidification of particle surfaces at the initial conditions in the drying tower to retain free-flowing properties of particles toward powder outlet and to avoid stickiness and caking of particles in the equipment (**Figure 9**). The formation of solid structures requires a rapidly increasing viscosity at the particle surfaces to extend contact times required for stickiness and adhesion (Downton et al. 1982). This can be achieved by glass-forming solutes such as lactose in dairy powders (Jouppila & Roos 1994) or drying aids such as maltodextrins (Roos 1995, Jaya & Das 2009). In encapsulation by spray drying, the glass-forming solutes become a solid continuous phase that can entrap volatiles and flavors as well as encapsulate dispersed components such as milk fat in dairy powders (Vega & Roos 2006, Gharsallaoui et al. 2007). Spray drying of solids with low glass transition temperatures is often difficult as the product outlet temperature must be lower than the glass transition of the solids. Storage of powders also requires temperatures below the glass transition (**Figure 3**). Solids with glass transition below typical ambient temperatures, e.g., several fruit juices, exhibit liquid properties of component sugars and cannot be dehydrated.

Agglomeration of spray dried materials is used to increase the particle size of powders and the process is often combined with spray drying either as an integrated or external process. Agglomeration uses a controlled plasticization of particle surfaces allowing particles to adhere, form interparticle liquid bridges, and agglomerate (Peleg & Mannheim 1977, Roos 1995, Palzer 2005).

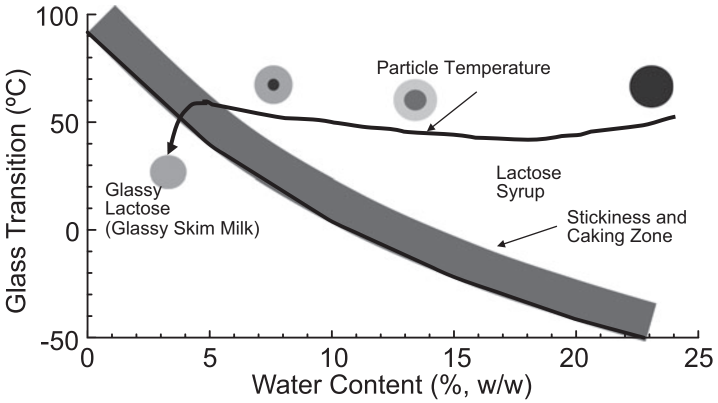

Figure 9

A schematic representation of dehydration of lactose containing particles in dairy solids. Lactose at high water contents exists as a supersaturated syrup that is dehydrated to a lactose glass at the end of spray drying. The temperature-water content corresponding to viscous flow of plasticized lactose at particle surfaces can result in stickiness, agglomeration, and caking.

The resultant agglomerates have channels between adhered particles enhancing water uptake in rehydration and formation of reconstituted liquid foods.

Freeze drying. Freeze drying involves freezing of water in a material followed by dehydration through sublimation of the ice. Freeze drying has been recognized as a process allowing production of fully amorphous structures of carbohydrates (Simatos & Blond 1975, Roos 1997). The process is often considered to include primary drying for the sublimation of ice and secondary drying for the removal of unfrozen water (Tang & Pikal 2004). However, these processes are concomitant in a vacuum sublimation process as a material containing ice and unfrozen water associated with highly freeze-concentrated solids is dehydrated. The freezing step preceding freeze drying must ensure full solidification of the unfrozen phase, i.e., the material must achieve a maximally freeze-concentrated state. The maximally freeze-concentrated state ensures that the unfrozen phase is able to support its own weight and resist flow (collapse) during sublimation of ice (Pehkonen & Roos 2008). The collapse in freeze drying results from viscous flow above the onset temperature of ice melting in a maximally freeze-concentrated systems, T'_m (Bellows & King 1973, Roos 1997). Successfully freeze-dried materials can be produced only at drying conditions at which the ice temperature is kept lower than the T'_m, typically by the control of dehydration pressure, which determines the ice sublimation temperature.

The structure of properly freeze-dried materials is controlled by the freezing process. It may be assumed that the unfrozen phase, possibly with dispersed components, such as lipids and flavors, or suspended solids, including probiotic bacteria cells, forms a continuous phase surrounding ice crystals in frozen systems (**Figure 10**). The freeze-drying process retains the solid state of the unfrozen material that approaches an anhydrous, glassy solid state at the end of the freeze-drying process. Retention of the solid structure of the solids, as well as any of the entrapped components (**Figure 10**), requires that the temperature of the unfrozen and dehydrated solids phase is lower than its glass transition during and after dehydration. Hence, no material with a glass transition below normal storage temperatures of freeze-dried materials can be dehydrated (**Figure 3**). For example, solutions of several monosaccharides and polyols cannot be freeze dried (or spray dried), as their anhydrous glass transitions are lower than room temperature (Roos 1993a,

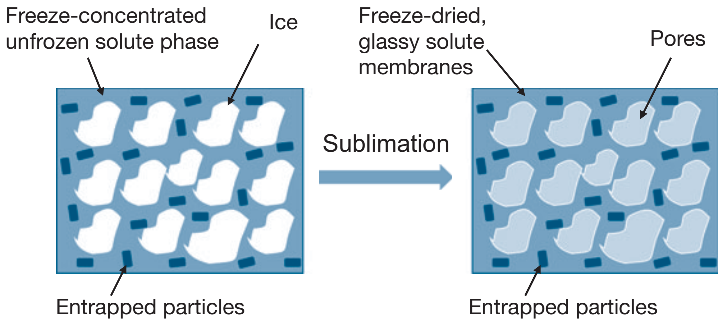

Figure 10

Structure formation and particle entrapment in freeze drying. A solid freeze-concentrated glass phase with entrapped particles (solid components, dispersed phase, bacteria cells, etc.) is formed in the prefreezing step of a freeze-drying process. The solid, glassy structure is maintained throughout the dehydration process to avoid viscous flow and collapse. The dehydrated solids form membranes around voids left by the ice crystals and retain entrapped components in the dehydrated, glassy solids.

Talja & Roos 2001). When freeze-dried materials are exposed to atmospheric conditions, they show significant water plasticization, which may result in collapse of the freeze-dried structures as the glass transition is depressed to below ambient temperature (Roos 1995).

Extrusion

Extrusion in the food industry can vary from production of pasta to various confectionary processes and manufacturing of numerous puffed cereal- and starch-based foods. Production of extruded puffed snacks is based on a similar behavior of food solids to that of synthetic polymers. For example, starch can be gelatinized by using a high temperature and limited water content (Olkku et al. 1978). At a high temperature during extrusion, water in a starch paste exhibits high pressure and the material behaves as a polymer melt (**Figure 3**). At the die, this paste is extruded to atmospheric conditions allowing a flash evaporation of the water and a concomitant expansion caused by the water vapor release from the paste. This rapid release of water with evaporative cooling results in the vitrification of the amorphous starch with other components and formation of crispy membranes typical of the puffed structure. Roos et al. (1998) produced a model extruded snack from wheat flour and maltodextrin. This system showed a clear glass transition that allowed the study of the relationship of sensory crispness and the glass transition. It was observed that the crispness was lost at water contents depressing the glass transition to below room temperature. Harris & Peleg (1996) used the Fermi's relationship to model water activity dependence of textural characteristics of cellular cereal foods. They also observed that the stiffness of the materials could increase at low water contents followed by a significant decrease around glass transition. It was noted that different mechanical properties change differently around the glass transition. It has also been observed that crispness may decrease in the glassy state of white bread (Champion et al. 2000), but as noted by Harris & Peleg (1996), the glass transition in cereal systems occurs over a wide temperature range, and no single temperature responsible for the transition can be defined.

Baking and Cereal Foods

Glass transition studies of cereal systems have reported glass transition data for starch or protein components of cereals (e.g., Zeleznak & Hoseney 1987, Madeka & Kokini 1996) with little information on the use of glass transition data on baking and cereal processing. Levine & Slade (1995) published numerous papers on the use of glass transition in baking of cookies. This concept has shown the possibilities of using various sugars to explain and manipulate the quality of cookies (Kweon et al. 2009). Icoz & Kokini (2008) summarized state diagrams and explained structure formation by cereal proteins in baking and extrusion. Baking and cereal foods is a challenging area for the understanding of material properties, component interactions, and formation of complex structures at high protein and starch contents. The formation of structure typically takes place as a result of changes in temperature and decreasing water content leading to water plasticized structures of gelatinized starch and proteins (**Figure 3**). Starch may also be plasticized by sugars and other small molecular weight carbohydrates. It may be assumed that, for example, baking of a cake requires an increase of viscosity of the dough to form a continuous phase that can support its own weight. A similar change takes place in baking of dough to bread in which the crust approaches a glassy state of starch, and the crumb forms an elastic amorphous structure of gluten and starch. The glass transition may also be used to explain retrogradation of starch as it affects the rate of amylopectin crystallization during storage (Jouppila & Roos 1997).

Edible Films

Edible films are typically produced from proteins, such as casein, whey proteins, cereal proteins, or polysaccharides, including starch. These can be plasticized by small molecular weight polyols, sugars, and water, and they may behave as typical polymer films (Gontard & Ring 1996). The amorphous state of biopolymers is preferred as crystallization results in brittleness and poor structural characteristics. Various plasticizing components are added to biopolymer films to decrease their brittleness and to decrease component crystallization (Talja et al. 2007).

Encapsulation

Encapsulation requires entrapment of food components or dispersed particles in a continuous phase. This continuous phase is often a solid matrix formed by glass-forming food components, particularly sugars and other carbohydrates. Encapsulation in glass-forming food matrices can be carried out using freeze drying, spray drying, other dehydration processes, and extrusion as the key processes available to the food industry (Roos 1995).

Several studies have addressed entrapment of volatiles and flavors in dehydrated matrices. Flink & Karel (1970) proposed that flavor retention in freeze drying was based on the formation of microregions in freezing and encapsulation of the components in freeze-dried amorphous matrices. Thijssen (1971) introduced the selective diffusion theory emphasizing rapid diffusion of water compared with volatiles that were selectively retained. The retention was improved with increasing molecular weight of the components. The selective diffusion in maltodextrin systems could also be related to their glass transitions. An improved entrapment and reduced diffusion was likely as the maltodextrin systems approached their glass transition (Roos 1995). Numerous recent studies have discussed the glass formation of amorphous matrices in encapsulation processes (Vega & Roos 2006) and emphasized the importance of the glass-forming ability of the encapsulant in protecting sensitive components (Ubbink & Krüger 2006).

Food properties, stability, and shelf life. Food processing aims at satisfying the needs of a safe food supply with the best possible shelf-life of food ingredients and foods. The food polymer science approach emphasized the importance of the glass transition and water plasticization to the food processing and stabilization. The introduction of the polymer science principles to the studies of food materials by Slade & Levine (1991) has been followed by numerous investigations of the role of glass transitions in the control of mechanical properties and mobility (Roudaut et al. 2004), crystallization (Roos & Karel 1992, Jouppila & Roos 1997, Hartel 2001, Ronda & Roos 2008), collapse (Roos & Karel 1991c), and diffusion and reaction kinetics (Shimada et al. 1991, Acevedo et al. 2008).

Flow Properties of Powders

Free-flowing properties are crucial in powder production and handling. Numerous studies have investigated factors affecting stickiness and glass transition of dehydrated materials (Roos & Karel 1991c) and caking properties of powders above the glass transition (Chuy & Labuza 1994). Roos & Karel (1991c) suggested that stickiness of amorphous powders was likely to take place approximately 20°C above the onset temperature of glass transition (**Figure 9**). This suggestion has been confirmed by several studies (Boonyai et al. 2004). Downton et al. (1982) considered stickiness as a surface phenomenon that was affected by viscosity and contact time. Stickiness properties in dairy powders have been studied extensively as spray drying and storage of powders may significantly be affected by changes in flow characteristics (Paterson et al. 2005). Stickiness is often affected by the carbohydrate components of food powders. In dairy systems, lactose vitrifies in spray drying if the water content is decreased to sufficiently low levels. The water content must be lower than that at which the glass transition occurs at the observation temperature to maintain solid properties of the material. This is described in **Figure 11**. Silalai et al. (2009) measured glass transition, dielectric, dynamic-mechanical, and stickiness properties of dairy powders at various protein and maltodextrin contents. The results confirmed their sensitivity to stickiness at increasing water contents. However, it seemed that differences in flow behavior occurred also as a result of composition although in general, stickiness occurred when the glass transition temperature of lactose was lower than the observation temperature. It seems that more studies are needed to establish effects of carbohydrates, proteins, their molecular weight, and water content on the glass transition, particle flow, and stickiness of powders.

Crystalization and Recrystallization Phenomena

Amorphous materials exhibit a strong driving force for a change from the nonequilibrium state to the equlibrium crystalline state. This change in state may occur when molecules of the noncrystalline material gain translational mobility around and above the glass transition (**Figure 4** and **Figure 11**). Slade & Levine (1991) suggested that rates of nucleation and crystal growth were differently affected by the glass transition. Crystallization is a dramatic change in amorphous materials resulting in a complete change of physicochemical properties (**Figure 12**). Crystallization of amorphous lactose is typical of dairy powders at high storage humidities or temperatures (Roos & Karel 1992). It may be observed from changes in water content or water activity taking place in water sorption studies (Roos 1995). Roos & Karel (1992) showed that lactose crystallization was time-dependent above the glass transition. Jouppila et al. (1997) showed further that a maximum crystallization occurred at an intermediate water activity of 0.7 a_w, suggesting that the rate of crystallization decreased as conditions for possible dissolution of lactose were approached.

Another crystallizing food component is starch, which is known to exist as a partially crystalline polymer showing crystallinity in its amylopectin and amylose components (Jouppila & Roos 1997). Amylose forms strong crystals that are difficult to dissolve in water even at high temperatures. Amylopectin is a branched glucose polymer that shows slow crystallization in bread and starch pastes. Melting of the amylopectin crystals occurs in gelatinization of starch. This occurs partially

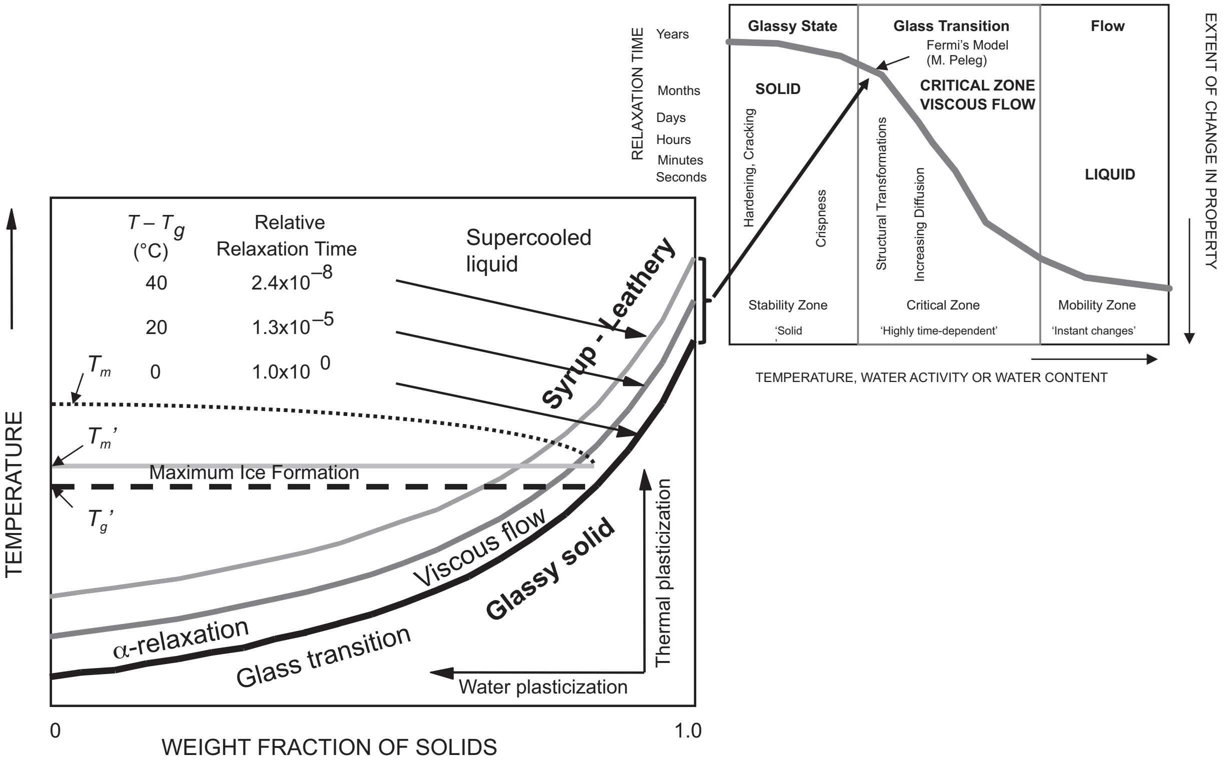

Figure 11

State diagram with zones for decreasing relaxation times above the glass transition at various water contents and temperatures according to the Williams-Landel-Ferry relationship. The relaxation times around the glass transition decrease as a result of thermal or water plasticization, which may also be described by the Fermi's Model.

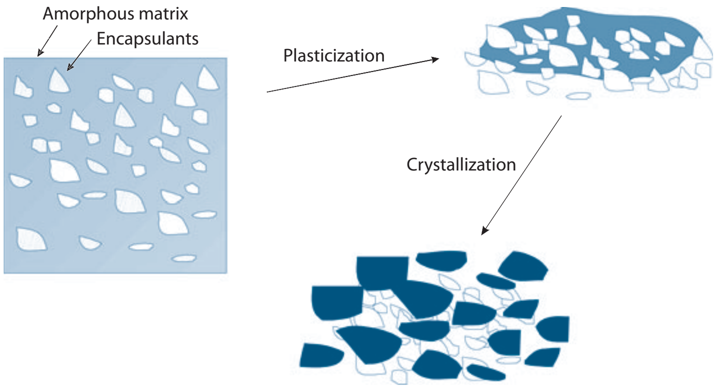

Figure 12

Crystallization of amorphous food materials with encapsulated components. Plasticization of solids (encapsulants) by temperature or water to exceed the glass transition results in viscous flow and loss of structure with some loss of encapsulated components. Crystallization of the amorphous components, e.g., lactose in dairy systems, leads to complete separation of the crystalline material from encapsulated components and possible other solids.

at intermediate water contents at temperatures below 100°C, e.g., in bread crumb during baking. In cooling and storage of bread, recrystallization of amylopectin is enhanced, showing a very favorable T-T_g for recrystallization at refrigeration temperatures (Jouppila & Roos 1997, Ronda & Roos 2008).

Reaction Kinetics and Glass Transition

The introduction of WLF kinetics in the food science areas suggested that reaction rates, such as nonenzymatic browning, enzymatic reactions, and oxidation, at temperatures above the glass transition of a food matrix may increase according to the WLF relationship (Slade & Levine 1991). Karmas et al. (1992) suggested that several foods at high solids contents showed increasing nonenzymatic browning reaction rates with increasing water contents or temperatures. It was suggested that reactions had low rates below the T_g and a change in the activation energy occurred around the T_g. At temperatures above the T_g, reaction rates became more temperature dependent than below the T_g. Several studies, however, have suggested that the reaction rates in food systems are affected by a number of factors, including the glass transition (LeMeste et al. 2002, Acevedo et al. 2008). These include temperature and water content, the nature of the reaction, and the type of food systems, i.e., low- or intermediate water or frozen foods, as reviewed by Roos (1995) and Le Meste et al. (2002). The effects of glass transition on reaction kinetics in food processing have not been well established, but it seems that food storage below glass transition often improves shelf life as diffusional limitations decrease reaction rates in glassy food systems during storage.

CONCLUSIONS

Food stabilization by the control of the physical state of food solids and their water plasticization is achieved in several food processes. These include the control of structure formation in confectionary with high sugar contents or in various baked products. Food dehydration results in a high level of noncrystalline solids in the dehydrated structures. The formation of a glassy state of the solids is necessary in dehydration by spray drying and in the prefreezing step of the freeze-drying process. The glassy state of food solids can maintain free-flowing properties in amorphous food powders. Freeze drying and stability of freeze-dried foods require the solid state of solids to reduce flow and collapse. Food extrusion requires controlled plasticization of low water solids and vitrification of the extruded solids at the end of the extrusion process. Agglomeration of food powders is often achieved by the control of flow properties and stickiness of the noncrystalline solids. Noncrystalline solids in foods often entrap dispersed components and volatiles, which may be lost as a result of changes in food structure. The glassy state contributes to diffusion of various components in food structures, and the glass transition is often a critical parameter for stability of low water and frozen foods during storage. Changes in food structure and component crystallization may result from the glass transition, whereas rates of chemical and enzymatic reactions in low water and frozen foods may depend on various other factors, including temperature and water content. Food processing has greatly benefited from understanding of glass transitions of food components and their impact on food characteristics, but variations in glass-forming properties, food composition, and structural heterogeneities are important factors to be addressed in future studies.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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**Annual Review
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Contents

A Promise Kept
W. James Harper 1

Whole Grains: Benefits and Challenges
Julie Miller Jones and Jodi Engleson 19

Water-Solids Interactions: Deliquescence
Lisa J. Mauer and Lynne S. Taylor 41

Food Formats for Effective Delivery of Probiotics
Mary Ellen Sanders and Maria L. Marco 65

Fate of Starch in Food Processing: From Raw Materials to Final Food Products
Jan A. Delcour, Charlotte Bruneel, Liesbeth J. Derde, Sara V. Gomand, Bram Pareyt, Joke A. Putseys, Edith Wilderjans, and Lieve Lamberts 87

Crosslinking Food Proteins for Improved Functionality
Johanna Buchert, Dilek Ercili Cura, Hairan Ma, Chiara Gasparetti, Evanthia Monogioudi, Greta Faccio, Maija Mattinen, Harry Boer, Riitta Partanen, Emilia Selinheimo, Raija Lantto, and Kristiina Kruus 113

Genetics of Yeast Impacting Wine Quality
Linda F. Bisson and Jonathan E. Karpel 139

Anthocyanins: Natural Colorants with Health-Promoting Properties
Jian He and M. Monica Giusti 163

An Update on the Health Effects of Tomato Lycopene
Erica N. Story, Rachel E. Kopec, Steven J. Schwartz, and G. Keith Harris 189

Food Powders Flowability Characterization: Theory, Methods, and Applications
Pablo Juliano and Gustavo V. Barbosa-Cánovas 211

Emulsion Design to Improve the Delivery of Functional Lipophilic Components
David Julian McClements 241

Biochemistry and Genetics of Starch Synthesis
Peter L. Keeling and Alan M. Myers 271

Functional Oligosaccharides: Application and Manufacture
R.A. Rastall 305

Food Safety: What Can We Learn From Genomics?
Máire Begley and Colin Hill 341

Mechanisms of Microbial Hydrogen Disposal in the Human Colon and Implications for Health and Disease
Noriko Nakamura, Henry C. Lin, Christopher S. McSweeney, Roderick I. Mackie, and H. Rex Gaskins 363

Genomic Evolution of Domesticated Microorganisms
Grace L. Douglas and Todd R. Klaenhammer 397

Edible Packaging Materials
Theeranun Janjarasskul and John M. Krochta 415

Phage and Their Lysins as Biocontrol Agents for Food Safety Applications
Brid Coffey, Susan Mills, Aidan Coffey, Olivia McAuliffe, and R. Paul Ross 449

Glass Transition Temperature and Its Relevance in Food Processing
Yrjö H. Roos 469

Functional Genomics for Food Fermentation Processes
E.J. Smid and J. Hugenholtz 497

Errata

An online log of corrections to *Annual Review of Food Science and Technology* articles may be found at http://food.annualreviews.org