

**A REVIEW OF METHODS, DATA AND APPLICATIONS OF STATE  
DIAGRAMS OF FOOD SYSTEMS**

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## **Abstract**

Understanding of the amorphous glassy state of food systems is often crucial in determining physicochemical characteristics and predicting stability of dehydrated and frozen foods. At the glass transition temperature ( $T_g$ ) of food components, transformation from the amorphous glassy state to the liquid like rubbery state occurs.  $T_g$  and ice melting temperatures ( $T_m$ ) of food systems are used to construct their state diagrams, in which the different physical states/phases and state/phase transitions of food components are presented in relation to temperature and concentration. A state diagram may be used to identify the appropriate processing and storage conditions of food systems. An overview of determination methods is carried out for glass transition temperature, ice melting temperature and conditions of maximum-freeze-concentration (glass transition temperature of maximum-freeze-concentrated solution,  $T_g'$  and onset of ice melting temperature,  $T_m'$ ) for food systems. The data as  $T_g$ ,  $T_m$ ,  $T_g'$  and  $T_m'$  are necessary for construction of state diagrams of foods. The advantages and limitations of the determination methods are discussed. Combined data for glass transition temperature, ice melting temperature and conditions of maximum-freeze concentration for selected food systems are presented in this study. The effect of food composition on glass line, freezing/melting curve, and maximum-freeze-concentration conditions is evaluated. The significance of the state diagrams in predicting the physical, chemical and microbial stability in foods is briefly examined. Glass transition concept and state diagrams are useful for describing the physical and structural stability of food systems at specific conditions, yet they are not considered as the only determining factors of chemical, biochemical and microbial stability of food systems.

**Key words:** Food stability, glass transition temperature, ice melting temperature, maximum-freeze-concentration, relaxation behavior, spectroscopic methods, unfrozen water, water activity

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## **Introduction**

The amorphous state of materials is a solid state, characterized by a short-range molecular order, whereas a crystalline state has a long-range molecular order. Many food processing techniques result in the partial or full development of an amorphous structure, caused by super-cooling of melt, mechanical creation such as milling, dehydration, or vapor condensation (Hancock and Zografi 1997). The most common food processing techniques that alter physical and molecular structures in foods include drying such as spray-drying, hot air-drying and freeze-drying; grinding, extrusion and rapid freezing. Components of many processed foods such as milk powder, instant coffee, infant formula, biscuits and cookies, extruded cereals, pasta, beverage mixes and culinary food powders exist in an amorphous state.

Over the years, rigorous scientific investigations have advanced our understanding of the amorphous nature of food biopolymers and state transitions (e.g., glass transitions). Glasses are often formed by progressive moisture removal, or when a liquid or a rubbery system is cooled rapidly with little or no time for the molecules to rearrange and pack into crystalline domains (Hutchinson 1995). Glassy amorphous solids have a high viscosity range ( $10^{12}$ - $10^{14}$  Pas), brittleness, high strength, short-range order and little molecular mobility (Rahman 1995). In the amorphous glassy state, long range cooperative motions are restricted, but vibrations and reorientation of small groups of atoms continue to occur (Le Meste et al. 2002). The temperature range where a reversible transformation from a brittle glassy state to a rubbery state occurs in an amorphous component is identified as glass transition temperature ( $T_g$ ). In the glass transition region, there is no discontinuity among primary thermodynamic properties such as volume, enthalpy, and free energy. However, the first derivatives of these thermodynamic properties undergo marked changes in the course of a small temperature range. Discontinuity in the coefficient of thermal expansion and specific heat at the crystallization temperature is often not detected during vitrification (Kasapis 2008). The glassy to rubbery state transition occurs over a temperature range without a first-order phase change, while it exhibits the characteristics of a second-order thermodynamic transition. The molecular mobility of a food system decreases as food solids transform from a rubbery state to a glassy state during cooling and/or removal of a plasticizer. The physical state and state/phase transitions of amorphous components of food biopolymers are integral to the characterization of molecular stability

during processing and storage. State diagrams are used to map the physical states during state/phase transitions in amorphous food components as a function of temperature and solid or water content. Scientific understanding of glass transition phenomena in materials has progressed significantly in the last 80 years. White and Cakebread (1966) first highlighted how glassy behavior in foods affects stability. Since then, many studies have explored the application of the glass transition concept to the description of food properties and various kinetic phenomena, including Slade and Levine (1988b; 1991), Karel et al. (1994), Roos (1995), Roos and Karel (1991a; 1991b), Blanshard (1995), Kalichevsky et al. (1992), Kokini et al. (1994; 1995), and Simatos et al. (1989; 1996). Glass transition involves rapid changes in the physical, mechanical, electrical, and thermal properties of foods. Calorimetric studies for the characterization of state transitions dominate the food literature (Roos 1995a; Rahman 2006). Mechanical methods including dynamic mechanical thermal analysis, thermo-mechanical analysis, and rheological techniques for the study of glass transition in food are increasingly more sensitive, but their applications to use with foods are limited. Kalichevsky et al. (1992) and Kasapis et al. (2000) investigated the use of mechanical spectroscopy for the study of glass transition in food biopolymers. Their studies used dynamic mechanical loss determinations and dielectric loss determinations to probe the time scales of molecular motion in the region of glass transition. These relaxation studies apply a sinusoidal external field and response of the material to the external field. In a mechanical experiment, the response is an oscillating stress or strain, while in dielectric studies, an oscillating electric field is determined as a function of the frequency of the applied field. The use of advanced spectroscopic methods, such as nuclear magnetic resonance (NMR) and electron spin resonance (EPR) have also been explored (Ablett 1992; Kalichevsky et al. 1992, 1993; Ruan et al. 1999; Rolee and Le Meste 1999; Buitink et al. 2000). The relaxation methods are introduced in which the decay in response to an applied pulse instead of a continuous sinusoidal wave is monitored. Data is then converted to a continuous wave format with Fourier transforms. This technique is used to determine  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic relaxation. Pulse sequences allow determination of the spin-lattice relaxation time of the system at the nuclear magnetic resonance frequency. Since this technique observes the rate of dissipation of nuclear spin energy into the molecular lattice, results are comparable with high frequency dielectric or mechanical determinations (Allen 1993).

In low and intermediate moisture food systems, water activity ( $a_w$ ) is traditionally used as a predictive tool for microbial, chemical and physical changes (Rahman and Labuza 1999, Maltini et al. 2003). However, the state of water and solids in foods, kinetic changes and the physico-chemical stability of intermediate moisture food polymers in a non-equilibrium state may be better explained with the glass transition concept (Franks, 1991; Slade and Levine, 1991; Roos 1995a; Roos 1995b). Studies of the relationship between glass transition, water content and food properties are advancing our understanding of physical changes (Roos and Karel 1991a; Kalichevsky et al. 1992; Karathanos et al. 1993; Aguilera et al. 1995; Peleg 1996; Bhandari and Howes 1999; Shrestha et al. 2008) and as well as chemical changes in foods (Shimada et al. 1991; Karmas et al. 1992; Nelson and Labuza 1994; Buera et al. 1995; Bell 1995; Schebor et al. 1996; Drusch et al. 2006; Sablani et al. 2007a).

Freezing increases the stability of foods at subzero temperatures by reducing the availability of the water for chemical, microbial and enzymatic reactions (Goff and Sahagian 1996). The amount of ice crystallized at temperatures below the initial freezing point depends on the temperature of the food system, the concentration of food solids, and the time and temperature history of the food. However, with decreasing temperatures under adequate cooling rates, maximum-freeze-concentration is reached, in which maximum ice crystallization occurs simultaneously with unfrozen water in the food matrix (Li et al. 1998). Maximum-freeze-concentration is characterized by high viscosity. Glass formation may start inside the food matrix at temperatures below  $T_m'$  (onset of ice melting). Type of food constituents and freezing temperature may also play a role in the nature and amount of ice crystallization (Wolfe et al. 2002; Simatos et al. 1989; Blond et al. 1997; Goff et al. 1993). The glass transition temperature corresponding to maximum-freeze-concentration is noted as  $T_g'$ , and the resulting water content from the state diagram is the unfrozen water in the matrix ( $X_w'$ ). This water is freezable and not bound, but remains unfrozen during the practical time frame of observation due to its increased viscosity (Franks, 1986b). Ice crystal growth is restricted due to the reduced translational and rotational motions of molecules. High viscosity rather than any binding force such as the presence of strong chemical bonds (hydrogen bonds) keeps the water from freezing (Franks, 1986b). Larger amounts of unfrozen water are present in foods with smaller effective molecular weight, such as fruits and vegetables. Unfrozen water may influence the physicochemical deteriorative reactions in foods since liquid water is less organized and more unstable than ice (Wolfe et al.

2002). Below  $T_g'$ , the viscosity becomes great enough to reduce rates of chemical reactions (Roos 1995c; Biliaderis et al. 1999). An increase in temperature above the  $T_m'$  may result in ice melting, an increase in the amount of unfrozen water, and reduced viscosity. This reduced viscosity results in an increase in molecular mobility and leads to enhanced rates of diffusion-controlled reactions (Biliaderis et al. 1999; Le Meste and Huang 1992). State diagrams can also be used to study the stability of frozen foods (Reid 1990; Goff 1995; Goff and Sahagian 1996; Brake and Fennema 1999; Bhandari and Howes 2000; Roos 2003; Hansen et al. 2004). For example,  $T_g'$  and  $T_m'$  can be used to predict loss of quality including changes in texture, aroma, caking and stickiness of freeze-dried foods (Roos and Karel 1991a; Roos 1997). A few excellent reviews cover selected aspects of the glass transition concept and state diagrams (Roos 1995a; Champion et al. 2000; Rahman 2006; Kasapis 2008). Our work reviews determination methods and data on glass transition temperatures, ice melting temperature, and conditions of maximum-freeze-concentration of food systems. Our work also explores the importance of state diagrams and how they affect the physical, chemical and microbial stability of foods.

### **State Diagrams**

State diagrams are graphical representations of the physical states of food constituents with respect to the temperature, water or solids content of foods at constant pressure for equilibrium and nonequilibrium systems (Roos 1995c). Figure 1 presents a typical state diagram. State diagrams of materials are similar to phase diagrams presenting physical states, temperature, pressure and volume of foods at equilibrium (Roos 1995c). State diagrams are extended phase diagrams, provide information on equilibrium phases and nonequilibrium states of food systems (Reid and Fennema 2007). State diagrams of food systems may be developed considering them as binary systems consisting of the water and the major solids or total solids present in food systems (Reid and Fennema 2007). State diagrams can be used to observe and predict state changes during processing and storage of fresh, frozen, intermediate moisture or low moisture foods. A dynamic map or dynamic state diagram includes the equilibrium and nonequilibrium thermodynamics of food systems using temperature (Figure 2), with solids content and time as axes (Slade and Levine 1991). The equilibrium regions are not time dependent, and can be represented using a phase diagram where nonequilibrium regions are kinetically dependent and represented using  $t/\tau$  as the third axis, where  $\tau$  is the

relaxation time. The dynamic map of food systems focuses on two aspects such as water dynamics and glass dynamics. Water dynamics deal with the reactivity and mobility of water as a diluent in the rubbery state of a food system. Nonequilibrium amorphous food systems approach equilibrium over extended time periods when they are stored below their glass transition temperature. Glass dynamics describe the time-temperature dependence on selected properties of a glassy food system. More details on glass and water dynamics are presented elsewhere (Slade and Levine 1988b, 1991).

State diagrams of plant and animal-based food systems developed during the last two decades highlight the relevance of state transition in foods during processing and storage. Heat and water are the major plasticizing agents in foods, and affect the physical states and functionalities of foods during processing and storage. Selection of appropriate temperatures and humidity conditions during food processing operations and storage is important for improving the quality and shelf lives of foods. However, since foods are complex mixtures of components with heterogeneous behavior, state diagrams may only partially explain physicochemical changes in food systems. Changes in food properties during processing and storage also depend on other factors including water activity, pH, presence/absence of oxygen, preservatives, antioxidants, and presence/absence of catalysts (Le Meste et al. 2002; Bell 2007; Rahman 2006; Rahman 2009).

### **Components of a State Diagram**

State diagrams present temperature-concentration relationships for both equilibrium and nonequilibrium states and represent selected physical states of foods (Figure 1). A state diagram may include a glass line that characterizes glass transition temperature and the solids content relationship of a polymer mixture, a melting/freezing curve that designates melting/freezing point depression dependent on solids concentration, a solubility curve of solids concentration in saturated aqueous solutions at given temperatures, eutectic temperature, boiling temperature, and maximum-freeze-concentration conditions corresponding to the temperature at the onset of ice melting ( $T_m'$ ), and the glass transition temperature at maximum ice formation conditions ( $T_g'$ ) (Rahman 2006). State diagrams are valuable tools in the characterization of amorphous food systems (Slade and Levine 1991; Roos 1995c). A state diagram can effectively be used to analyze deteriorative reactions in foods and optimize processing conditions for maximum utility (Rahman



2009). State diagrams are often based on equations such as the Gordon-Taylor and Clausius-Clapeyron equations for experimental data.

### **Glass Line**

The influence of water or solids content on glass transition temperature at constant pressure may be presented by plotting the glass line, with temperature as the ordinate and water content or solids content as the abscissa. Unlike the equilibrium lines in a phase diagram, the glass line in a state diagram differentiates the general states of non-equilibrium systems such as a stable glassy state and the metastable rubbery state. The glass line for a food system is dependent on composition, water content, molecular weight of the biopolymers, and degree of polymerization (Tolstoguzov 2000). The  $T_g$  of food solids increases as biopolymer molecular weights, size, rigidity, and cross linkages increase, and decreases as biopolymer chain flexibility increases. Incompatible constituents and heterogeneous complex food systems often lead to the detection of more than one glass transition temperature (Tolstoguzov 2000; Matveev et al. 2000). A small amount of free water can drastically lower the glass transition temperature of dry food solids. The plasticizing ability of water is attributed to its low molecular weight, and to its low glass transition temperature (-135°C), compared to the glass transition temperature and hydrogen bonding capacity of food biopolymers (Tolstoguzov 2000).

### **Glass Transition Theories**

Several theories including free volume, kinetics and thermodynamics attempt explain glass transition phenomena. Recent reviews by Abiad et al. (2009) and Roos (2010) present a detailed discussion of relevant theories. These theories are applied to predict glass transitions of foods and pharmaceuticals with some success (Abiad et al., 2009). A brief description of three major theories of glass transition is presented below.

#### **Free Volume Theory**

Free or unoccupied volume allows segmental mobility in a material, unlike occupied volume. Free volume theory considers a constant free or unoccupied volume is reached in a material at its glass transition temperature, and this free volume remains constant in the glassy state (Fox and Flory, 1950). To pinpoint

the glass transition temperature, the free volume theory was employed in a quantitative fashion to interpret glassy phenomena in terms of molecular processes (Dlubek et al. 2000). According to free volume theory,  $T_g$  is located at the end of a glass transition region, where free volume declines to ~3% of the total volume of a material (Ferry 1980; Ward and Hadley 1993). At this volume, the coefficient of thermal expansion of free volume undergoes a discontinuity, reflecting a change in slope of the linear plot of the total volume as a function of temperature. Conformational rearrangements below  $T_g$  are small in the experimental time frame and attributed to a very small free volume. The Doolittle equation empirically relates free volume to the viscosity of the system. The temperature dependence of viscosity in the glass transition region described by William-Landel-Ferry (WLF) equation may be derived with free volume theory using the Doolittle equation (Gedde 1995). The WLF equation is used to describe changes in relaxation times above the glass transition temperature. The free volume concept is used extensively by material scientists to develop a mechanistic understanding of the rubber to glass transition based on the concept of macromolecular volume. However, free volume theory does not explain the heating/cooling rate dependence on glass transition temperatures or the kinetic nature of glass transition temperatures (Roos 2007).

### **Kinetic Theory**

Kinetic theory assumes that glass transition is a dynamic process. Kinetic theory describes the molecular relaxation time of a selected polymer chain and the time scale of the experiment exhibit an equivalent order of magnitude at the glass transition temperature (Gedde 1995). Glass transition is influenced by the heating or cooling rate during the experiment. Glass transition is observed at a lower temperature when slow heating rates are used. Slow heating rates are associated with long experimental time scales, wherein conformational rearrangements occur (Abiad et al. 2009). Kinetic theory explains heat capacity change greater than and less than glass transition temperatures and change in  $T_g$  with heating/cooling rates (Roos 2007).

### **Thermodynamic Theory**

Thermodynamic theory assumes that glass transition as a second order phase transition, and that equilibrium properties of glass transitions are achieved at infinite experimental time frames. According to this theory, a true equilibrium thermodynamic transition is reached when the conformational entropy of the system becomes zero at a temperature 50°C below the experimentally determined  $T_g$  (Gibbs and DiMarzio 1958; Gedde 1995). Thermodynamic theory explains changes in  $T_g$  dependent on plasticizer content, molecular weight and cross link density (Roos 2007).

### **Characterizing Glass Transition**

Glass transition is a change in state associated with a considerable change in molecular mobility and relaxation time in amorphous food solids. Properties of a food system are dramatically changed as the food system transforms from a glassy state to a rubbery state. Determination of the glass transition temperature is based on observation of changes in thermal, mechanical, dielectric, and volumetric properties and molecular mobility over the glass transition temperature range. In food biopolymers, free volume, specific heat, specific volume, or the thermal expansion coefficient increase, while the elastic modulus and viscosity decrease during this transition. The glass transition temperature of food systems is dependent on the method of observation and is not always well defined. Each analytical technique probes material properties at a selected distance scale to analyze glass transition. Glass transition temperature is also affected by the heating or cooling rate, the applied frequency of oscillation and the sample history. The most common techniques such as differential scanning calorimetry and mechanical spectroscopy provide an indication of a transition at a macroscopic level, while nuclear magnetic resonance and electron spin resonance provide information on the molecular mobility in selected phases and microstructural locations. Determination of glass transition temperature for food products is further complicated because of their chemical and microstructural complexity. Glass transitions often occur over a large temperature range due to a broad distribution of relaxation times and/or to unresolved transitions corresponding to different components (Le Maste et al. 2002). The glass transition temperature is taken as the onset temperature of the glass transition temperature range (onset  $T_g$ ) or as a temperature corresponding to a 50% change in heat capacity occurring over the transition (midpoint  $T_g$ ) in a differential scanning calorimetric determination. The temperature range of glass transitions, the changes around glass transitions, and material properties at temperatures

greater than the glass transition temperature are all highly dependent on food composition and molecular weights of the components. Small molecular weight components (for example, water and simple sugars), provide a glass transition over a relatively narrow temperature range (10-20°C), whereas large molecular weight food components such as proteins and starch exhibit glass transition over a broad temperature range (as large as 50°C) (Roos 1995c). Most foods are multiphasic systems, and therefore do not exhibit global glass transitions. Glass transitions are properties of food components and affected by component interactions. Distinct transitions associated with selected phases are observed with multi-component mixtures. For instance, Mousia et al. (2000) observed distinct  $\tan \delta$  peaks in the DMTA analysis of a mixture of gelatin, amylopectin and water with selected gelatin/amylopectin ratios indicating the presence of two phases. The degree of hydration of each food component differs depending on the thermodynamic compatibility of the component with water. Unlike homogeneous single phase systems, multicomponent systems are heterogeneous, so that unequal water distribution depends on food components (Mousia et al. 2000). Considering the physicochemical stability of multiphasic systems, lower glass transition temperatures may describe a critical limit.

Glass transition characterization methods may be classified as thermal (differential scanning calorimetry [DSC] and modulated differential scanning calorimetry [MDSC]), mechanical (dynamic mechanical thermal analysis [DMTA]), rheological determinations and thermal mechanical analysis [TMA]), dielectric (dielectric thermal analysis [DEA]), and spectroscopic (nuclear magnetic resonance [NMR]), and electron spin resonance spectroscopy [ESR]) based on the properties determined (Roos 2009). DSC traces vitrification processes by providing a direct, continuous determination of a material heat capacity, while mechanical spectroscopy probes the relaxation behavior of synthetic and biopolymers over a large temperature range and frequency scale. The mechanical loss of a material results from conformational changes leading to a phase shift between stress and strain during periodic excitation and a damping of a free vibration sample. The phase shift increases as damping increases. Damping reaches its maximum when the period of molecular motion approaches the time scale of the experiment. These mechanical loss peaks are used to pinpoint different relaxation processes (Wu and Zhu 2009). Spectroscopic techniques such as NMR and EPR monitor the motional properties of molecules by detecting the relaxation characteristics of the active nuclei and the spin probe dissolved in the sample. Spectroscopic

techniques are also used to characterize glass transition in biopolymers. Glass transition and relaxation determination methods are reviewed extensively in recent review articles by Abiad et al. (2009) and Roos (2010).

### **Differential Scanning Calorimetry (DSC)**

DSC is the most extensively used technique for thermal transition analysis of food systems because of its unique characteristics and simplicity. DSC determines the enthalpy and temperature changes between a sample and reference during the phase and state transitions. Information on transition temperatures, enthalpy of melting/freezing, specific heat and latent heat are obtained from DSC temperature scanning of food systems (Rahman 1995). Gelatinization of starch, phase transitions, crystallization or melting of polysaccharides and lipids, and the quantity of unfrozen water may be determined by using a differential scanning calorimeter. Quality assurance, adulteration of food materials and freezing-induced denaturation of food proteins may also be studied with DSC (Farkas and Mohacsi-Farkas 1996).

Thermal transition experiments of low and high-moisture foods are conducted with a differential scanning calorimeter after calibrating the calorimeter with selected standards. An empty, sealed aluminum pan is used as a reference in each experiment. A common procedure for DSC determinations involve a thermal scan of a small quantity (~10 mg) of food over a selected temperature range, dependent upon the food composition and water content. Glass transition temperature is kinetically governed and the rate of the thermal scan of the food influences the  $T_g$ . Scan rates of 5 and 10°C/min are commonly used for determination of glass transition temperatures. A typical DSC thermogram is presented in Figure 3a. The glass transition temperature ( $T_g$ ) is identified as the step transition in the heat flow curve of the DSC thermogram, presenting the variation in heat flow with temperature. The midpoint of step transition is generally determined for  $T_g$ ; however, most recent studies reported temperatures (onset,  $T_{gi}$ ; midpoint,  $T_{gm}$ ; and end point,  $T_{ge}$ ) of glassy to rubbery state transitions. The onset glass transition temperature may be suitable for predicting food storage stability and shelf life. High moisture foods are annealed to identify clear and accurate glass transition temperature ranges, achieve maximum-freeze-concentration conditions, and avoid exothermic crystallization peaks (Rahman 2004). A nearly complete state diagram of food systems can be constructed by plotting the glass line and melting curve using DSC results. The state diagrams of most food systems published in the literature were developed using DSC. The DSC provides

direct determinations of enthalpy change during phase transitions (Farkas and Mohacsi-Farkas 1996). The plasticization effects of water and interactions with food components may be studied by fitting Gordon-Taylor model with the glass transition temperature-water content data (Roos 1995c).

The advantages of using DSC include convenient preparation, rapid analysis, applicability to low and high-moisture foods, and a broad range of temperatures (Farkas and Mohacsi-Farkas 1996). Characterizing the  $T_g$  of the individual components of food systems is relatively difficult with the DSC. Glass transition temperatures of complex food systems determined with DSC may not be accurate, although the concentrations of individual components may determine the  $T_g$  of the food system. The DSC may not provide precise specific heat transitions for foods containing food components of large molecular weight, such as starches or proteins. DSC determination of  $T_g$  is most suitable for sugar-rich foods of small molecular weight (Roos 1995c; Sablani et al. 2007c; Rahman et al. 2007). The kinetics of thermal transitions depends on the heating rates selected for DSC analysis, because of the thermal lag associated with the heating rates (Farkas and Mohacsi-Farkas 1996; Simatos et al. 1996). Foods in the DSC are more uniformly heated when slower scan rates are applied, resulting in a small temperature lag during the analysis. A higher  $T_g$  is observed when rapid heating rates are used. Finally, DSC analysis may not be sufficiently sensitive to recognize weak glass transitions (Farkas and Mohacsi-Farkas 1996). Optimizing conditions for DSC determinations is necessary to provide accurate  $T_g$  results.

### **Modulated Differential Scanning Calorimetry (MDSC)**

Modulated differential scanning calorimetry (MDSC) is an extension of conventional DSC and a very useful method for thermal characterization of heterogeneous food biopolymer systems. Modulated DSC is more sensitive in the detection of glass transition temperatures than conventional DSC, due to the rapid heating rate produced by sine wave modulations (Lai and Lii 1999). Sinusoidal oscillations in heating and cooling rates produce sample temperatures that change with time in a nonlinear fashion (Modulated DSC™ Compendium). The underlying principle of MDSC is that sine wave modulations deconvolute the total heat flow to reversible heat flow events related to heat capacity, and non-reversible heat flow signals related to irreversible events during heating (Coleman and Craig 1996). Heat capacity evaluation of foods is relatively easy and rapid with MDSC. Thermal transition experiments are conducted after calibrating the

modulated differential scanning calorimeter with standard temperatures and enthalpies of fusion for indium and sapphire, as in conventional DSC. The experimental protocol involves thermal scanning of a food over a selected temperature range similar to DSC experiments. In addition, modulation temperature amplitude and modulation periods are specified. Total heat flow is made up of two components: a thermodynamic component (reversing heat flow signal in MDSC) that involves the heat capacity and rate of temperature change in a material, and a kinetic component (non-reversing heat flow signal in MDSC) that involves the temperature of the material and time (Modulated DSC™ Compendium). The MDSC is useful for separating complex thermal events such as thermodynamic and kinetic relaxations. The heat capacity of the material can be calculated using heat flow amplitude, temperature amplitude, and modulation period. Reversible heat flow is the product of heat capacity and average heating rate (Modulated DSC™ Compendium). The average modulated heat flow obtained with MDSC is taken as the total heat flow. The nonreversing heat flow is the difference of total and reversing heat flows (Modulated DSC™ Compendium). With the reversing heat flow, transitions with step change in the heat capacity, thermodynamic characteristics such as melting, and glass transitions are analyzed, and with non-reversing heat flow, kinetic characteristics such as molecular relaxations, crystallization and decomposition are identified (Figure 3b) (Cuq and Lcard-Verniere 2001). The glass transition and melting temperatures of a material are determined using the reversing heat flow curve plotted against change in temperature. Various operational parameters such as heating and cooling rates, modulation period, and modulation amplitude influence the observed transitions in MDSC. Like DSC, the rate of thermal scanning may significantly affect the glass transition temperatures determined from MDSC thermograms. The amplitude of modulation temperature and modulation period may also influence the determination of glass transition temperatures. Advantages of MDSC include better detection of glass transition temperature in high moisture foods, increased sensitivity to observe weak transitions, simplification of overlapping complex transitions, and increased resolution (Modulated DSC™ Compendium). Limited studies relate the use of MDSC for determination of glass transition temperatures in food systems, since MDSC is a relatively new technique.

#### **Dynamic Mechanical Thermal Analysis (DMTA)**

At temperatures near to or greater than the glass transition temperature, the solid state is transformed to a supercooled liquid state with rapid time-dependent flow. In DMTA, sinusoidal oscillatory strain or stress

input is applied in foods and the resulting stress or strain is determined (Chartoff et al. 1995; Abiad et al. 2009). DMTA describes the viscoelastic characteristics of food materials by determining the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and mechanical loss factor ( $\tan \delta = E''/E'$ ) with the frequency of oscillating deformation as a function of temperature during state transitions of foods.  $E'$  and  $E''$  are the ratio of in-phase and out-of-phase stress to the corresponding applied strains (Chartoff et al. 1995).  $E'$  is also related to recoverable elastic energy stored in the material, while  $E''$  is related to deformation energy dissipated as heat of friction (de Graaf et al. 2003). The temperature range encompassing a sudden decrease in storage modulus ( $E'$ ), a maximum of  $E''$ , or  $\tan \delta$  is identified as the glass transition temperature (Chartoff et al. 1995). The onset glass transition temperature is identified as the temperature where tangents from glassy and transition regions meet in the storage modulus curve, or the temperature where the maximum  $E''$  is observed (Chartoff et al. 1995). Various determination geometries with selected modes of operations such as tension, compression, shear, or bending are available for the determination of viscoelastic properties of food materials (Chartoff et al. 1995). In the case of parallel plate geometry, food systems are placed onto the plates and coated with a silicone grease to reduce water loss. The foods are heated in the selected temperature range at fixed strain sweeps (0.05%) and at selected frequencies ranging from 0.001 to 200 Hz with a dynamic mechanical thermal analyzer (DMTA) (Kalichevsky et al. 1992, 1993; Nikolaidis and Labuza 1996). The viscoelastic properties of food powders are characterized using a powder cell in DMTA (Abiad et al. 2009).  $E'$  and  $E''$  are components of tensile elasticity, determined when axial forces are applied. A decrease in  $E'$  and a maximum in  $E''$  as well as  $\tan \delta$  of polymers are observed at the temperature corresponding to  $\alpha$  relaxations (Champion et al. 2000) (Figure 4). A suitable frequency must be selected to insure that a DMTA peak coincides with the glass transition temperature (Blanshard 1995). At greater frequencies, higher glass transition temperatures are identified, since glass transition is a relaxation transition (Chartoff et al. 1995). DMTA is more sensitive than the calorimetric method for detection of glass transition temperatures, particularly for complex food biopolymers, semicrystalline and cross-linked polymers where the change in heat capacity is small (Chartoff et al. 1995). However, additional sample preparation for dynamic mechanical thermal analysis limits its applicability. For instance, food powders are melt-mixed by adding water and heated to a specific temperature and dried in molds before being subjected to analysis (Forssell et al. 1997). Samples of required dimensions are prepared



for DMTA. Also, tablets are commonly prepared for DMTA by pressing at high pressures (Abiad et al. 2009). Large quantities of low-moisture solid materials are generally selected for DMTA analysis. Use of DMTA in sub-ambient temperature ranges may be challenging, due to potential condensation (Chartoff et al. 1995). Also, the temperature associated with the  $\tan \delta$  peak in DMTA may be higher than the glass transition temperature observed in calorimetry, due to water loss during sample preparation and heating (Rahman et al. 2007). Also, high  $T_g$  may be attributed to slow heating rates (5-10°C) used in calorimetry, comparable to static heating (Rahman et al. 2007; Di Gioia et al. 1999).

### **Rheological Determinations**

Rheology is used extensively by Kasapis and coworkers (Kasapis et al. 2000; Kasapis 2004, 2008; Kasapis and Sablani 2005) to characterize glassy behavior of food systems. The procedure involves time-temperature superposition of mechanical spectra (shear storage modulus  $G'$  and shear loss modulus  $G''$ ) obtained from rheological determinations, as well as calculating the data with the Williams-Landel-Ferry (WLF) equation based on free volume theory and the Arrhenius equation to identify glass transition temperature (Kasapis and Sablani 2005). Rheological determinations provide the shear storage modulus ( $G'$ ), which makes up the elastic component of the network, the shear loss modulus ( $G''$ ), which makes up the viscous component, and the dynamic viscosity ( $\eta^*$ ). They are performed using a controlled strain rheometer. A small quantity (10-12 g) of food is loaded on a circular plate and coated with a silicone fluid to minimize water loss during experiments. The food is cooled below its expected  $T_g$  and scanned at 1°C/min to a temperature higher than its  $T_g$ . The isothermal mechanical spectra are obtained at selected temperature intervals (~3°C) between 0.1 and 100 rad/s. In these experiments, the applied strain on shear may vary from 0.0005% in the glassy state to 1% in the rubbery plateau to accommodate large changes in food stiffness. A strain sweep is performed to confirm that the small deformation analysis is carried within the linear viscoelastic region.

Figure 5a presents thermal profiles of  $G'$ ,  $G''$  and  $\tan \delta$  for a biopolymer matrix containing 5% gelatin, 25% sucrose and 50% glucose syrup. Area I represents the glassy state with a dominant elastic component ( $G'$ ) greater than the viscous component ( $G''$ ), with values of  $G'$  greater than  $10^9$  Pa. Area II represents the glass transition state, and the dominant loss modulus or viscous component ( $G''$ ) occurs with heat loss.

Area III represents the rubbery state with value of  $\tan \delta$  less than one (Kasapis and Sablani 2005). Mechanical spectra (frequency vs.  $G'$  and  $G''$ ) are combined to produce a master curve of reduced frequency (frequency x shift factor) versus the superpose of shear modulus ( $G'$  and  $G''$ ) (Kasapis and Sablani 2005). A computerized calculation minimizing a multiple regression correlation coefficient is used to shift mechanical spectra and produce a master curve for viscoelasticity. The shift factor is plotted against the temperature. The portion of the temperature dependent on the shift factor (glass transition state) is modeled using the WLF equation, while another portion (glassy state) is fitted to the Arrhenius equation (Figure 5b). According to free volume theory,  $T_g$  is located at the end of the glass transition state, where the free volume declines to insignificant volumes (~3% of the total volume of the material). Rheological determinations may provide  $T_g$  and demarcate the onset of the glassy state from the glass transition region. In the glass transition region, transverse string-like vibrations of polymeric chains diminish with reduced temperature, whereas in the glassy state (or temperatures less than  $T_g$ ), relaxation processes are heavily controlled by specific chemical features (Kasapis 2004).

The mechanical transitions in several food systems, such as dried fish proteins and fruit carbohydrates, are difficult to determine (Rahman et al. 2003; Kasapis 2004; Sablani et al. 2004; Sablani and Kasapis 2006). To circumvent the problem of a decreased glass transition temperature in dehydrated foods, another approach was suggested to assess the temperature dependence of state changes (Rahman et al. 2003; Kasapis 2004; Sablani et al. 2004; Sablani and Kasapis 2006). Kasapis (2004) observed that for gelatin and sugar mixtures, the  $T_g$  obtained with the time-temperature superposition principle coincides with the minimum of the storage modulus. A procedure was therefore recommended in which a plot of the first derivative of  $\log G'$  as a function of sample temperature is prepared and the minimum of the storage modulus is defined as the mechanical glass transition temperature (Figure 5b). Mechanical transition procedures are used to determine glass transition temperatures in dehydrated fish and fruits (Kasapis 2004).

### **Thermo Mechanical Analysis (TMA)**

Softening or loss of mechanical rigidity of low-moisture solids during state transitions of food systems may be determined by a thermo mechanical analyzer (TMA). TMA is a simple and relatively inexpensive methodology. In TMA, changes in physical dimensions (volume, length) of the foods under non-oscillatory

stress are recorded as a function of temperature and time during temperature scanning (Roos 1995c; Abiad et al. 2009; Earnest 1994). Selected geometries and modes of operation such as compression, tension, flexure or torsion are possible with TMA (Abiad et al. 2009; Earnest 1994). To observe consistent dimensions, parallel geometry of the food systems is used (Goff et al. 1993). A dilatometer is placed in the sample holder of the thermomechanical analyzer and compression or expansion mode with selected force (normally 20-50 mN for penetration mode) is maintained for 5 min at room temperature before heating. Food systems are heated over a selected temperature range at a rate of 5°C/min and the change in the volume/length of the sample is determined by using an expansion probe during heating (Earnest 1994). Thermograms presenting the glassy and rubbery regions in the materials are analyzed and  $T_g$  is assigned as the temperature at the intersection of the tangent lines along the glassy and rubbery regions (Perdon et al. 2000). TMA provides greater sensitivity than DSC in recognizing state transitions of amorphous and semicrystalline food components. Disadvantages of TMA include water loss during sample preparation and heating, difficulty in controlling the heating and cooling rates, and inaccuracy in assigning glass transition temperatures in porous foods (Farhat, 2004).

A simple thermal mechanical compression test (TMCT) technique consisting of a thermally controlled sample cell attached to a texture analyzer is developed for the characterization of glass transition for food powders (Boonyai et al. 2006; Boonyai et al. 2007). Glass transition characterization is carried out in a thermally controlled cell using a thermal compression test in creep mode, where food is subjected to a constant compression force while it is heated, and the probe displacement is determined as a function of temperature. At the glass to rubber transition, a sudden increase in displacement is observed. The glass transition temperature is determined using the slope of linear regression line greater than the transition and a displacement value less than the transition in the displacement-temperature diagram during heating (Figure 6). In figure 6, to determine  $T_g$ , the mean value of displacement is taken from points 1 to 2 below transition and the linear regression equation of the data points above transition (from 3 to 4). The TMCT method was tested with the standard DSC, DMTA/TMA techniques, using skim milk powder adjusted to water contents in the range of 2-5% (kg water/kg dry solids). The method was found to be accurate and sensitive for the determination of the glass transition temperatures in selected food powders (Boonyai et al. 2006; Boonyai et al. 2007). The TMCT method provides glass transition temperatures for foods with  $T_g$

greater than ambient temperatures. The TMCT method must be validated with a wide range of powders such as modified proteins and starches.

### **Dielectric Thermal Analysis (DEA or DETA)**

The DEA/DETA method determines the relaxation behavior of a food system as it is subjected to a temperature scan over a selected polarizing frequency range (Laaksonen and Roos 2000; Abiad et al., 2009). The dielectric cell used in DEA/DETA varies dependent on the application and material of interest (Vassilikou-Dova and Kalogeras 2009). Experiments are performed with a dielectric analyzer. A typical geometry of DEA is the parallel plate electrode system. Expansion and contraction of a food system during heating and cooling are the associated problems of this geometry (Vassilikou-Dova and Kalogeras 2009).

The food system is placed between the two electrodes of a capacitor and the impedance of the capacitor is determined during a thermal scan at selected frequencies. The food system is heated over a selected temperature range at a heating rate of approximately 1 to 5°C/min for selected frequencies of 0.001, to 10<sup>6</sup> Hz. Dry nitrogen gas is used to avoid condensation of water on the foods. The absorption maximum corresponds to the glass transition temperatures obtained similar to the DMTA method. A suitable frequency must be selected to insure that the DEA/DETA peak coincides with the  $T_g$ . In dielectric techniques, dielectric constant or permittivity ( $\epsilon'$ ), the degree of alignment of dipole molecules to the electric field, dielectric loss constant ( $\epsilon''$ ), the energy needed to align the dipole molecules, and  $\tan \delta (= \epsilon''/\epsilon')$  of food as a function of temperature/frequency for an applied stress, are detected by using alternating current (Bidstrup and Day 1994; Rasanen et al. 1998; Abiad et al. 2009). Glass transition temperatures ( $T_g$ ) are assigned to the temperature corresponding to an increase in the permittivity or the peak of  $\tan \delta$  - temperature diagram. During glass to rubber transitions, the polar groups of the food components attain mobility, resulting in increased permittivity (Bidstrup and Day 1994). The characteristic relaxation time ( $\tau$ ) associated with the increased mobility of polar groups is determined by the permittivity of the food system (Bidstrup and Day, 1994). To make accurate determinations, the electrodes and sample food system must stay in good contact and avoid electrode polarization. Samples with large surface areas and small thicknesses are selected to improve the sensitivity of DEA/DETA. Also, electric current leakage must be minimized at the edges (Bidstrup and Day, 1994). The DEA/DETA techniques are more sensitive than

DSC and DMTA for observing phase and state transitions in a wheat dough (Laaksonen and Roos 2003). However, DEA is not used extensively in the determination of phase and state transitions of food systems.

### **Nuclear Magnetic Resonance (NMR)**

NMR is a spectroscopy technique based on the magnetic properties of atomic nuclei and is used to detect molecular motion by determining the relaxation characteristics of the NMR active nuclei, such as  $^1\text{H}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{23}\text{Na}$  and  $^{31}\text{P}$  (Ruan et al. 1998; Kou et al. 1999). Using  $^1\text{H}$  NMR, the mobility of water was examined with respect to the  $T_g$ . A shift in the relaxation time of water that coincides with a shift in relaxation time at  $T_g$  was observed (Ablett 1992; Kalichevsky et al. 1992, 1993). However, solid state NMR studies to determine the mobility of chemical reactants and correlation of this mobility with reaction rates are lacking (Sherwin et al. 2002). NMR determines the time constant  $T_1$  (spin-lattice relaxation time), indicating longitudinal relaxation and a time constant  $T_2$  (spin-spin relaxation time), indicating transverse relaxation. Figure 7 presents typical relaxation times ( $T_1$  and  $T_2$ ) of water as a function of temperature. When foods undergo transitions from the glassy to the rubbery state due to plasticization by water or heat, molecular mobility increases significantly and may be represented by a steep slope of the  $T_2$ -temperature relationship. However, the  $T_1$ -temperature relationship of foods is presented as a negative slope as temperature increases and reaches  $T_g$ . In general, foods exhibit an abrupt change in slope in the  $T_1$ -temperature relationship as temperature increases above  $T_g$  (Ruan et al. 1998). The relaxation time-temperature plots of liquids is a straight line with positive slope, while on relaxation time-temperature plots for solids,  $T_1$  increases significantly beyond specific temperatures and  $T_2$  exhibits a minimum value at a specific temperature corresponding to the rigid lattice limit ( $T_{RL}$ ) (Lin et al. 2006; Blanshard 1995). Some studies report that NMR observed  $T_2$  relaxation times may not always approximate glass transition temperatures (Blanshard 1995; Kaletunc & Breslauer 2003). However, the difference between  $T_{RL}$  and  $T_g$  may be attributed to different distance scales/levels in which different methods observe glass transition temperature. For instance, DSC presents the macroscopic mobility of a food system by determining the step change in heat capacity at the glass to rubber transition, while NMR determines the microscopic/molecular level mobility approximations in a food system. Often the  $T_g$  values approximated from NMR are lower than the  $T_g$  value obtained using DSC (Kalichevsky et al. 1992; Schmidt 1999). For instance, Kalichevsky

et al. (1992) reported that the midpoint  $T_g$  of amylopectin maize starch at 15% water content obtained from DSC was 56°C, while the  $T_g$  approximated using NMR was 38°C. The  $T_g$  observed by different methods is dependent on various factors, including principle and procedure involved in the method, sample preparation, and the various experimental parameters controlling the observation (Schmidt 1999). The selection of a method for the observation of  $T_g$  is often dependent on the application, the information required, and the material of interest (Schmidt 2007; Schmidt 2004).

### **Electron Spin Resonance Spectroscopy (ESR)**

ESR is a good method for the study of molecular motion in biological glasses, and provides information on the rotational mobility of dissolved spin probes (Buitink et al. 2000). The rotation mobility of the probes is expressed in the rotational correlation time. ESR is closely related to nuclear magnetic resonance spectroscopy. When electromagnetic radiation is applied to food systems, some amount of energy is absorbed, resulting in the discharge of unpaired electrons or free radicals that are paramagnetic. The absorption of the electromagnetic radiation attributed to free unpaired electrons in the presence of an externally applied magnetic field is determined and amplified to provide an ESR spectrum (Gray 1995). A change in the ESR spectral shape represents molecular mobility during glass transitions in amorphous systems (Roos 1995c). The spin probe rotational correlation time ( $\tau_R$ ) is determined during a thermal scan by inserting a probe of nitroxide radicals inside the food (Buitink et al. 1999). The  $\tau_R$  is calculated using signal components of the ESR spectra (Buitink et al. 2000). An increase in temperature reduces  $\tau_R$  and represents increased molecular mobility. An increased  $\tau_R$  observed in the glassy state of foods represents decreasing molecular mobility. A sharp change in the slope of the linear relationship between  $\log \tau_R$  and temperature is an indicator of glassy to rubbery state transitions. A decrease in  $\tau_R$  values is observed in the rubbery state (Figure 8) because of the increase in free volume and the decrease in the viscosity of the food system (Buitink et al. 2000). The use of ESR for observation of state and phase transitions in food systems is limited. Rolee and LeMeste (1999) analyzed the rotational diffusion coefficient for starch-water systems of intermediate moisture contents at selected temperatures using ESR. One disadvantage of ESR is that the rotational relaxation time and the molecular mobility of the external probe introduced into the matrix is

approximated using the component signals rather than the relaxation times of matrix itself, unlike NMR which approximates the relaxation time and molecular mobility of the food (Buitink et al. 2000).

### **Characterizing the Effects of Water and other Plasticizers**

Water is the universal solvent, a common additive and a plasticizing agent in food systems. Adding thermal energy can also plasticize foods and decrease the  $T_g$  of the food systems by increasing the molecular energy as well as the entropy of food systems. The extent of the  $T_g$  decreasing capacity of the plasticizing agent in foods depends on the concentration of plasticizing agent, its molecular weight, glass transition temperature, viscosity and compatibility with food solids (Roos 1995b; Kalichevsky et al. 1993; Ruan & Chen 1998).

The plasticizing effect of water is attributed to a large dielectric constant and the ability to promote hydrogen bonding among hydrophilic molecules during plasticization (Matveev et al. 2000). In dry and intermediate moisture food systems, the  $T_g$  of the system decreases sharply with increase in water content, while in foods containing large quantities of water, little change in  $T_g$  of foods is observed when water content is increased. (Figure 1). Adding water increases the free volume among food molecules and results in molecular relaxation in the system (Reid & Fennema 2007). In comparison with food solids, water exhibits a small molecular weight and a low  $T_g$  (-135°C) (Johari et al. 1987) and therefore depresses the total  $T_g$  of food systems. However, water reacts with individual food macromolecules differently. For example, carbohydrates and proteins are hydrophilic, while lipids are hydrophobic and immiscible with water. Other common plasticizers added to foods are glycerol, sorbitol and low molecular weight sugars such as glucose and fructose. The effects of other plasticizers are less significant than that of water (Pouplin et al. 1999). High molecular weight additives compatible with the food solids are added to increase the  $T_g$  of foods.

Water plasticization effects and therefore the stability of foods during processing and storage may be predicted by selected models. The Gordon-Taylor equation (Gordon & Taylor 1952) is most commonly used for experimental data. For binary food systems such as food solids and water, Gordon-Taylor equation is expressed as

$$T_{gm} = \frac{X_s T_{gs} + k X_w T_{gw}}{X_s + k X_w} \quad (1)$$

$T_{gm}$ ,  $T_{gs}$  and  $T_{gw}$  of aqueous binary mixtures are the glass transition temperatures of the mixture, solids and water, respectively;  $X_w$  and  $X_s$  are the water (w.b.) and total solids contents, and  $k$  the Gordon-Taylor parameter. The curvature of glass transition temperature-solids content relationship is described by  $k$ , denoting the strength of interaction between water and the foods solids (de Graaf et al. 1993). A larger  $k$  for a binary mixture indicates that the solids are more plasticized by water than food mixtures with a smaller  $k$  and equivalent water content. Increases in  $k$  in the Gordon-Taylor model indicate greater plasticization for an equivalent amount of water, presenting a decrease in glass transition temperature. If  $k = 1$ , the glass transition temperature-solids content relationship is a straight line. If  $k > 1$ , the nature of the graphical relationship between glass transition temperature and solids content is more concave, and for  $k < 1$ , the nature of the relationship is convex. Starches exhibit a smaller  $k$  than sugar or food proteins, and in some instances,  $k < 1$ . The shape of the glass transition temperature-water content relationship is dependent on  $k$  and on the structure and composition of the solids in food systems. According to free volume theory (Kelley & Bueche 1961)  $k = \Delta\beta_{gs}/\Delta\beta_{gw}$ , where  $\beta$  is the free volume expansion coefficient and the subscripts  $s$  and  $w$  represent solids and water, respectively. The model parameters ( $k$  and  $T_{gs}$ ) of Equation (1) are estimated using non-linear regression analysis, where  $T_{gw} = -135^\circ\text{C}$ . At any water concentration in a binary mixture, the Gordon-Taylor model is used to calculate the glass transition temperature of the mixture, if the values of  $T_{gs}$  and  $k$  are available. For instance, the  $T_{gs}$  and  $k$  values of glucose-water solution are  $31^\circ\text{C}$  and 4.07 respectively (Truong et al. 2002). Using the Gordon-Taylor equation (1), the glass transition temperature of the glucose-water solution containing a water concentration of 0.1 is calculated as  $-20.7^\circ\text{C}$ . Mixtures containing more than two components may not be calculated with the Gordon-Taylor equation because a large number of experiments are necessary for adequate data collection.

The Couchman and Karasz equation (Couchman & Karasz 1978) is based on the thermodynamic theory used to explain water plasticization in food systems. The parameter  $k$  in the Gordon-Taylor model is equivalent to the ratio of the change in specific heats of the components of binary mixture i.e. water ( $C_{pw}$ ) and food solids ( $C_{ps}$ ), from a thermodynamic standpoint. The Couchman and Karasz equation (2) is similar to the Gordon-Taylor equation with the parameter  $k = \Delta C_{pw} / \Delta C_{ps}$ .



$$T_g = \frac{X_s \Delta C_{ps} T_{gs} + X_w \Delta C_{pw} T_{gw}}{X_s \Delta C_{ps} + X_w \Delta C_{pw}} \quad (2)$$

This equation is used to calculate the glass transition temperature of the mixture, if the  $\Delta C_p$  values of the components are available. For instance, the  $\Delta C_p$  values of glucose and water in a mixture are 0.58 and 1.94 J/g°C respectively (Truong et al. 2002). Using the Couchman and Karasz equation, the glass transition temperature of the glucose-water mixture containing a water concentration of 0.1 is calculated as -13.9°C. Unlike the Gordon-Taylor equation, the Couchman and Karasz equation can be used to predict the behavior of glass transition temperature-solids content relationship for multicomponent mixtures.

Cuq and Lcard-Verniere (2001) used the Kwei equation successfully to explain water plasticization phenomena in wheat semolina. However, the Kwei equation (Equation 3) is mainly used to model the water plasticization behavior in sugar rich foods such as fruits (Table 1). The Kwei equation is also similar to the Gordon-Taylor equation, with the addition of one more component ( $qX_wX_s$ ), indicating specific interactions in food systems or the interactions of water molecules with solids in heterogeneous food systems (Micard & Guilbert 2000). The Kwei equation is

$$T_{gm} = \frac{X_s T_{gs} + kX_w T_{gw}}{X_s + kX_w} + qX_s X_w \quad (3)$$

where the parameter  $q$  is a constant representing the effect of intermolecular forces such as hydrogen bonding present in a heterogeneous mixture, or heterogeneous formations of food systems of large water concentrations (Kwei, 1984; Micard & Guilbert 2000; Cuq & Lcard-Verniere 2001). A value of  $q > 0$  indicates that water-food solids interactions are strong compared to solid-solid interactions, while  $q < 0$  indicates solid-solid interactions are prominent, resulting in immiscibility of water in the food matrix (Lin et al. 1989).

### **Melting/Freezing Curve**

A melting/freezing curve, representing melting/freezing point depression with an increase in solids content, is plotted as one of the main components of a state diagram of food systems. Differential scanning calorimetry and cooling curve methods are commonly used for determination of the melting/freezing point. In the case of DSC determinations, the temperature at which the last ice crystals in the food systems are melted when cooled down to an adequately low temperature ( $< T_m' \sim -60^\circ\text{C}$  for fruits) is designated as the

ice melting temperature ( $T_m$ ), and the temperature at which melting of the first crystals occurs is designated as the onset of ice melting ( $T_m'$ ). When considering the freezing temperature of water to ice in food systems, as in the case of the cooling curve method, the initial crystallization temperature is designated as the initial freezing point ( $T_f$ ). This is located as the onset of ice crystallization, where there is an abrupt increase in temperature due to the release of latent heat (Rahman et al. 2002). In the cooling curve method,  $T_m'$  is designated as the endpoint of freezing. At the melting/freezing point, the vapor pressure of the solid and liquid are equal, and both phases exist in equilibrium. The freezing point of water or the melting point of ice is an equilibrium process, where neither cooling nor heating rate affect the phase transition point of ice crystallization. Like the glass line, the nature of melting/freezing curve is strongly dependent on food composition. Moreover, the  $T_m'$  as well as the glass transition temperature of the maximum-freeze-concentration solution ( $T_g'$ ) is identified with a melting/freezing curve.

### **Characterizing Melting/freezing Temperature**

A differential scanning calorimetry method is used extensively to characterize the onset of ice melting ( $T_m'$ ) and the decrease in melting temperature ice crystals, due to increasing solids content in foods (Rahman et al. 2005; Rahman et al. 2002). Thermograms provide melting endotherms and glass transition temperatures of maximum freeze-concentrated solutions for foods containing freezable water (Figure 9). The ice melting temperature ( $T_m$ ) of foods is taken as the peak temperature of the melting endotherm as presented in Figure 9 (Goff et al. 1993; Arvanitoyannis et al. 1993). However, in foods with broader endotherms, a tangent to the left side of the melting endotherm curve is plotted.  $T_m$  is identified as the point where maximum slope of the endotherm is observed (Rahman et al. 2009; Rahman 2004; Bai et al. 2001). However, the DSC is conducted with only a small quantity of food sample and may not represent actual melting scenarios, since foods are complex mixtures of various components (Rahman et al. 2002).

Use of the cooling curve method to determine initial freezing temperature ( $T_f$ ) is simple and inexpensive compared to the DSC method. Complex and multicomponent food systems may not be completely represented by the small food quantity of 5-15 mg in the DSC (Rahman et al. 2002). Initial freezing temperature ( $T_f$ ) and  $T_m'$  can be precisely determined with the cooling curve method (Rahman et al. 2002). In the cooling curve method, a metallic cylinder containing the food system is placed in a freezer

maintained at low temperatures ( $< -60^{\circ}\text{C}$ ). The temperature at the geometric center of the food sample is determined at selected time intervals using a thermocouple. Figure 10 shows a typical cooling curve. The solid line represents the temperature of the material during cooling while the dotted line represents the slope of the cooling curve. At point *a* (onset of ice crystallization), temperature abruptly increases due to the release of latent heat to point *b*, which is considered the initial freezing temperature ( $T_F$ ). At the initial freezing temperature, the slowest cooling rate is observed. The cooling curve method was used to obtain the freezing curve of dates (Kasapis et al. 2000), garlic (Rahman et al. 2005), abalone (Sablani et al., 2004) and tuna flesh (Rahman et al. 2003). This method can be used for solids, liquids and viscoelastic materials. The cooling curve method is relatively inexpensive, and sample preparation is relatively easy (Rahman et al. 2002). However, the cooling curve method is less accurate when materials contain smaller amounts of freezable water (Rahman et al., 2002).

#### **Characterizing conditions of Maximum-Freeze-Concentration Solutions**

The crystallization of water in foods occurs at temperatures lower than  $0^{\circ}\text{C}$ , since freezing temperature depression relates to the concentration of solids. As temperature is decreased and water is removed from a food in the form of ice, the solutes in the unfrozen water are freeze-concentrated. An increase in the viscosity of the unfrozen phase occurs, thus decreasing the diffusion properties of the system and hindering additional ice crystallization. This highly concentrated unfrozen solution goes through a glass transition if temperature is decreased further. Maximum-freeze-concentrated conditions in foods correspond to maximum ice formation at low temperatures. These conditions are characterized by two temperatures: the onset of ice melting ( $T_m'$ ) and the glass transition temperature for maximum-freeze-concentration ( $T_g'$ ), both which are lower than  $0^{\circ}\text{C}$ . At  $T_m'$ , the viscosity of the maximum-freeze-concentrate lies in the range of  $10^7$  Pas (Roos & Karel 1991a). The difference between  $T_m'$  and  $T_g'$  is often very small, and the two temperatures may coincide for high molecular weight food components (Roos 1995c). The water content corresponding to  $T_g'$  is the unfrozen water.  $T_m'$  and  $T_g'$  also increase with increasing molecular weight of food components.

The ice formation in freeze-concentrated solutions is time-dependent, and therefore, determination of characteristic temperatures ( $T_m'$  and  $T_g'$ ) of freeze-concentrated solutions is challenging. It is difficult to

observe small changes in unfrozen water associated with ice melting at temperatures close to  $T_m'$  (Sacha & Nail 2009). Thermograms of high-water foods generally exhibit multiple transitions, and the lower transition temperature is commonly assigned as  $T_g'$  (Roos & Karel 1991c; Ablett et al. 1992). However, the assignment of  $T_m'$  and  $T_g'$  of maximally freeze-concentrated solutions is a subject of debate (Goff & Sahagian 1996; Blond et al. 1997; Fonseca et al. 2001; Reid & Fennema 2007). The complex behavior of maximally freeze-concentrated solutions is attributed partly to the excess enthalpy resulting from the molecular relaxations near  $T_g'$  (Goff & Sahagian 1996). Generally, the onset temperature of ice melting ( $T_m'$ ) is determined by plotting a base line linear to the endotherm. The intersection point of the baseline with the left side of the endotherm is defined as the  $T_m'$  (Figure 9). Annealing is performed at a temperature ( $T_m'-1$ ) for systems containing freezable water, allowing maximum ice formation to avoid the crystallization endotherm. Annealing time must be optimized to achieve maximum freeze-concentrated solutions. After annealing, the foods are cooled from ( $T_m'-1$ ) to a low temperature and scanned to a preselected temperature range depending on the food system. The  $T_m'$  and  $T_g'$  are determined from a single thermogram. However, accuracy of this technique may depend on selected factors, such as heating and cooling rates or annealing conditions (Rahman et al. 2002). Also, the value of  $T_m'$  is dependent on the intersection point of the baseline with the left side of the endotherm (Fonseca et al. 2001). A state diagram may be better utilized to assess the temperatures and states of the food system at maximum-freeze-concentration conditions. The value of  $T_g'$  for a specific food is normally determined by extending the freezing curve to the glass line in a state diagram, as presented in Figure 1. However,  $T_g'$  observed using the results from DSC analysis may be considerably different from the  $T_g'$  determined from state diagram (Blond et al. 1997; Syamaladevi et al. 2009). A procedure similar to the initial freezing point determination is followed to identify the onset of ice melting ( $T_m'$ ), using the cooling curve method. At point *c* (Figure 10), the slope of the cooling curve changes and a maximum cooling rate is observed. Point *c* is regarded as the onset of ice melting ( $T_m'$ ). The  $T_m'$  obtained with the cooling curve method is comparable to that determined with DSC (Rahman et al. 2002). However, the cooling curve method for determination of  $T_m'$  is less sensitive than DSC for concentrated foods (Rahman et al. 2005).

An approach similar to the determination of the glass transition temperatures of low moisture food systems, mechanical analysis with annealing at temperatures below  $T_m'$  may be used to determine the glass

transition temperatures of high moisture foods ( $T_g'$ ). At glass transition temperatures ( $T_g'$ ), a maximum value of  $E'$  (or  $G'$ ),  $E''$  ( $G''$ ) and  $\tan \delta$  of foods is observed. Melting temperatures of ice also may be obtained with DMTA. The peak in the value of  $E'$  (or  $G'$ ) at a high temperature represents the melting of ice while the peak in the value of  $E'$  (or  $G'$ ) at a low temperature represents the  $T_g$  of food solids (Laaksonen & Roos 2003). DEA/DETA is considered a more sensitive method to determine  $T_g'$  than DSC or DMA. In dielectric techniques, the dielectric constant or permittivity ( $\epsilon'$ ) expresses the degree of alignment of dipole molecules to the electric field. The dielectric loss factor ( $\epsilon''$ ) expresses the energy needed to align the dipole molecules. The  $\tan \delta$  ( $= \epsilon'' / \epsilon'$ ) of foods is a function of temperature/frequency for an applied stress, and is detected by alternating current (Rasanen et al. 1998). The melting temperatures of ice and glass transition temperatures are determined using DEA. A peak in  $\tan \delta$  provides glass transition temperatures at maximum-freeze-concentration conditions ( $T_g'$ ) (Laaksonen & Roos 2000).

#### **Characterizing Unfrozen Water ( $X_w'$ )**

Unfrozen water ( $X_w'$  or  $1-X_s''$ ) in frozen foods may result in deterioration during long-term storage due to its molecular mobility. Three different approaches may be followed to calculate the concentration of unfrozen water in frozen foods. In the first approach, the change in enthalpy during ice-melting of is determined (Levine & Slade 1986). Using Equation 11, the area under the ice melting endotherm is determined and the quantity of unfrozen water ( $X_w'$ ) are calculated.

$$X_w' = X_w^0 - \frac{(\Delta H_m)_{frozen\ food}}{(\Delta H_m)_{water}} \quad (11)$$

where  $X_w^0$  is the water content of the frozen food,  $(\Delta H_m)_{frozen\ food}$  is the change in enthalpy during melting of ice in the frozen food and  $(\Delta H_m)_{water}$  is the change in latent heat of melting of ice (334 kJ/kg).

A second approach is to plot the linear relationship between  $(\Delta H_m)_{frozen\ food}$  and the water content of annealed high-moisture foods (Simatos et al. 1975). The unfrozen water is considered the water content corresponding to  $(\Delta H_m)_{frozen\ food} = 0$ . The most common and reliable approach for the determination of unfrozen water is to extend the freezing curve to the glass line of the food system on a state diagram following the curvature of the freezing curve (Franks 1986a; Ablett et al. 1993). The temperature and water concentration at the intersection point of the glass line and the freezing curve are considered as  $T_g'$  and the

quantity of unfrozen water, respectively (Figure 1). The accuracy and utility of the three approaches for the determination of unfrozen water is discussed in the literature (Blond et al. 1997; Fonseca et al. 2001; Rahman 2004). The unfrozen water quantities obtained by the three approaches vary depending on the assignment of onset or midpoint glass transition temperatures in the thermograms (Blond et al. 1997). Also, the assignment of melting and glass transition temperatures determines the quantity of unfrozen water (Blond et al. 1997; Fonseca et al. 2001). Blond et al (1997) attributed the difficulty in defining a true intersection between the freezing curve and the glass line to differences in the onset and midpoint glass transition temperatures. Studies relating molecular mobility and viscosity of the unfrozen phase to diffusion-induced mechanisms may provide a better understanding of  $T_g$  and unfrozen water in frozen food systems (Blond et al. 1997).

### **Characterizing the Effects of Solids Content on Equilibrium Melting Temperature**

A number of empirical and theoretical models are available for relating the equilibrium melting/freezing temperatures with solids content of food biopolymers (Rahman 1995). The Clausius-Clapeyron equation and the Chen equation are used extensively to predict equilibrium melting temperatures of selected food systems. The Clausius-Clapeyron equation (4)

$$\delta = -\frac{\beta}{\lambda_w} \ln \left[ \frac{1 - X_s}{1 - X_s + EX_s} \right] \quad (4)$$

where  $\delta$  is the melting/freezing temperature depression relative to increasing total solids concentration,  $\beta$  is the molar freezing temperature constant for water (1860 kgK/kg mol),  $\lambda_w$  is the molecular mass of water,  $X_s$  is the solids mass fraction in a food system, and  $E$  is the molecular mass ratio of water to solids ( $\lambda_w/\lambda_s$ ).

The Clausius-Clapeyron equation is applicable to ideal systems, but multicomponent systems are normally non-ideal in nature. The Chen equation (Chen 1986), is an extension of the Clausius-Clapeyron equation and may be used to predict the freezing temperature for non-ideal systems. The Chen equation (5) is expressed as:

$$\delta = -\frac{\beta}{\lambda_w} \ln \left[ \frac{1 - X_s - BX_s}{1 - X_s - BX_s + EX_s} \right]$$

(5)

Where a new parameter  $B$ , the ratio of unfrozen water to the total solids concentration, and the parameter  $E$  are estimated using non-linear optimization analysis.

A set of theoretical equations (6 to 10) was developed to predict the  $T_g'$  and corresponding solids content  $X_s''$  on a state diagram for aqueous solutions of mono-, oligo- and polysaccharides. These are derived from standard glass transition temperatures of anhydrous solids and specific heat changes for mixtures of pure solids and water based on a water clustering model (Matveev & Ablett 2002).

$$\frac{T_{gw}}{T_g'} = 1 - 0.145f(y) \quad (6)$$

$$X_s' = 0.55z(2.645 - y)^{0.5} \quad (7)$$

The function  $f(y)$  and  $y$  are calculated from following equations using iterative procedures.

$$6.896K_2(z-1)z = (zK_2 - 1)zf(y) + \varphi(y) \quad (8)$$

$$f(y) = \ln\left(2y^{1.5}\left(\left(1.55y^{0.5} - 1\right)^3 + 1/3\right)\right) \quad (9)$$

$$\varphi(y) = 1.819f(y)(2.645 - y)^{-0.5} \quad (10)$$

where  $z = T_{gs}/T_{gw}$  and  $K_2 = \Delta C_{ps}/\Delta C_{pw}$

These equations were further modified to accurately calculate  $T_g'$  and  $X_s''$  values for frozen aqueous solutions of proteins and solutions of polysaccharides (Matveev 2004).

## STATE DIAGRAM DATA

The following sections discuss the Gordon-Taylor equation constants ( $T_{gs}$  and  $k$ ) obtained from glass transition temperature-solids content relationships (glass line), Chen equation constants ( $E$  and  $B$ ) obtained from melting/freezing point-solids content relationships (melting/freezing curve), and conditions of maximum-freeze-concentrations ( $T_g'$ ,  $T_m'$  and  $X_w'$ ) of foods. Tables 1-5 present the state and phase transition data.

## Sugars

Studies of glass transitions and applications are more often conducted for sugars than for starches or proteins. In fruits, glass transitions are detected due to the presence of sugars including glucose, fructose and sucrose. State diagrams of fruits are similar to their major amorphous components. State diagram data ( $T_g'$ ,  $T_m'$ ,  $T_{gs}$ , and  $k$  values) of monosaccharide and disaccharide solutions and selected fruit solids are presented in the literature (Rahman 1995, Roos 1993a). Calorimetric methods are widely used for development of the state diagrams of sugars (Tables 1). Glass transition temperatures in amorphous sugars are easily detected by DSC. Single and narrow range glass transition temperatures are commonly observed for fruit solids, and attributed to compatible and simple structures. The Gordon-Taylor equation and the Kwei equation are commonly used to characterize the plasticization effect of water on sugars. Glass transition temperatures of dry fruit solids ( $T_{gs}$ ) range from -29 to 107°C and from -16.3 to 142.7°C for sugars and fruit solids, respectively (Table 1). The  $T_{gs}$  of fruit solids (mainly sugars) are smaller than the  $T_{gs}$  of food protein or starch because of differences in molecular weight. Within sugars, trehalose exhibits a high  $T_{gs}$  (100°C), which is attributed to high molecular weight. Maltose and lactose also exhibit high glass transition temperatures ( $T_{gs}$ ). However, high molecular weight may not be the sole cause of high anhydrous glass transition temperatures. For instance, glucose and fructose exhibit equivalent molecular weights and their  $T_{gs}$  are 31 and 5°C, respectively (Table 1). Normally, fruit solids exhibit large  $k$  values, indicating that sugars are easily plasticized by water. The  $k$  values of pure sugars range from 3.02 to 6.56, while fruit solids exhibit  $k$  values ranging from 0.21 to 6.69. Trehalose and lactose exhibit larger  $k$  values than other pure sugar components. The larger  $k$  value (4.52) for glucose compared to the  $k$  value (3.76) of fructose also exhibits a greater decrease in glass transition temperatures with small additions of water compared to fructose.

Chen and Clausius–Clapeyron equations are used to fit the melting/freezing point depression of fruits. The parameter  $E$  in Chen and Clausius–Clapeyron equations relates to the molecular mass ratio of water to solids ( $\lambda_w/\lambda_s$ ). The value of  $E$  is dependent on the type of food solids. For instance, date flesh consists of approximately 75% of a solids mixture of sucrose, glucose and fructose. The mean molecular weight of the food solids of dates obtained from the parameter  $E$  is 200 (Table 1). The constant  $B$  in the Chen equation presents the ratio of unfrozen water to total food solids. The constant  $B$  only provides an approximate value of unfrozen water. The values of  $E$  ranged from 0.064 to 0.129 for selected fruits, while  $B$  values ranged



from -0.062 to 0.429. The negative value of  $B$  indicates that a fraction of solids is behaving as a solvent. Chen (1986) indicated that melting/freezing point depression results from the complex interaction between solutes and water, and can be expressed by equivalent increases in free water. Thus, the values of  $B$  can either be positive or negative depending on the behavior of food constituents.

The  $T_g'$  of freeze concentrated solutions of fruit solids range from -60 to -40°C, while the  $T_m'$  range from -52 to -24°C (Table 1).  $T_g'$  and  $T_m'$  of small molecular weight sugars as well as fruit solids are lower than the  $T_g'$  and  $T_m'$  of proteins and starches (Table 1). Dissimilar values of  $T_g'$  and  $T_m'$  for pure sugars may be attributed to experimental conditions and methods. The  $T_m' - T_g'$  of fruit solids range from 0.4 to 15°C. Normally, fruit solids consist of more unfrozen water than starch or protein rich foods. The unfrozen water content of selected sugars ranges from 0.172 to 0.535 kg water/kg sugars. A state diagram of amorphous sucrose is presented in Figure 11. Amorphous sucrose may be prepared by many methods, including freeze drying (Roos 2009). The variation of glass transition temperature ( $T_g$ ) and ice melting temperature ( $T_m$ ) of amorphous sucrose solutions with solids content are presented as a glass line and melting curve in the state diagram (Roos 1991c). Figure 12 presents a state diagram of raspberry solids. Here the glass line and melting curves are modeled using Gordon-Taylor and Chen equations, respectively. (Syamaladevi et al. 2009).

## **Starches**

Calorimetric and mechanical determinations are often used to study the glass transition of starch systems (Table 2). Both the Gordon-Taylor and Couchman-Karasz equations are used to model the plasticization influence of water on starches. The  $T_g$  of high molecular weight starches are relatively higher than the  $T_g$  of sugars.  $T_{gs}$  of selected starches range from 75 to 281°C (Table 2). High glass transition temperatures ( $T_{gs}$ ) of starches may be attributed to biopolymer interactions, limiting molecular motion and increasing molecular rigidity and viscosity. The  $T_g$  increases with an increase in molecular weight, occupied volume, rigidity, polarity of side chain groups, covalent and non-covalent bonds and cross linkages among biopolymers (Di Gioia et al. 1999). Moreover, as molecular weights increase, the cross-linking density of biopolymers increases the stiffness of the biopolymers, reducing the mobility and increasing  $T_g$  of starches. (Tolstoguzov 2000). Starches exhibit broad glass transition temperature ranges ( $T_{gi} - T_{ge}$ ) attributed to large

molecular weights and incompatibility of constituents, while many small molecular weight sugars exhibit glass transition ranges ( $T_{gi}$ - $T_{ge}$ ) of a few degrees (Tolstoguzov 2000). Multiple glass transition temperatures are observed in many starch-rich foods. Perdon et al. (2000) observed three apparent glass transition temperatures of rice kernels at specific water contents attributed to the structural characteristics of heterogeneous starch as well as the coexistence of the crystalline/semicrystalline and amorphous regions of starch.

Mean  $k$  values in the Gordon-Taylor equation for starches ranging from 2.39 to 6.38 are relatively smaller than the mean  $k$  values for proteins and sugars (Table 1 and 2). Starch may absorb less water than readily plasticized hydrophilic and amorphous proteins or polysaccharides (Matveev et al. 2000). Plasticization of foods by water depends on many factors, including the hydrophilicity of the food constituents, the quantity of water in food systems, and the thermodynamic compatibility of water with food constituents. Statistical models are better suited to correlate glass transition temperatures with the water or solids content. The extrapolation of the relationship to foods containing zero water provides glass transition temperatures for dry starches (Bindzus et al. 2002). Extruded starches exhibit higher  $T_{gs}$  than  $T_{gs}$  of native starches. Bindzus et al. (2002) reported that starches may exhibit similar states and state transitions, regardless of their botanical origin or processing conditions.

Starches normally exist in both amorphous and crystalline states. For example, linear amylose in starch basically exhibits an amorphous structure, while amylopectin exhibits a crystalline/semicrystalline structure. The amorphous portion undergoes glassy to rubbery transitions and the crystalline portion of the starches melts during heating. Amylopectin in waxy maize exhibits a high  $T_g$ . Amylose exhibits a lower  $T_g$  than amylopectin, attributed to the smaller molecular mass of amylose and the smaller degree of polymerization (de Graaf et al. 2003). Zhong and Sun (2005) report that gelatinized corn starch exhibits a higher glass transition temperature than native corn starch. Tan et al. (2004) report that the glass transition temperature of waxy maize starch overlaps with the peak gelatinization temperature attributed to the loss of crystallinity. Glass transition and gelatinization temperatures are reduced by the addition of water content. Moreover, Tan et al. (2004) report that the addition of glycerol to maize starch increases the glass transition and gelatinization temperatures at small water contents.

Semicrystalline portions of starch may crystallize with time during storage. Storing of starch-rich foods at a temperature lower than glass transition temperatures may reduce the rate of crystallization due to the large viscosity of starches. The extent of crystallization of starches depends mainly on the difference between storage temperature and the glass transition temperature of the particular starch ( $T-T_g$ ) (Jouppila & Roos 1997). Li et al. (1998) reported loss of crispness in glassy corn cakes. Recently, Van Nieuwenhuijzen et al. (2008) reported that the loss of crispness of bread crust is more dependent on water content than water activity, though both may influence crispness. Proton mobility, representing water mobility determined by NMR, was not influenced by water activity at constant water concentrations in bread crust.

Glass transition temperatures at maximum-freeze-concentration ( $T_g'$ ) of starches are higher than the glass transition temperatures of sugars or proteins (Table 1, 2 and 3).  $T_g'$  and  $T_m'$  of common mono-, di-, oligo- and polysaccharides were determined and the difference in the temperatures ( $T_m' - T_g'$ ) ranged from 10 to 15°C. ( $T_m' - T_g'$ ) was consistent for polysaccharides. However, little information about  $T_g'$  and  $X_w'$  of starches is available in the literature.  $T_g'$  of selected starch systems ranged from -3 to -11°C (Table 2). Melting/freezing curves and  $T_m'$  of limited starch systems are provided in Table 2. Previously, equivalent values for  $T_g'$  and  $T_m'$  were adopted for starch systems (Roos & Karel 1991b). The quantity of unfrozen water for selected starch systems ranging from 0.185 to 0.3 kg water/kg starch is in the general range for unfrozen water of many other food systems, such as proteins and fruit solids (Table 2). Unfrozen water is lowest in pure starches compared to food solids consisting of small molecular weight constituents. The semi-crystalline and hydrophobic nature of starch is related to the small quantity of unfrozen water in starch-rich foods. Compared to the ordered structure of starch, proteins and sugars exhibit a hygroscopic amorphous nature and greater quantities of water adsorption than starch (Kokini et al. 1994). **Figure 13 presents the state diagram of amorphous gelatinized corn starch. The glass line is modeled using Gordon-Taylor. The  $T_g'$  and  $T_m'$  values of corn starch are -11°C respectively, which are greater than typical values for sugars.**

### **Plant Proteins**

Proteins exhibit complex structures and large molecular weights ranging from thousands to millions. Structurally, proteins are amino acids bound by peptide linkages into long chains. Plant proteins play a

major role in the human diet and are necessary for the growth of cells. Protein denaturation is sensitive to temperature changes during processing and storage. Research on state diagrams of plant proteins is concentrated on gliadin, glutenin and gluten (Micard & Guilbert 2000; Pouplin et al. 1999; De Graaf et al. 1993; Noel et al. 1995; Nikolaidis & Labuza 1996). DMTA, DSC and MDSC are the most useful methods to determine the  $T_g$  of plant proteins. Kokini et al. (1994) reported that the combined use of DSC and DMTA allows researchers to study state transitions of proteins in a broad range of temperatures and water contents. State diagrams with different states (glassy, rubbery, entangled polymer flow, reaction zone and softening) of selected proteins (gliadin, zein, and glutenin) are developed (Kokini et al. 1994).

Like starches, glass transition temperatures of dry proteins ( $T_{gs}$ ) are high, attributed to large molecular weights. Studies on glass transition in many anhydrous proteins and polysaccharides are difficult due to denaturation and decomposition of the biopolymers during heating (Roos et al. 1996). However, the mean  $T_{gs}$  obtained for the selected plant proteins ranged from 114 to 187°C (Table 3). The  $T_{gs}$  of plant protein-rich foods were greater than the  $T_{gs}$  of sugars and smaller than the  $T_{gs}$  of starches and animal proteins. There are inconsistencies in the  $T_{gs}$  of wheat gluten, the most studied plant protein for glass transition analysis (Table 3). This may be attributed to the choice of methods and experimental conditions. Mean  $k$  values ranging from 0.2 to 6.72 for proteins systems are greater than  $k$  values for carbohydrates or starches (Table 1, 2 and 3). Most of the proteins are hydrophilic in nature and highly plasticized by water compared to starches. The  $k$  values of soy globulins (6.72 and 6.66 for 7S and 11S, respectively), are larger than the  $k$  values for selected plant proteins (Table 3). Micard and Guilbert (2000) reported that for gluten, the value of  $k$  is between the  $k$  values of gliadin and glutenin. The smaller  $k$  values of hydrophobized gluten are attributed to less plasticization. The plasticizing effect of glycerol and sorbitol added to wheat gluten proteins is less prominent than the plasticizing effect of water (Pouplin et al. 1999). Due to the smaller molecular weights and smaller concentrations of hydrophilic amino acids in gliadin, the decrease of  $T_g$  for gliadin with added water was smaller than the decrease of  $T_g$  for gluten and glutenin (De Graaf et al. 1993). Plasticization of proteins by water is important, since plasticization affects the quality of protein-based edible films and food systems, and the stability of protein rich foods during frozen storage (Roos 1995a).

$T_m'$ ,  $T_g'$  and melting curve information for protein-rich foods is limited (Table 3).  $T_g'$  of selected plant proteins ranged from -15 to -30°C and was higher than the  $T_g'$  of sugars and fruit solids (Table 1 and 3).

Maximum-freeze-concentration conditions ( $T_g'$  and  $T_m'$ ) are not available for many plant protein systems. Future research is needed to develop state diagrams with melting curves and concentrations of unfrozen water in protein systems. Figure 14 presents a state diagram for zein (to water concentrations from 0 to 35%), developed using glass transition and pressure rheometry results (Kokini et al. 1995).

### **Animal Proteins**

Rheological, mechanical and calorimetric studies are conducted to analyze state transitions in animal proteins.  $T_{gs}$  values of selected animal protein foods range from 95 to 235°C, higher than the  $T_{gs}$  of sugars (Table 4). Hashimoto et al. (2004) reported the glass transition temperatures of whole fish muscle is less than the  $T_g$  of extracted proteins, probably due to the plasticizing effect of small molecular weight materials such as salts and sugars. Glass transition temperatures of dry fish proteins ranged from 130 to 180°C. Mean  $k$  values for animal protein systems range from 0.43 to 8.57 (Table 4). Cooling curve methods are used to obtain the freezing temperature depression of selected animal protein systems (Rahman et al. 2002). The data obtained from cooling curve methods is modeled using Chen, as well as the Clausius–Clapeyron equations in selected animal proteins (Sablani et al. 2004 and 2007b; Rahman et al. 2003). The Chen equation parameter  $E$  ranges from 0.0275 to 0.071, while parameter  $B$  ranges from 0.303 to 0.383 for selected animal protein systems.

Generally, the  $T_g'$  of animal proteins are lower than that of plant proteins (Table 3 and 4). However, Kalichevsky et al. (1993) reported that the  $T_g$  of casein is greater than the  $T_g$  of amylopectin or gluten at equivalent water content. The  $T_g'$  of selected animal proteins ranges from -44.3 to -11.3°C, while the  $T_m'$  for selected animal proteins ranges from -18 to -13.3°C (Table 4). The positive difference between  $T_g'$  and  $T_m'$  ( $T_g'-T_m'$ ) range from 4 to 40°C in selected animal protein systems. The quantity of unfrozen water in the selected animal protein systems ranges from 0.312 to 0.390 kg water/kg protein (Table 4). However, the quantity of unfrozen water for many animal protein systems is not available. Similar to starches, broad ranges in glass transition temperatures ( $T_{gi}-T_{ge}$ ) were observed in proteins, attributed to the complex molecular structure of proteins (Cuq et al. 1997). A state diagram of protein-rich abalone is presented in Figure 15. The  $T_g'$  and  $T_m'$  are -44.3 and -18°C, respectively.

Figure 16 presents the approximate ranges of  $T_m'$ ,  $T_g'$ ,  $X_s''$  and  $T_{gs}$  of starch, protein and sugar-based systems in a state diagram based on the data in Table 1-5. The  $T_g'$  and  $T_m'$  of many food constituents ranged from -5 to -70°C, while the  $T_{gs}$  ranged from 30 to 300°C. The unfrozen water of many food constituents varies between 20-30% (w.b.). Starches and proteins exhibit similar glass transition temperature ranges, while sugar systems exhibit a smaller range for glass transition temperatures.

### **Importance and Applications**

State diagrams of food systems can be used to optimize processing and storage conditions by analyzing their glass lines, conditions of maximum-freeze-concentration, and melting/freezing curves. Devitrification or glassy to rubbery transition is kinetic and promotes loss of quality and physiological activity in foods. Optimal processing conditions including temperature and relative humidity during selected food processing operations (e.g., freeze-drying, extrusion, baking, frying, freeze concentration, storage and cryopreservation) can be predicted using state diagrams of the dominating food constituents. Sorption isotherms in combination with state diagrams may be useful for predicting adequate packaging requirements, optimal temperatures and relative humidities during storage.

### **Physical Stability**

The major physical and structural deteriorative reactions that occur during processing and storage of foods are collapse of structure during freeze- and vacuum-drying (Bhandari & Howes 1999; Karathanos et al. 1993), stickiness of food powders during spray, hot air, and fluidized bed drying and storage (Bhandari & Howes 1999; Adhikari et al. 2005), caking of food powders during storage (Fitzpatrick et al. 2007), crystallization of sugar (Chiou & Langrish 2007; Shrestha et al. 2008), or loss of crispness (Roudaut et al. 2002). Caking and crystallization are time-dependent and irreversible, while collapse and stickiness development are time-independent (Maltini et al. 2003; Bhandari & Howes 1999).

The main reasons for collapse during or after dehydration and freeze-drying are low glass transition temperatures and high hygroscopicity, leading to undesirable quality attributes of foods (Roos 1997; Bhandari & Howes 1999; Krokida et al. 1998; Sablani & Rahman 2002). Most fruit solids exhibit a  $T_g'$  value between -10 and -60°C, and their collapse temperature is also in this temperature range. Maintaining

freeze-drying temperatures below the  $T_g'$  may avoid collapse and deterioration of the fruit structure. Sticking among food powder particles and the walls of containers often leads to poor product utility and productivity (Bhandari & Howes 1999).

The combined effect of temperature and water affects the cohesion and stickiness of sugar-rich food powders (Foster et al. 2006). For a storage temperature  $T$ , beyond a specific  $(T-T_g)$ , amorphous components of food powders are sticky even after short time periods (Paterson et al. 2005). The magnitude of positive  $(T-T_g)$ , rather than conditions resulting in differences between ambient and glass transition temperatures are important for the development of stickiness in amorphous lactose during processing and storage. Temperature and water in amorphous components of food powders affect plasticization and structural relaxation, resulting in sticky powders at a temperature called the sticky point temperature. Normally the  $(T-T_g)$  is not greater than 10-20°C, since the sticky point temperature of food powders occurs in this range (Bhandari & Howes 1999).

Aguilera et al. (1995) explained the stages of the caking phenomena in amorphous components of food powders. Positive values defining the differences between storage and glass transition temperatures  $(T-T_g)$  and relative humidity act as the driving forces that initiate caking over time. Fitzpatrick et al. (2007) indicated that the cake strength of skim milk powder increases considerably when the  $(T-T_g)$  is greater than 20°C. Along with glass transition temperature, many other factors such as time, storage temperature, water content and composition affect the caking behavior and cake strength of food powders.

Crystallization of sugars in carbohydrate-rich food systems is another concern of food technologists, since this adversely affects the physical quality, consumer acceptability, and acceptable shelf life of many foods. Amorphous components of food powders may crystallize over time to approach greater stability. The crystallized state is organized with regular lattice structures, unlike the randomly arranged amorphous glassy structures. During crystal formation, adsorbed water in amorphous powders is released, resulting in plasticization of the amorphous material. The release of adsorbed water increases the water activity of foods, resulting in potential physicochemical deterioration in foods. Crystallization is a kinetic phenomena, and the temperature at which crystallization occurs is between the glass transition temperature and melting temperature of the amorphous components (Le Meste et al. 2002). Suitable conditions to attain the crystallized state include high relative humidity (RH) and ambient temperature. As the difference between

storage temperature and glass transition temperature increases, the rate of release of adsorbed water from food increases, and crystallization occurs. Crystallization occurs at temperatures greater than and less than the glass transition temperature, but rates of crystallization are significantly different (Yu et al. 2008). Crystallization may be delayed by storing foods and pharmaceuticals at safe storage temperatures referred as zero mobility temperature ( $T_o$ ) (Hancock & Zografi 1997; Yu et al. 2008). It is assumed that at  $T_o$ , no molecular relaxations are observed.  $T_o$  also corresponds to the theoretical Kauzmann temperature of approximately 50 K below  $T_g$ . The value of  $T_o$  can be approximated with the Vogel-Tammann-Fulcher equation (Hancock & Zografi 1997). Along with this, storage time, food composition, and molecular weight can also affect food crystallization (Chiou & Langrish 2007). The rate of crystallization is slow for high molecular weight components. Crystallization of amorphous components of food powders results in reduced solubility over time. A number of studies report crystallization of amorphous lactose and components of skim milk powder at temperatures greater than their glass transition temperatures (Jouppila & Roos 1994; Jouppila et al. 1997). Lactose crystallization was observed in milk powders stored at temperatures greater than their glass transition temperatures or at critical water activities corresponding to their glass transition temperatures (Jouppila & Roos 1994). Like caking and stickiness, rate of crystallization also increases as water content or the difference between storage and glass transition temperature increases (Roos & Karel 1991a). Crystallization and wall deposition of spray dried food polymers may be reduced by producing spray dried food polymers at a temperature less than the glass transition temperature (Chiou & Langrish 2007).

Crispness is another sensory attribute that affects consumer acceptability. Loss of crispness in carbohydrate-rich foods during storage is related to depressed glass transition temperatures less than storage temperatures (Roudaut et al. 2002). High molecular weight additives such as maltodextrins and gum arabic are encapsulating ingredients mixed with fruit juices for the retention of volatile ingredients. These additives increase glass transition temperatures during dehydration and storage (Righetto & Netto 2005). The retention of volatiles in spray-dried microcapsules using mesquite gum reached the maximum when the microencapsulates were stored at temperatures lower than their  $T_g$  (Beristain et al. 2003). Spray-drying removes water and transforms food powders to the glassy state, improving flavor retention and reducing caking due to rapid drying and evaporative cooling (Zasytkin & Porzio 2004).



By controlling the processing and storage temperature ( $T$ ) of foods well below the glass transition temperatures and by adding high molecular weight ingredients with high  $T_g$ , adverse structural changes can be prevented to ensure acceptable food quality (Karel et al. 1994). The temperature regions where stickiness, collapse, and crystallization occur can be represented in a state diagram (Maltini et al. 2003). Maximum utilization of state diagrams is made by choosing optimum temperature and water concentrations to avoid detrimental effects of structural changes. Sorption isotherms and state diagrams along with ( $T-T_g$ ) may be used to predict the physical stability of foods during processing, transport, packaging and storage (Fitzpatrick et al. 2007).

### **Chemical Stability**

Molecular motions are reduced considerably and the rates of chemical reactions are also reduced in the glassy state of food polymers (Shimada et al. 1991). Several chemical and biochemical reactions in foods such as sucrose hydrolysis (Buera et al. 1995; Schebor et al. 1995), enzyme inactivation (Schebor et al. 1996; Chen et al. 1999a and b), non-enzymatic browning (Karmas et al. 1992; Bell 1995), vitamin degradation (Bell & White 2000; Sablani et al. 2007a), protein denaturation (Bell & Hageman 1996; D'Cruz & Bell 2005) and oxidation (Labrousse et al. 1992; Shimada et al. 1991; Drusch et al. 2006) are investigated in relation to glass transition temperatures and water mobility. The rates of many chemical reactions are influenced by water concentrations in foods. For example, rates of thiamin and vitamin C degradation, lipid oxidation and the Maillard reaction increase as water concentrations increase, and can be predicted by the glass transition temperatures and physical states of foods (Bell et al. 1998; Bell & White 2000; Drusch et al. 2006; Sablani et al. 2007a). However, several studies indicate that selected chemical reactions occur in the glassy state, suggesting that  $T_g$  alone cannot be considered an absolute threshold temperature for the chemical stability of foods. The influence of glass transition temperature on selected chemical reactions is not clear, because water exhibits multiple functions in foods as a plasticizer, solvent, reactant or product of chemical reactions (Buera et al. 1995). The analysis of the impact of  $T_g$  on water mobility and chemical stability of polyvinylpyrrolidone (PVP) by nuclear magnetic resonance indicates that water mobility is not influenced by  $T_g$  (Bell et al. 2002). Water mobility was observed in the glassy state of the PVP model system. Moreover, Bell et al. (2002) reported that water mobility in the food system cannot

be used as an indicator to explain the chemical stability of foods. Glass transition temperatures and the physical state of a system are not the only way to clarify complex chemical degradation reactions in food systems. Other factors, such as food constituents and constituent concentrations, play a major role in predicting and explaining deterioration resulting from chemical reactions.

### **Microbial Stability**

Water activity is considered the single most valuable parameter in defining the microbial stability of intermediate and low-moisture foods. Foods with low water activities are normally in the amorphous glassy state, and the glassy state or low water activity may contribute to microbial stability. Slade and Levine (1987) suggested that the glass transition concept or water dynamics may provide an alternative to water activity for the prediction of the microbial stability of low-moisture and intermediate-moisture foods. Chirife and Buera (1994) concluded that the glass transition concept is not useful in predicting microbial growth in foods. They explained that water activity is a solvent property, whereas the glassy state is a solute and structure-related property, and both water activity and physical state in foods are required for understanding food-water relationships. Buera et al. (1998) reported the presence of xerophilic molds in white bread in the glassy state stored at adequate water activities. They suggested that glassy and rubbery states may exist in food matrices with incompatible constituents. Chirife and Buera (1994) indicated that molds may grow in substrates of relatively high  $T_g$  due to the presence non glassy microregions. Champion et al. (2000) also indicated that macroscopic heterogeneities in food materials can induce areas with greater water mobility. It is unlikely that the glass transition concept defining biopolymer mobility will be an adequate predictor of water activity, water mobility, microbial growth and survival, or food safety. Additional studies are needed to probe the utility of the glass transition concept to explain microbial stability.

### **Frozen Food Stability**

Temperatures below  $T_g'$  are desirable for safe storage of high water-content food systems, since they consist of ice, glass and solute. (Champion et al. 2000; Roos et al. 1991c). The  $T_g'$  of most foods ranges from -10

to  $-70^{\circ}\text{C}$ . It may not be economically feasible or practical to store sugar-rich foods such as fruits at temperatures below their  $T_g'$  ( $-40$  to  $-70^{\circ}\text{C}$ ). Maximum ice formation in the food systems during freezing takes place when systems are stored between their  $T_m'$  and  $T_g'$ . At temperatures greater than  $T_m'$ , the food system may be plasticized by the melting of ice. This condition may result in a partial-freeze-concentration in the matrix and may not be suitable for long-term storage of foods. Both  $T_m'$  and  $T_g'$  are independent of initial food solids concentration (Goff & Sahagian 1996). The unfrozen water plasticizes the freeze-concentrated food matrix, so the quantity of unfrozen water provides valuable information for stable frozen storage of foods (Roos 1995a). Unfrozen water is available to the solutes in the food system, unlike bound water, which is structurally and chemically bound to the solutes and unavailable for reactions. Ice recrystallization in foods may be reduced and food quality may be improved by storing the foods below their glass transition temperature (Rahman 1995).  $T_m'$  and  $T_g'$  are important in cryostabilization and cryoprotection of foods at varied process and storage conditions. Reaction rates may be a function of  $(T - T_g')$  and may increase with an increase in  $(T - T_g')$ , where  $T$  is the storage temperature.

Ferrero and Zaritsky (2000) studied the amylopectin retrogradation and textural changes in frozen starch-sucrose-water systems after slow freezing and frozen storage. Amylopectin retrogradation was observed at storage temperature greater than  $T_g'$ . The addition of hydrocolloids such as gums did not inhibit the amylopectin retrogradation. Akkose and Aktas (2008) reported that the total volatile basic nitrogen (TVB-N) and the thiobarbituric acid-reactive substances (TBARS) in ground beef differed significantly when stored above the  $T_g'$  for six months. However, storage studies of anthocyanins and soluble phenols in berry juices during frozen storage (between  $-10$  to  $-30^{\circ}\text{C}$ ) for six months showed that the stability of anthocyanins and soluble phenols are influenced by storage temperature and storage time (Rizzolo et al. 2003). The glass transition temperature of maximum-freeze-concentrated phases exhibited no influence on the stability of anthocyanins and soluble phenols. Torreggiani et al. (1999) reported that no simple relationship was observed between anthocyanin loss in strawberry juices and the difference in the storage and glass transition temperature of maximally freeze concentrated phase ( $T_g'$ ). Other factors such as freeze concentration level and pH may play a role in the anthocyanin stability in strawberry juice (Torreggiani et al. 1999). Terefe and Hendrickx (2002) reported that the kinetics of pectin methylesterase catalyzed de-esterification of pectin were less influenced by  $T_g'$ . Therefore, glass transition temperature may not be the

single parameter controlling the frozen storage stability of foods, and more critical studies on stability of foods during frozen storage are needed.

### **Other Applications**

Kaletunc and Breslauer (1996) demonstrated the use of state diagrams in characterizing the physical states of wheat flour in selected unit operations prior to or during extrusion processing. They explained the influence of post-extrusion storage conditions on the state of extrudate by using a state diagram. State diagrams identify the temperature and water content at which the protein components of extruded or baked products become crispy by changing the glassy state (Kokini et al. 1994). Adulteration of honey, milk and fruit juices may be identified using the glass transition temperature concept analyzed by DSC (Cordella et al. 2002; Goswami & Gupta 2008). Including sorption isotherms in a single, modified state diagram can help researchers analyze, design and optimize process conditions, and select the packaging and storage environments (Rahman, 2006). The glass transition concept is applied to select the appropriate processing conditions such as drying temperature, relative humidity for maximum head rice yield and milling quality. The head rice yield decreases when drying is conducted in the rubbery state without tempering (Yang et al. 2003; Yang and Jia 2004; Cnossen et al. 2002).

### **Summary and Future Research**

State diagrams describing the physical states and state transitions of foods can function as significant tools to help food scientists, food engineers and food packaging researchers develop processing protocols and determine storage conditions. Various thermal analytical and spectroscopic techniques are available for modeling and characterizing food components and relating observed transitions to food stability. This article described methods for determining and understanding state transitions of food component mixtures. Calorimetric determinations are the most common methods for characterization of phase/state transitions in food systems. Mechanical determinations combined with the free volume theory provide mechanistic understanding of rubber to glass transition in biomaterials. Spectroscopic methods such as NMR and EPR are used less often, yet they help researchers directly probe molecular mobility. Glass transition temperatures are often perceived as dependent on the method of observation and not well defined. There

are some discrepancies in  $T_g$  determined using selected analytical techniques, since each technique probes material properties at atomic, micro and macro scales to identify glass transition temperatures. More research is needed to develop standard experimental protocols for characterization of accurate glass transition temperatures with each determination technique.

We presented state diagrams for many pure food ingredients. State diagrams including glass transition and freezing curve data are mainly limited to fruits. Significant variations in glass transition temperatures obtained for the same food constituents are attributed to differences in determination techniques. Therefore, it is difficult to generalize and use the state diagrams for the design of processes and storage conditions. We also presented glass transition temperature data for proteins and carbohydrates, but little information is available related to melting and the condition of maximum-freeze-concentration ( $T_m'$  and  $T_g'$ ). Large molecular weight solutes increase the glass transition temperature ( $T_g$ ), initial melting point,  $T_g'$  and  $T_m'$  of foods. The glass transition temperature concept is used to predict physical changes including crystallization, caking, stickiness and collapse; however the relationship of glass transition temperature to chemical reactions is not clear. A better fundamental understanding of the kinetic state of food biopolymers and information on the factors affecting the chemical reactions in foods is needed. A limited number of studies report chemical stability in high moisture foods stored below  $T_m'$  and  $T_g'$ . The molecular mobility in foods below the glass transition temperature is characterized by using an enthalpy or mechanical relaxation method. This may elucidate rates of biopolymer reactions in the glassy state. Due to limited information on the relaxation kinetics of food materials, the relationship of relaxation kinetics to food stability is still largely unexplored. The use of state diagrams that include glass transition temperatures, melting curve data, and relaxation kinetics data can help improve the processing and storage of food materials.

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## LEGENDS TO FIGURES

- Figure 1 A typical state diagram presenting selected regions and states of food systems. The state diagram presents glass line (dependence of  $T_g$  on water content), freezing curve (freezing point depression), solubility,  $T_{bw}$ , boiling point;  $T_{ms}$ , melting point of dry solids;  $T_u$ , eutectic point;  $T_m'$ , onset ice melting temperature in a maximally freeze concentrated solution;  $T_g'$ , glass transition temperature in a maximally freeze concentrated solution;  $T_{gs}$ , glass transition temperature of dry solids.
- Figure 2 A three dimensional dynamic map or dynamic state diagram presenting equilibrium and nonequilibrium regions of food systems in relation to the temperature, solids content and time. The kinetic dependence of nonequilibrium thermodynamics of food systems may be described using a dynamic map (Adapted from Slade and Levine, 1988b).
- Figure 3a DSC thermogram of amorphous raspberry solids presenting heat flow versus temperature curves during desorption at selected water activities ( $a_{wl} = 0.113$  to  $0.86$ ) where  $T_{gi}$  = initial glass transition temperature. Glass transition temperature decreased as water activity increased. At higher water activities, the melting endotherms were observed indicating the presence of ice where  $\Delta H$  is the enthalpy of melting. (Syamaladevi et al. 2010)
- Figure 3b A typical MDSC thermogram presenting total heat flow, reversing heat flow and non-reversing heat flow versus temperature  $T_{gi}$  = initial glass transition temperature, and  $T_{ge}$  = end point glass transition temperature
- Figure 4 A typical DMTA thermogram presenting  $E'$ ,  $E''$  and  $\tan \delta$  versus temperature
- Figure 5a A schematic diagram presenting the variation of  $G'$ ,  $G''$  and  $\tan \delta$  with temperature in a biopolymer mixture containing 5% gelatin, 25% sucrose and 50% glucose syrup
- Figure 5b A schematic diagram presenting the deviation of  $\log a_T$ , first derivative of  $\log G'$  and  $\log G''$  with temperature
- Figure 6 A typical TMCT thermal mechanical responses during glass transitions. Glass transition temperature ( $T_g$ ) is observed at the temperature where sudden change in displacement occurs.  $T_g$  is determined using the data points below transition and linear regression equation of the data points above transition (Adapted from Boonyai et al. 2007).
- Figure 7 A schematic diagram presenting NMR state diagram presenting spin-lattice relaxation time ( $T_1$ ) and spin-spin relaxation time ( $T_2$ ) of solids as a function of temperature. A sudden decrease in  $T_1$  to certain temperature ( $T_{RLL}$ ) and a sudden increase is observed. The change in  $T_2$  is small at low temperatures while a sudden increase in  $T_2$  is observed after a certain temperature ( $T_{RLL}$ ) (Adapted from Lin et al. 2006)
- Figure 8 A schematic diagram presenting  $\log \tau_R$  as a function of temperature by ESR study. Glass transitions observed ( $T_{g1}$  and  $T_{g2}$ ) for different water contents ( $X_{w1}$  and  $X_{w2}$ )



- Figure 9 A typical DSC thermogram of food systems with freezable water presenting ice melting temperature ( $T_m$ ) taken as the peak temperature of melting endotherm and onset of ice melting temperature ( $T_m'$ ) taken as the intersection point of the baseline with the left side of the endotherm.
- Figure 10 A typical cooling curve presenting initial freezing point ( $T_F$ ) and onset of ice melting ( $T_m'$ ). At point *a* sudden increase in the temperature due to the release of latent heat to point *b*, considered the initial freezing temperature ( $T_F$ ). The point *c* greatest slope of the cooling curve is observed, is considered as the onset of ice melting ( $T_m'$ ).
- Figure 11 State diagram of sucrose presenting glass line and freezing curve;  $T_m'$ , onset ice melting temperature in a maximally freeze concentrated solution;  $T_g'$ , glass transition temperature in a maximally freeze concentrated solution;  $X_s''$ , solids content corresponding to  $T_g'$  (Adapted from Roos and Karel 1991c)
- Figure 12 State diagram of raspberry solids presenting glass line and freezing curve;  $T_m'$ , onset ice melting temperature in a maximally freeze concentrated solution;  $T_g'$ , glass transition temperature in a maximally freeze concentrated solution (Adapted from Syamaladevi et al. 2009).
- Figure 13 State diagram of gelatinized corn starch presenting glass line;  $T_m'$ , onset ice melting temperature in a maximally freeze concentrated solution;  $T_g'$ , glass transition temperature in a maximally freeze concentrated solution; (Adapted from Jouppila and Roos 1997)
- Figure 14 State diagram of zein presenting various transitions including glass to rubber, rubber to entangled polymer flow; the increase in temperature and water results in enhancement of mobility, reaction rate and softening of zein system (Adapted from Madeka and Kokini 1996).
- Figure 15 State diagram of abalone proteins presenting glass line and melting curve;  $T_m'$ , onset ice melting temperature in a maximally freeze concentrated solution;  $T_g'$  (Adapted from Sablani et al. 2004).
- Figure 16 State diagram presenting  $T_g'$ ,  $T_m'$ ,  $T_{gs}$ ,  $X_s''$  and  $X_s'$  range of food systems with selected major constituents.  $T_g'$ ,  $T_m'$ ,  $T_{gs}$  values of sugars and fruit solids are the lowest among the group while food systems with large molecular weight components such as starches and proteins have greater  $T_g'$ ,  $T_m'$ ,  $T_{gs}$  values.  $X_s''$  and  $X_s'$  values of sugars appear to have a broad range.

Table 1. Glass line and melting curve data of sugars and sugar systems

Product	Glass line				Freezing curve		References
	$T_g'$ (°C)	$X_s'$ (kg dry solids/kg food)	G-T model parameter $T_{gs}$ (°C)	G-T model parameter $k$	$T_m'$ (°C)	$X_s'$ (kg dry solids/kg food)	
Arabinose	-66	0.793	-2	3.55	-53	0.793 <sup>1</sup>	Roos (1993b)
Ribose	-67	0.814	-20	3.02	-53	0.814 <sup>1</sup>	Roos (1993b)
Xylose	-65	0.789	6	3.78	-53	0.789 <sup>1</sup>	Roos (1993b)
Fructose	-57	0.825	5	3.76	-46	0.825 <sup>1</sup>	Roos (1993b)
Fucose	-62	0.784	26	4.37	-48	0.784 <sup>1</sup>	Roos (1993b)
Galactose	-56	0.805	30	4.49	-45	0.805 <sup>1</sup>	Roos (1993b)
Glucose	-57	0.8	31	4.52	-46	0.800 <sup>1</sup>	Roos (1993b)
Mannose	-58	0.801	25	4.34	-45	0.801 <sup>1</sup>	Roos (1993b)
Rhamnose	-60	0.828	-7	3.4	-47	0.828 <sup>1</sup>	Roos (1993b)
Sorbose	-57	0.810	19	4.17	-44	0.810 <sup>1</sup>	Roos (1993b)
Maltitol	-47	0.829	39	4.75	-37	0.829 <sup>1</sup>	Roos (1993b)
Sorbitol	-63	0.817	-9	3.35	-49	0.817 <sup>1</sup>	Roos (1993b)
Xylitol	-72	0.802	-29	2.76	-57	0.802 <sup>1</sup>	Roos (1993b)
Glucitol	-63	0.817	-9	3.35	-49	0.817 <sup>1</sup>	Roos (1993b)
Lactose	-41	0.813	101	6.56	-30	0.813 <sup>1</sup>	Roos (1993b)
Lactose	28	0.592	-	-	-	-	Slade and Levine (1991)
Maltose	-42	0.816	87	6.15	-32	0.816 <sup>1</sup>	Roos (1993b)
Maltose	-29.5	0.8	-	-	-	-	Slade and Levine (1991)

Melibiose	-42	0.817	85	6.1	-32	0.817 <sup>1</sup>	Roos (1993b)
Melibiose	-30.5	-	-	-	-	-	Slade and Levine (1991)
Sucrose	-46	0.817	62	5.42	-34	0.817 <sup>1</sup>	Roos (1993b)
Sucrose	-32	0.641	-	-	-	-	Slade and Levine (1991)
Trehalose	-40	0.816	100	6.54	-30	0.816 <sup>1</sup>	Roos (1993b)
Trehalose	-29.5	0.833	-	-	-	-	Slade and Levine (1991)
Sucrose	-46	0.800	65	4.9	-35	-	Singh and Roos (2005)
Sucrose/Albumin (1:1)	-50	0.810	121	8.5	-30	-	
Sucrose/Gelatin (1:1)	-54	0.760	95	5.9	-26	-	
Sucrose/Corn Starch (1:1)	-48	0.760	83	4.9	-25	-	
Sucrose/Gelatin / Corn Starch (1:1:1)	-49	0.760	124	6.2	-24	-	
Dried banana	-	-	Two glass transition temperatures were detected. $T_{gs1} = 46 \pm 1$ and $T_{gs2} = 0 \pm 1$	$k_f = 1.6 \pm 0.2$ and $k_s = 0.9 \pm 0.1$	-	-	Katekawa and Silva (2007)
<sup>2</sup> Dates	-50	0.700	57.4	3.2	-	-	Kasapis et al. (2000)
Fructose	-48	0.790	-	-	-	-	Ablett et al. (1993)
Air dried apple at 30 C	-	-	-8.7	2.6	-	-	Welti-Chanes et al. (1999)
Air dried apple at 60 C	-	-	-1.9	3.6	-	-	
Freeze-dried apple	-	-	-13.3	2.7	-	-	
Freeze-dried apple juice	-	-	-16.3	2.4	-	-	
Freeze-dried Raspberry	-61.6	0.780	42.6	4.73	-38	0.780	Syamaladevi et al. (2009)
Freeze-dried pineapple	-51.6	-	57.9	0.21	-52	0.700	Telis and Sobral (2001)
Dried apple	For food	0.736	For food	3.59	-50.3	-	Bai et al. (2001)

slices	containing non-freezable water $T_g = -55.08$  For food containing freezable water (without annealing), $T_g = -59.7 \pm 1.7$		containing non-freezable water $T_{gs} = 41.3$  For food containing freezable water (without annealing), $T_{gs} = 70.07$	1.5			
Freeze dried plums	-57.5	-	102.7	3.76	-	-	Telis et. al. (2006)
Fresh and freeze dried Chinese gooseberry	-57.2	-	23.2	5.72	-41.8	-	Wang et.al. (2008)
Freeze dried garlic	-38.6	-	40.1	3.7	-24	-	Rahman et.al. (2005)
Freeze dried apple	-	-	-1.70	2.34	-	-	del Valle et al. (1998)
Freeze dried camu camu	-58.8 °C and -40.1 °C for natural pulp and pulp with maltodextrin, respectively	-	74.59 for natural fruit 125.45 for fruit with 30% maltodextrin	3.92 for natural fruit 5.52 for fruit with 30% maltodextrin	-	-	Silva et al. (2006)
Freeze dried and air dried tomato	-59 ±3 for freeze dried tomato	0.59	330.9 142.7	9.35 for freeze-dried and 6.10 for air dried tomato with osmotic pretreatment	-	-	Telis and Sobral (2002)
Freeze dried onion, grape and strawberry	-58.3 for onion -50.3 for grape -50.1 for strawberry	0.751 for onion, 0.803 for grape and 0.816 for strawberry		4.3, 3.3 and 4.0 for onion, grape and strawberry respectively	-	-	Sa and Sereno (1994)
Date flesh	-46.4	0.762	63.8	4.0	-43.6	-	Rahman (2004)
Freeze dried strawberries	-	-	34.2	3.52	-	-	Khalloufi et al. (2000)
blueberries	-	-	22.0	4.02	-	-	
raspberries	-	-	47.8	2.85	-	-	
blackberries	-	-	40.2	4.12	-	-	
Spray dried tomato pulp	-	-	139.8	6.69	-	-	Goula et al. (2008)

Honey	-60.5 for Tree honey from Germany -62.5 for and mixed floral honey from Hungarian source	-	-	-	-	-	Kantor et al. (1999)	
Honey		-	15	3.14	-	-	Lazaridou et al. (2004)	
Surimi-Trehalose mixture			123	5	-	-	Ohkuma et al. (2008)	
Trehalose		-	107	6.5	-	-	Roos (1995b)	
water extractable arabinoxylans (WEA)	-17 for high molecular weight and -35 for low molecular weight	-	-	-	-	-	Fessas and Schiraldi (2001)	
Maltose		-41	0.825 <sup>3</sup> , 0.752 <sup>4</sup>	87	6	-31	0.825 <sup>1</sup>	Roos and Karel (1991b)
Maltodextrins with different dextrin equivalents (DE) M365		-43	0.794 <sup>3</sup> , 0.781 <sup>4</sup>	100	6	-28	0.794 <sup>1</sup>	
M200		-31	0.797 <sup>3</sup> , 0.787 <sup>4</sup>	141	6.5	-19	0.797 <sup>1</sup>	
M100		-23	0.811 <sup>3</sup> , 0.781 <sup>4</sup>	160	7	-13	0.811 <sup>1</sup>	
M040		-15	0.729 <sup>3</sup> , 0.794 <sup>4</sup>	188	7.7	-11	0.729 <sup>1</sup>	

<sup>1</sup> $X_s'$  and  $X_s''$  are equivalent in the study

<sup>2</sup>Rheological test under low amplitude oscillatory shear

<sup>3</sup>From Gordon-Taylor model

<sup>4</sup>From extrapolated  $\Delta H_m$  values

Table 2. Glass line and melting curve data of starch systems

Product	Glass transition curve				Freezing curve		References
	$T_g'$ (°C)	$X_s'$ (kg dry solids/kg food)	G-T model parameter $T_{gs}$ (°C)	G-T model parameter $k$	$T_m'$ (°C)	$X_s'$ (kg dry solids/kg food)	
Extruded wheat	-	-	281	-	-	-	Bindzus et al. (2002)
Extruded corn	-	-	281	-	-	-	
Extruded rice starch	-	-	281	-	-	-	
Corn starch	-11	0.730	243	5.6	-11	0.730	Jouppila and Roos (1997)
Yellow corn cakes	-	-	128 for yellow corn cakes	2.58 for yellow corn cakes	-	-	Li et al. (1998)
White corn cakes	-	-	115 for white corn cakes	2.39 for white corn cakes	-	-	
Gelatinized waxy corn starch	-6	0.730	-	-	-6	-	Roos and Karel (1991b)
Gelatinized Corn starch	-	-	277.8	5.7	-	-	Zhong and Sun (2005)
Gelatinized wheat starch	-5	0.730	-	-	-5	-	Slade and Levine (1988a)
<sup>1</sup> Wheat semolina	-	-	$T_{gs}$ values are 162, 176 and 225 for heating, cooling and reheating respectively.	$k$ values are 3.4, 4.2 and 5.5 respectively for heating, cooling and reheating respectively	-	-	Cuq and Lcard-Verniere (2001)
cooked rice stick noodles	-4.0	-	-	-	-	-	Israkarn and Charoenrein (2006)
<sup>2</sup> Amylopectin-water mixture	-7.0	0.715	227	4.0	-	-	Brent et al. (1997)
Zein-water mixture	-48.0	0.815	137	-	-	-	
Extruded corn meal	-3	0.700	-	-	-	-	
Native corn starch	-6.6	-	-	-	-	-	Chung et al. (2004)

<sup>3</sup> Pea starch (Amylose:Am ylopecin = 2:1)	-	-	75	-	-	-	De Graaf et al. (2003)
Potato Starch (Amylose:Am ylopecin = 1:4)	-	-	152	-	-	-	
Wheat Starch (Amylose:Am ylopecin = 1:4)	-	-	143	-	-	-	
Waxy maize (Amylose:Am ylopecin = 1:99)	-	-	158	-	-	-	
Starch based wafers	-	-	133	5.54	-	-	Martinez- Navarrete et al. (2004)
<sup>4</sup> Rice	-11.6	-	158.5	6.38	-3.6	0.600	Sablani et al. (2009)

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<sup>1</sup>MDSC <sup>2</sup>DSC and DMTA <sup>3</sup>DMTA <sup>4</sup>Cooling curve

Table 3. Glass line and melting curve data of plant proteins

Product	Glass curve				Freezing curve		References
	$T_g'$ (°C)	$X_s'$ (kg dry solids/kg food)	G-T model parameter $T_{gs}$ (°C)	G-T model parameter $k$	$T_m'$ (°C)	$X_s'$ (kg dry solids/kg food)	
<sup>1</sup> Native wheat gluten hydrophobized wheat gluten gliadin and glutenin-rich fractions	-	-	173 for native gluten 174 for hydrophobized gluten 162 for gliadin rich fractions 175 for glutenin rich fractions	5.10 for native gluten 4.69 for hydrophobized gluten 4.48 for gliadin rich fractions 5.26 for glutenin rich fractions	-	-	Micard and Guilbert (2000)
<sup>2</sup> Wheat gluten plasticized with water, glycerol and sorbitol	-	-	187 for that plasticized by water, 187 for that plasticized by glycerol 187 for that plasticized by sorbitol	4.85 for that plasticized by water, 2.2 that plasticized by glycerol, 2.4 for that plasticized by sorbitol by Couchman-Karasz model	-	-	Pouplin et al. (1999)
<sup>2</sup> Gliadin	-	-	121.4	3.6	-	-	De Graaf et al. (1993)
High molecular weight glutenin	-	-	139	5	-	-	Noel et al (1995)
Alkylated glutenin	-	-	138	4.3	-	-	
$\alpha$ -gliadin	-	-	144	4.6	-	-	
$\gamma$ -gliadin	-	-	124	3.8	-	-	
$\omega$ -gliadin	-	-	145	4.2	-	-	
<sup>2</sup> Gluten	-	-	162	0.2	-	-	Kalichevsky et al. (1992)
<sup>3</sup> Wheat gluten	-20	0.760	127.6 $\pm$ 4.1	3.9 $\pm$ 0.24	-	-	Toufeili et al. (2002)
Green peas	-26 for young green peas -20 for old green peas	-	-	-	-	-	Lim et al. (2006)
Soy globulin (7S and 11S)	-67 for 7S globulin -17 for 11S globulin	-	114 and 6.72 160 and 6.66	6.72 6.66	-	-	Morales and Kokini (1999)
Gluten Soya protein	-	-	161.9 and 4.93 172.0 and 4.42	4.93 and 4.42	-	-	Bengoechea et al. (2007)



Sunflower protein	-	-	179	5.16	-	-	Rouilly et al. (2001)
Zein	-	-	139	6.24	-	-	Madeka and Kokini (1996)

<sup>1</sup>MDSC <sup>2</sup>DMTA <sup>3</sup>Mechanical spectrometry and pressure Rheometry

Table 4. Glass line and melting curve data of animal proteins

Product	Glass line				Freezing curve		References
	$T_g'$ (°C)	$X_s'$ (kg dry solids/kg food)	G-T model parameters $T_{gs}$ (°C)	G-T model parameters $k$	$T_m'$ (°C)	$X_s'$ (kg dry solids/kg food)	
Chicken meat	-16.8	0.924	-	-	-	-	Delgado and Sun (2002) Cuq et al. (1997)
<sup>1</sup> Myofibrillar proteins	-	-	235	6.06	-	-	
<sup>1</sup> Casein and Sodium Caseinate	-	-	144 for casein 130 for Sodium Caseinate	0.43 for casein 0.76 for Sodium Caseinate	-	-	Kalichevsky et al. (1993)
Mackerel	-13.3±0.5	-	-	-	-	-	Brake and Fennema (1999)
Cod	-11.7±0.6	-	-	-	-	-	
Beef muscle	-12.0±0.3	-	-	-	-	-	
King fish muscle	$T_g'$ varied from -21.4 to 25.5	0.688	-	-	-17.4	0.688	Sablani et al. (2007c)
<sup>3</sup> Tuna meat	-54.2	0.610	95.1	2.89	-13.3	0.610	Rahman et al. (2003) Sablani and Kasapis (2006)
<sup>3</sup> Freeze dried shark	-	-	152	5.35	-	-	
<sup>3</sup> Abalone	-44.3	0.680	-	-	-18	0.680	Sablani et al. (2004)
Whole milk powder	-	-	100.6	8.57	-	-	Vuataz (2002)
Skim milk powder	-	-	101	6.5	-	-	
Ovalbumin	-	-	207	-	-	-	Katayama et al. (2008)
Ribonuclease A	-	-	183	-	-	-	
Hydroxyl ethyl starch	-	-	225	-	-	-	
<sup>2</sup> Casein	-	-	206.4	4.97	-	-	Bengoechea et al. (2007)
<sup>3</sup> Gelatin	-	-	161	6.1	-	-	Kasapis and Sablani (2005)

<sup>1</sup>DMTA <sup>2</sup>PTA <sup>3</sup>Rheological Analysis

Table 5. Glass line and melting curve data of other polysaccharides/protein systems

Product	Glass line				Freezing curve		References
	$T_g'$ (°C)	$X_s'$ (kg dry solids/kg food)	G-T model parameter $T_{gs}$ (°C)	G-T model parameter $k$	$T_m'$ (°C)	$X_s'$ (kg dry solids/kg food)	
Chitosan	-	-	367.9	1.68	-	-	Lazaridou and Biliaderis (2002)
Starch-Chitosan mixture	-	-	363.7	1.97	-	-	
Pullulan Chitosan mixture	-	-	353.5	1.72	-	-	
<sup>1</sup> Pullulan	-	-	476.6 and 4.83 for DMTA	-	-	-	Diab et al. (2001)
Pullulan/sorbitol (P/S, 85:15 w/w)	-	-	425 and 3.78 for DSC	-	-	-	
Pullulan/sorbitol/sucrose (80:15:5)	-	-	422.6 and 3.55 for DMTA 375 and 3.33 for DSC	-	-	-	
			373.8 and 3.08 for DMTA 332.1 and 3.12 for DSC	-	-	-	

<sup>1</sup>DMTA

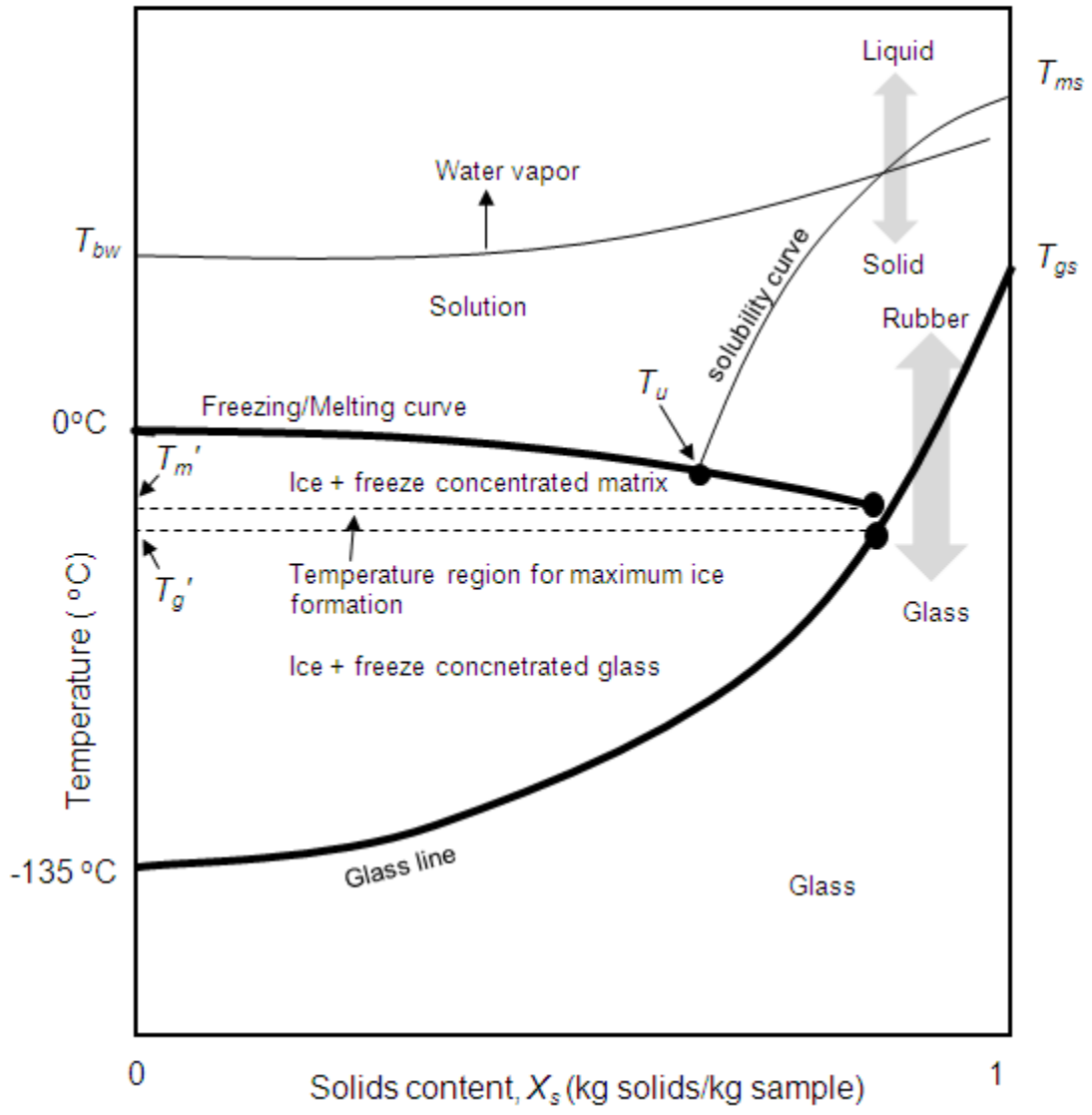


Figure1

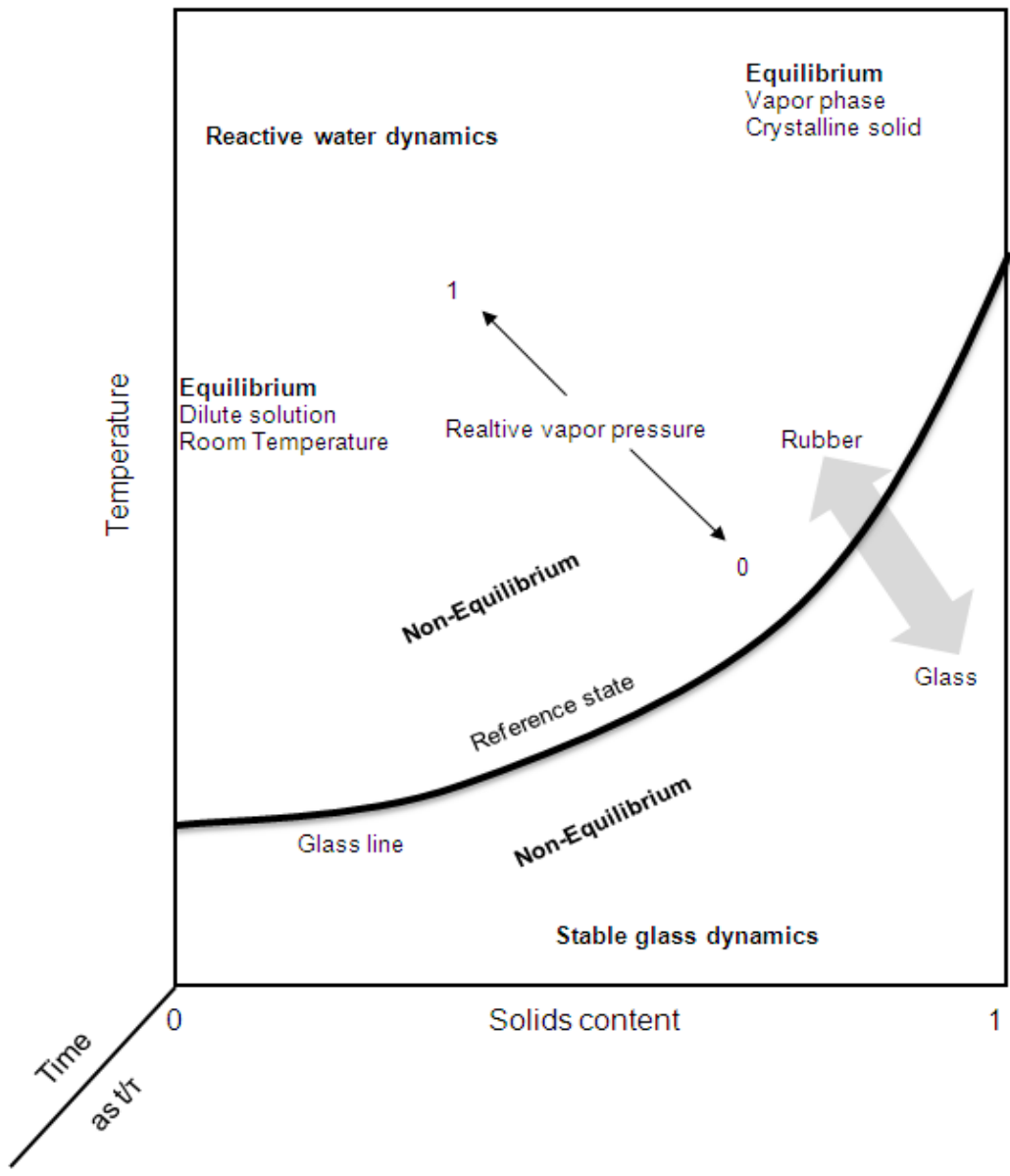


Figure 2

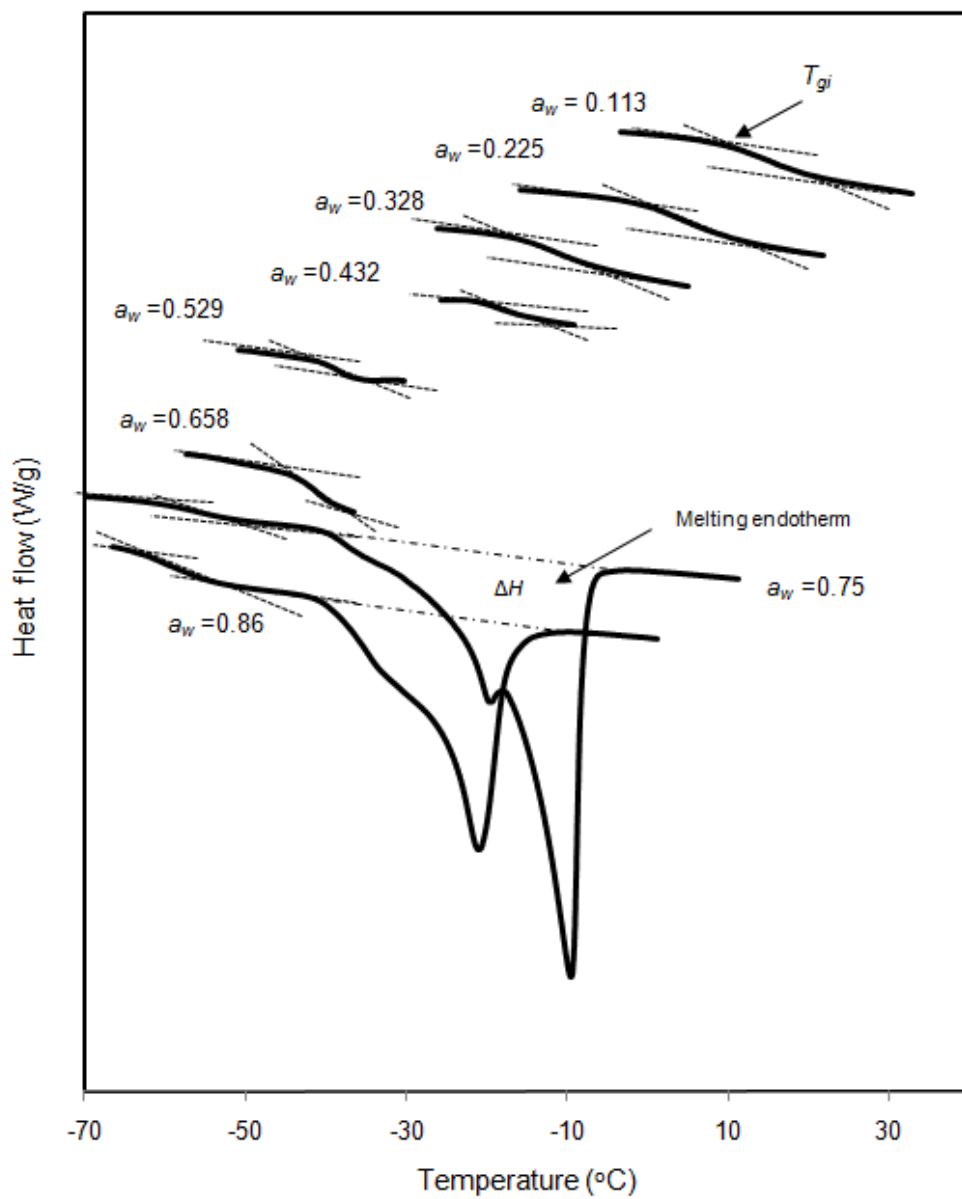


Figure 3a

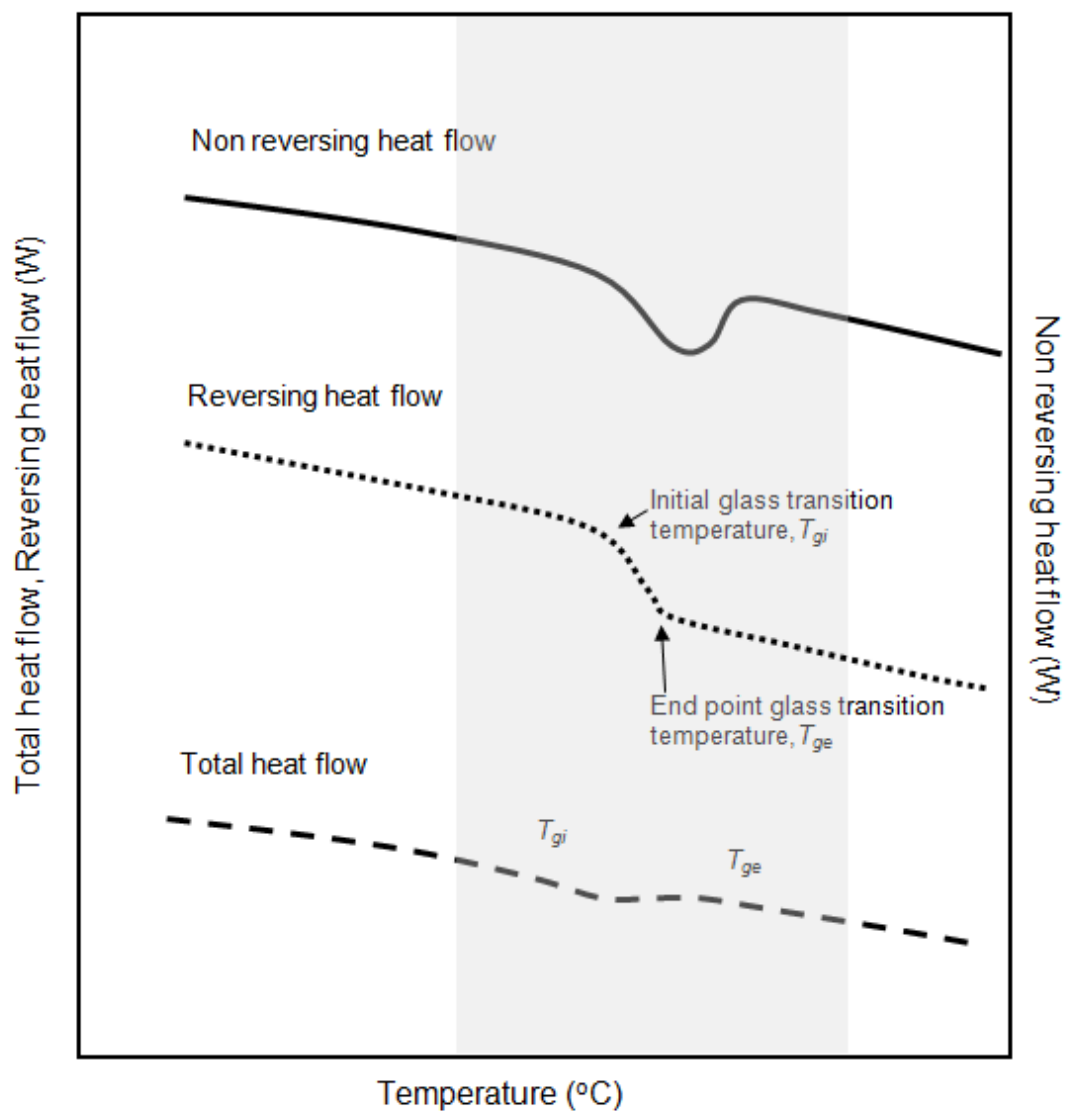


Figure 3b

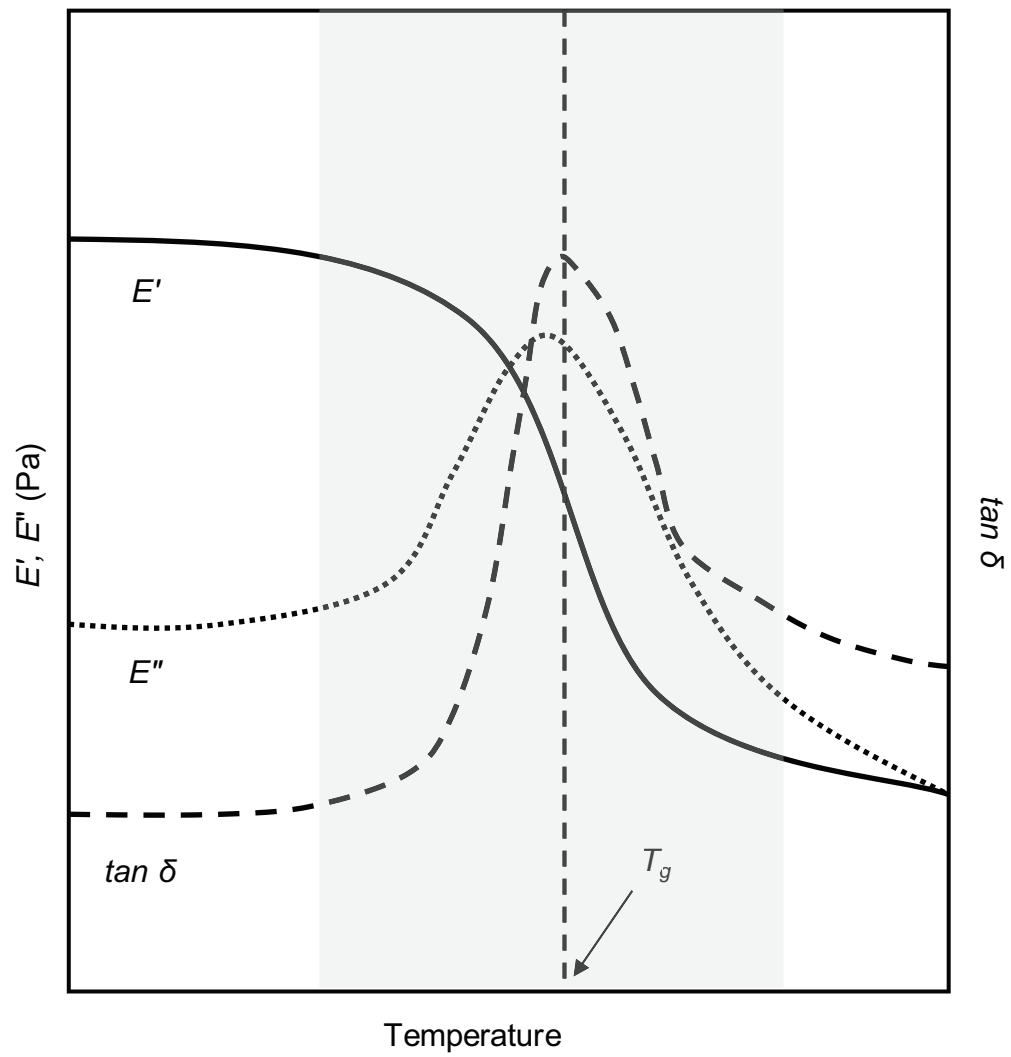


Figure 4



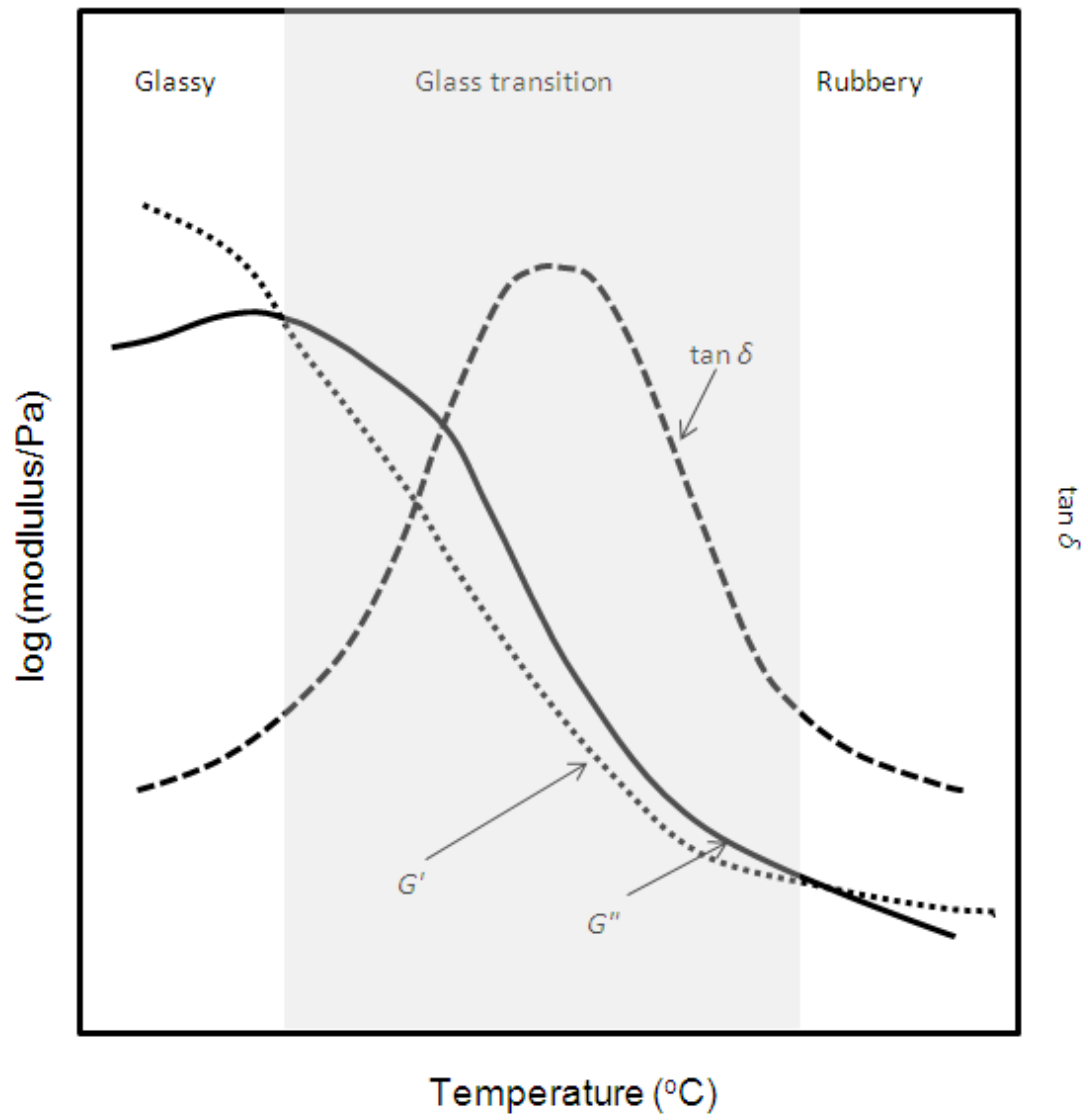


Figure 5a

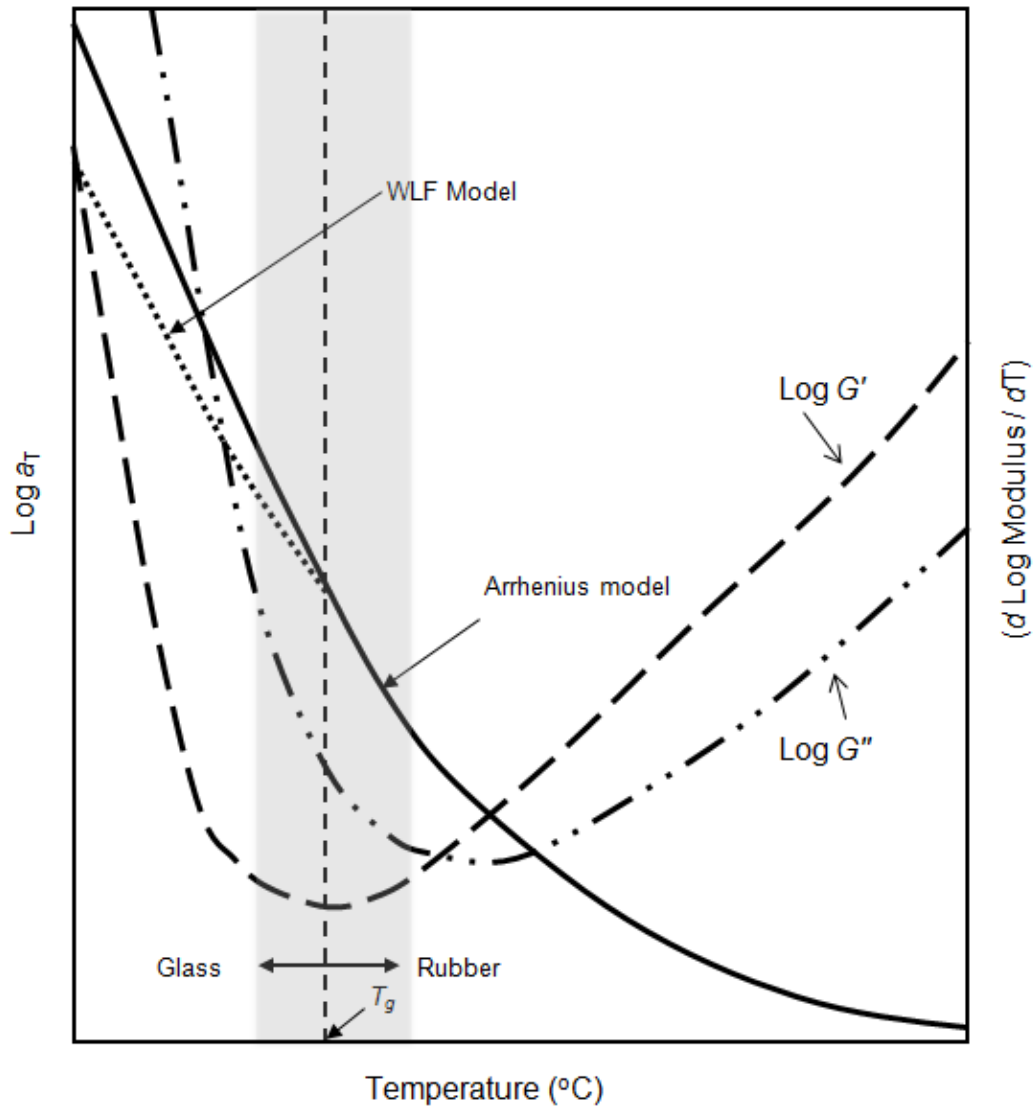


Figure 5b

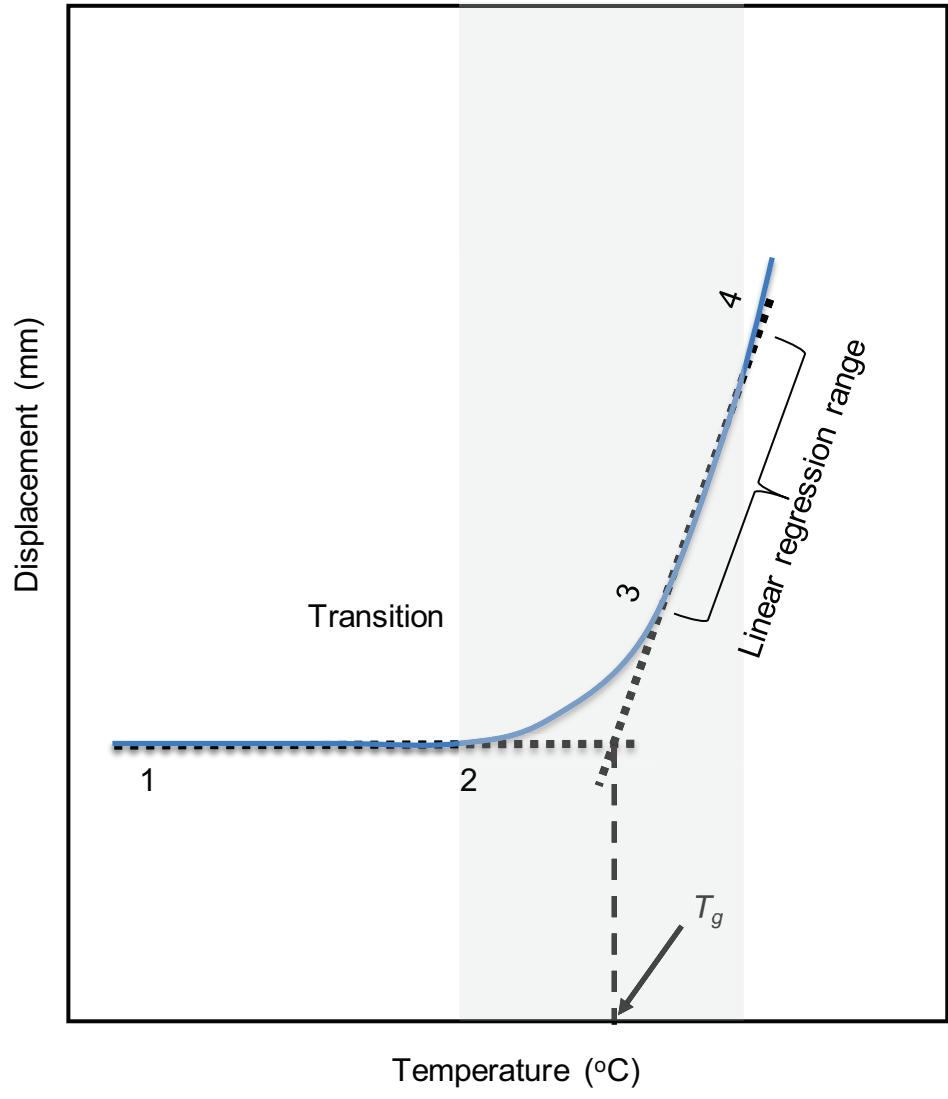


Figure 6

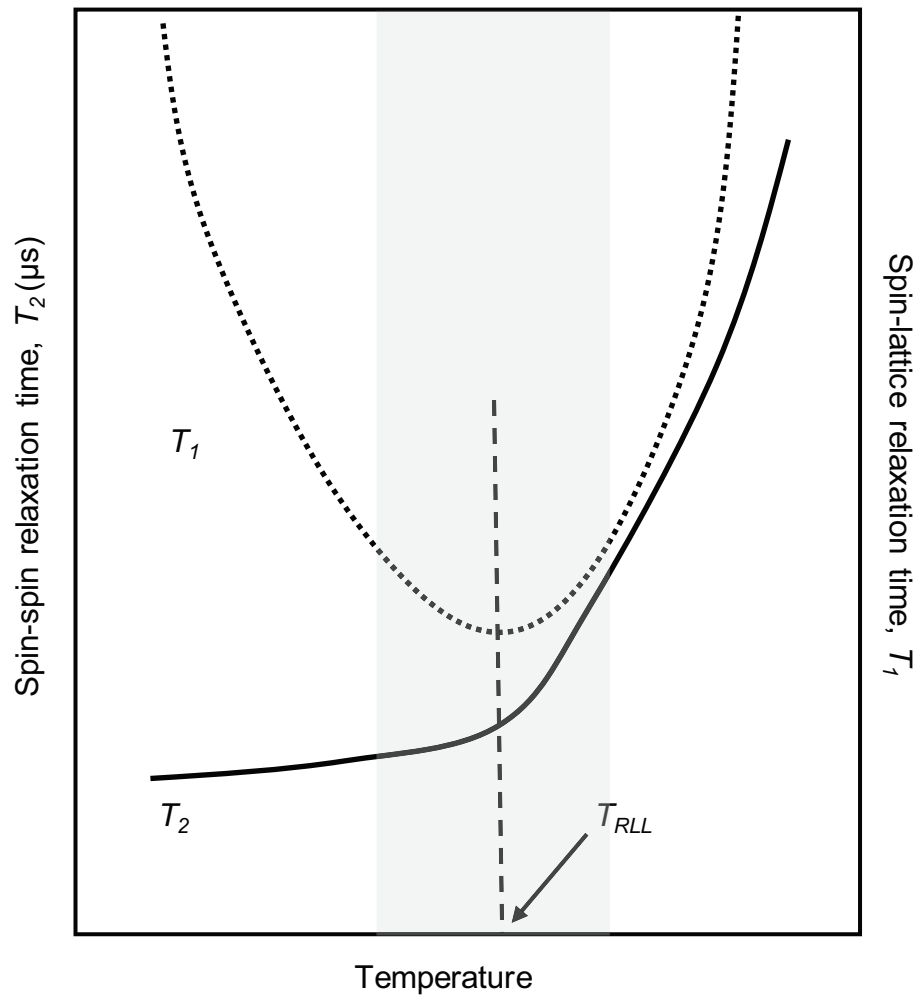


Figure 7

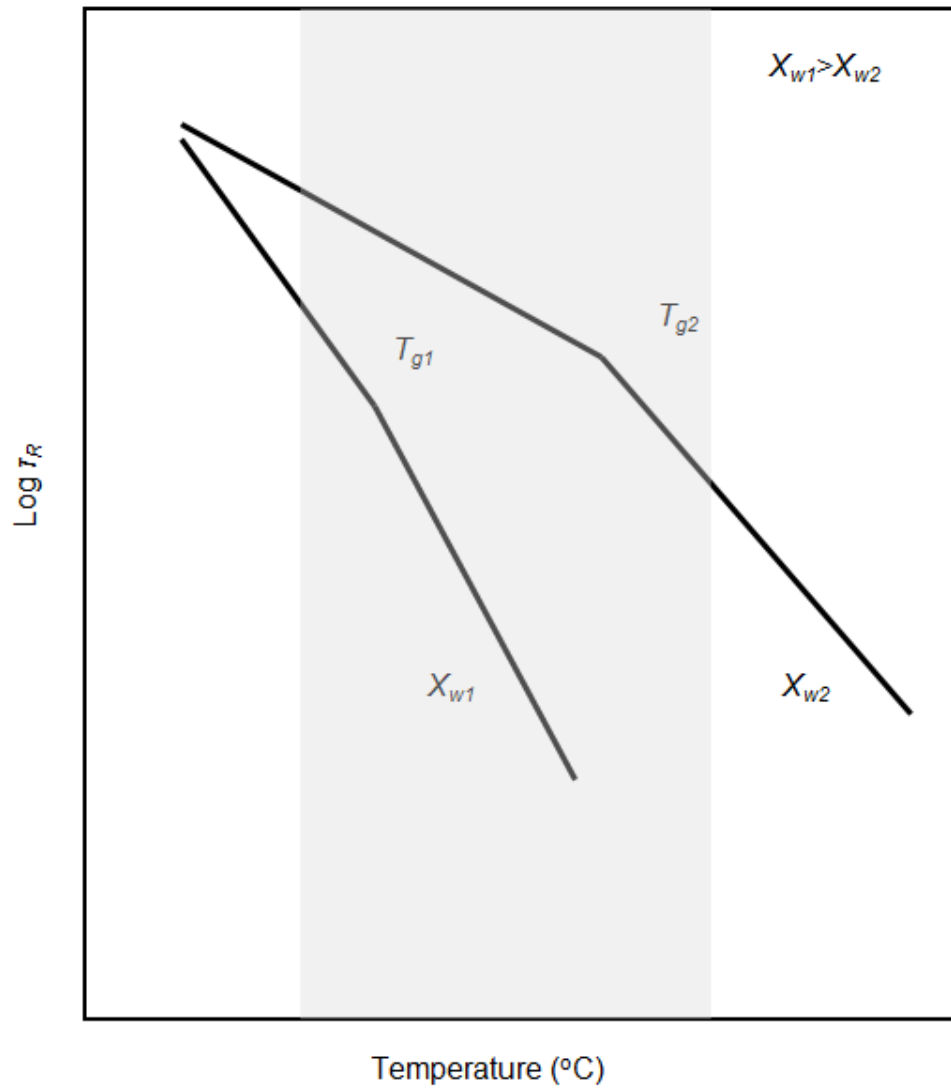


Figure 8

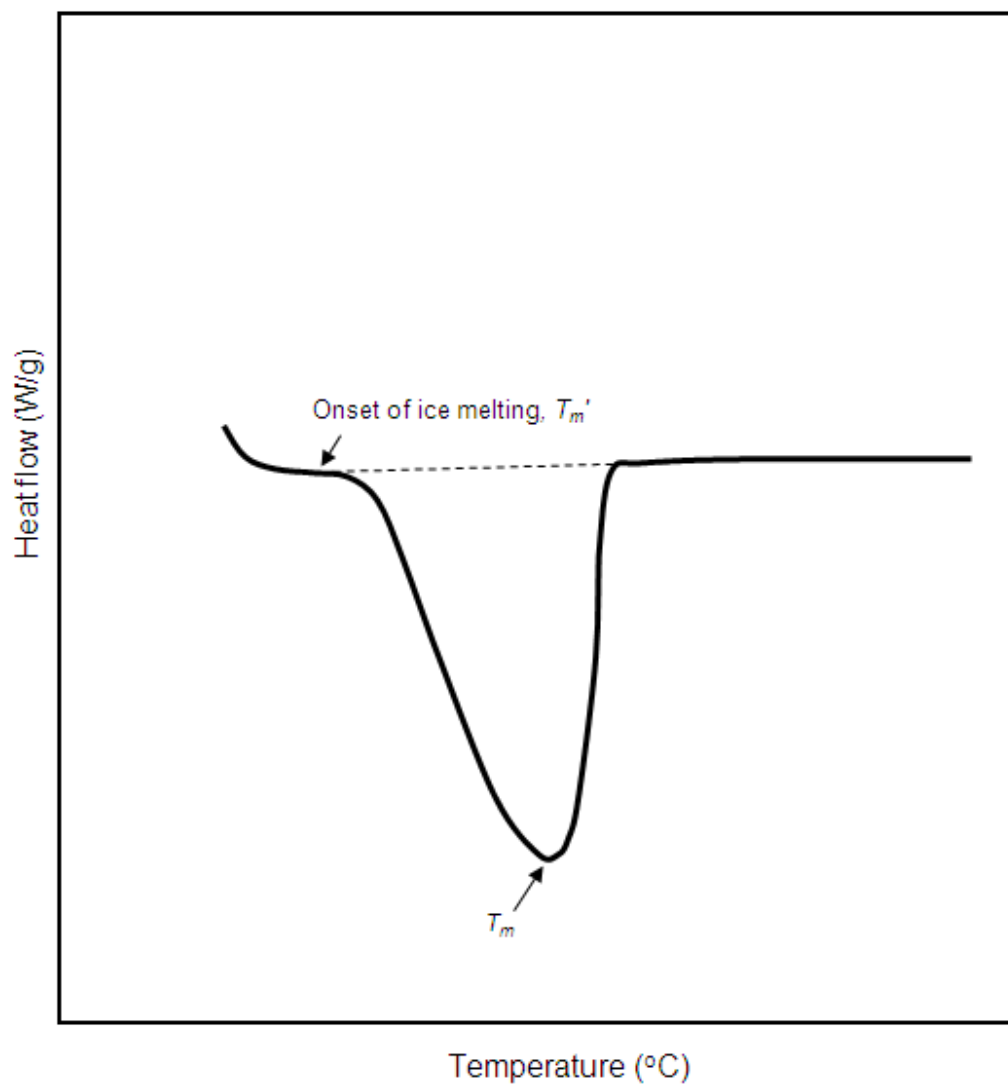


Figure 9

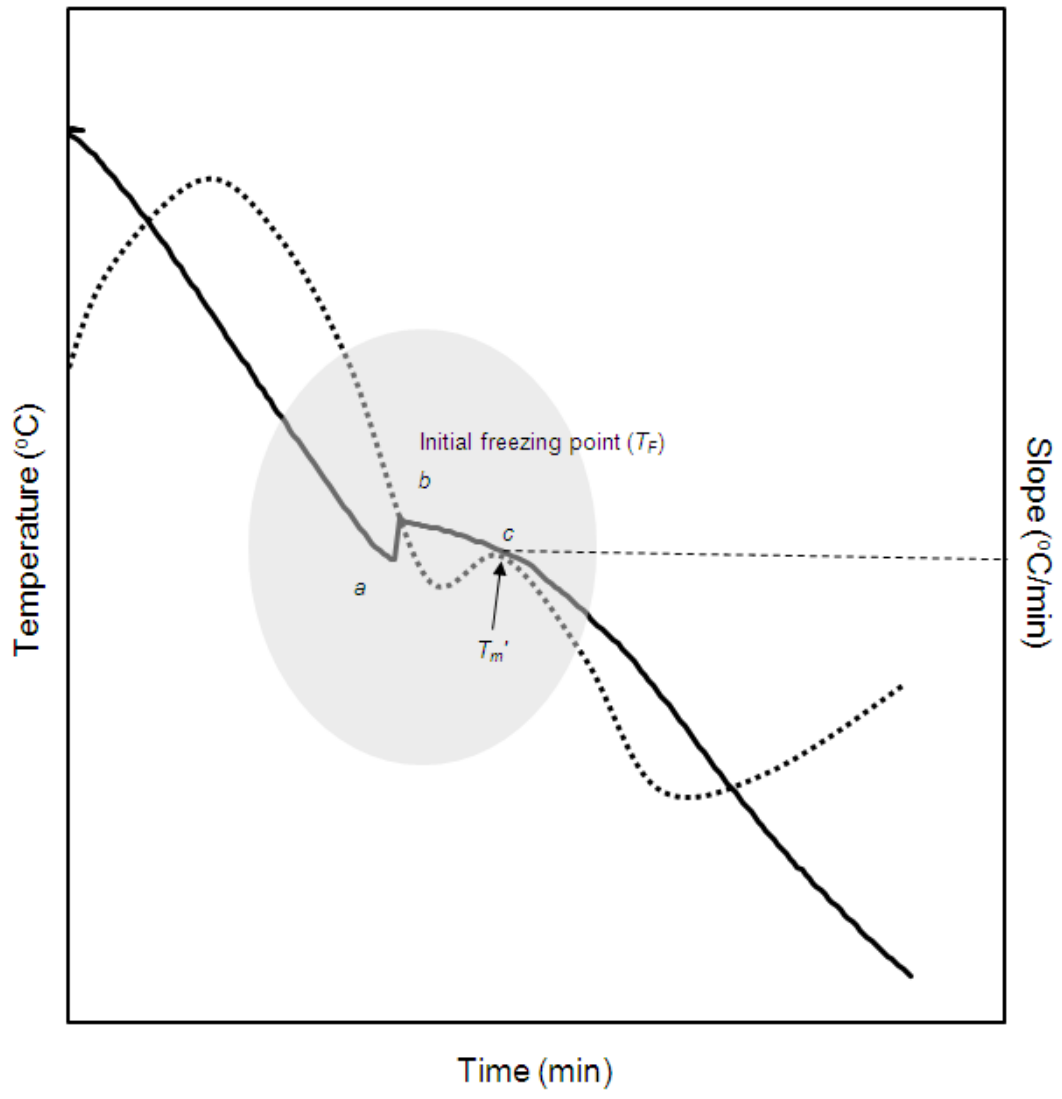


Figure 10

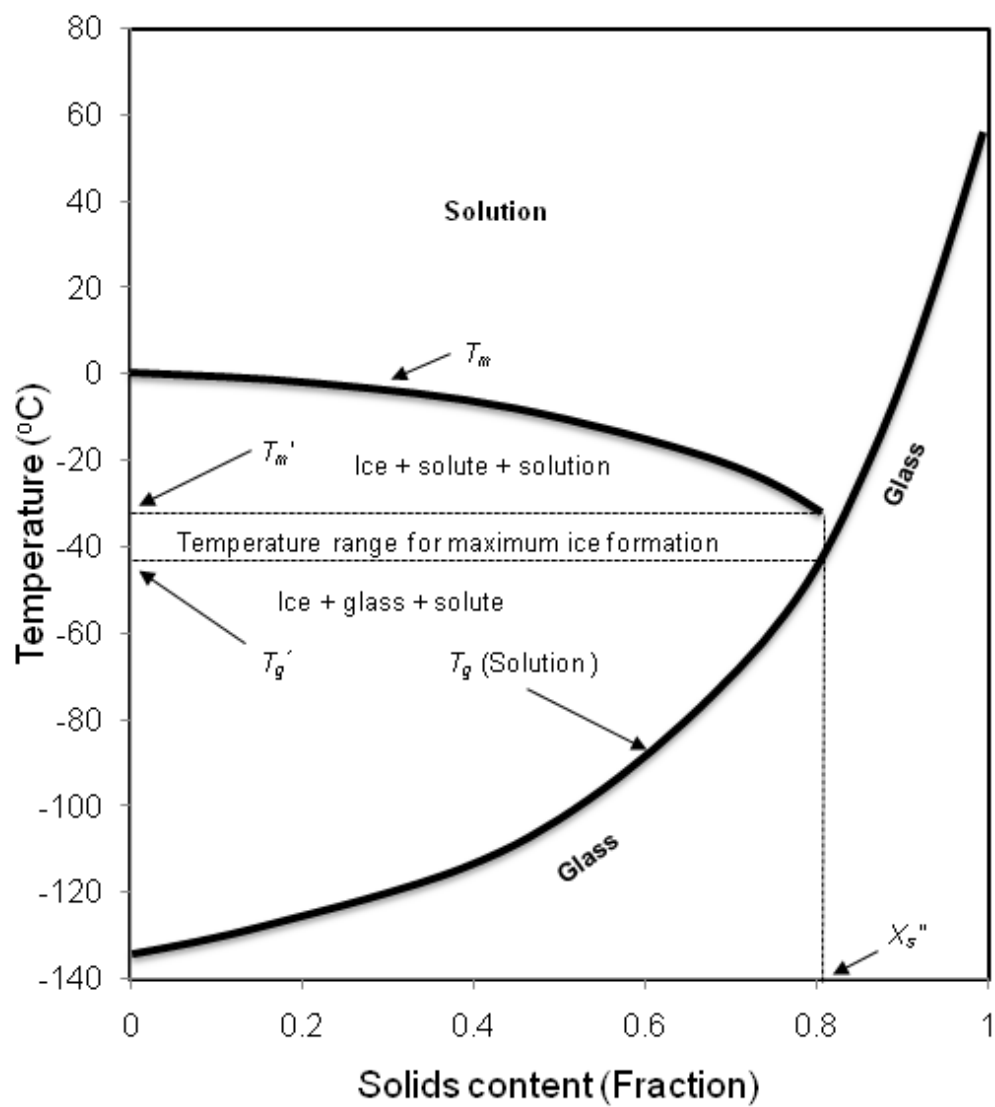


Figure 11



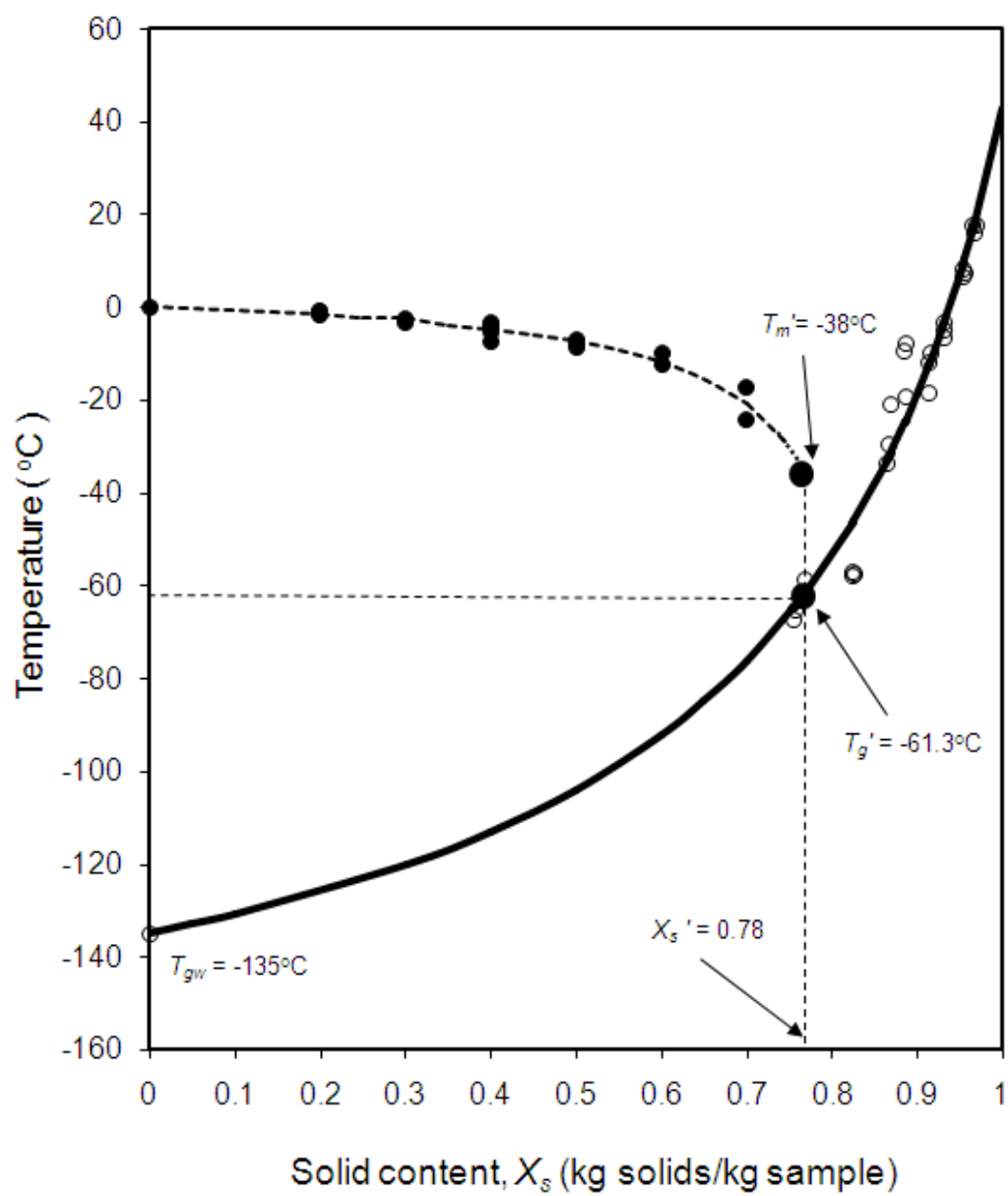


Figure 12

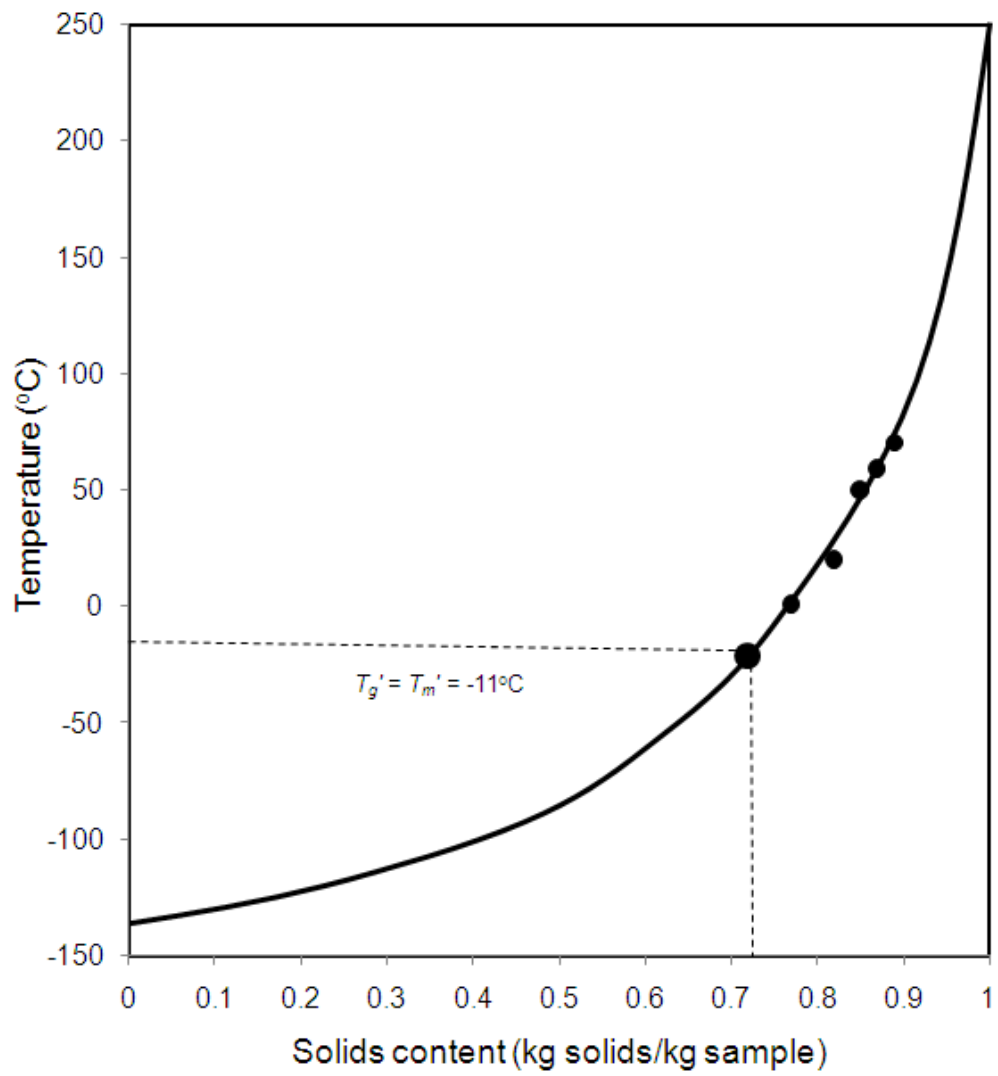


Figure 13

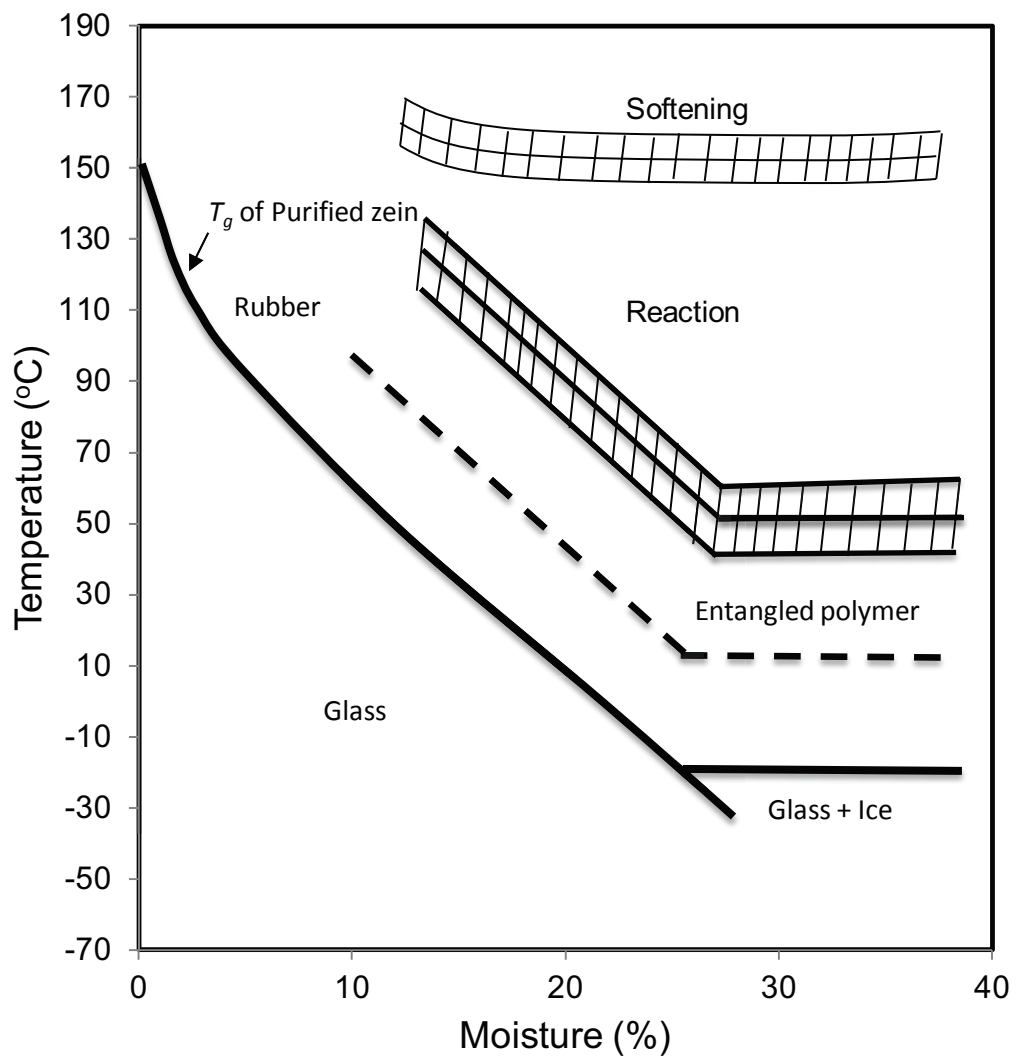


Figure 14

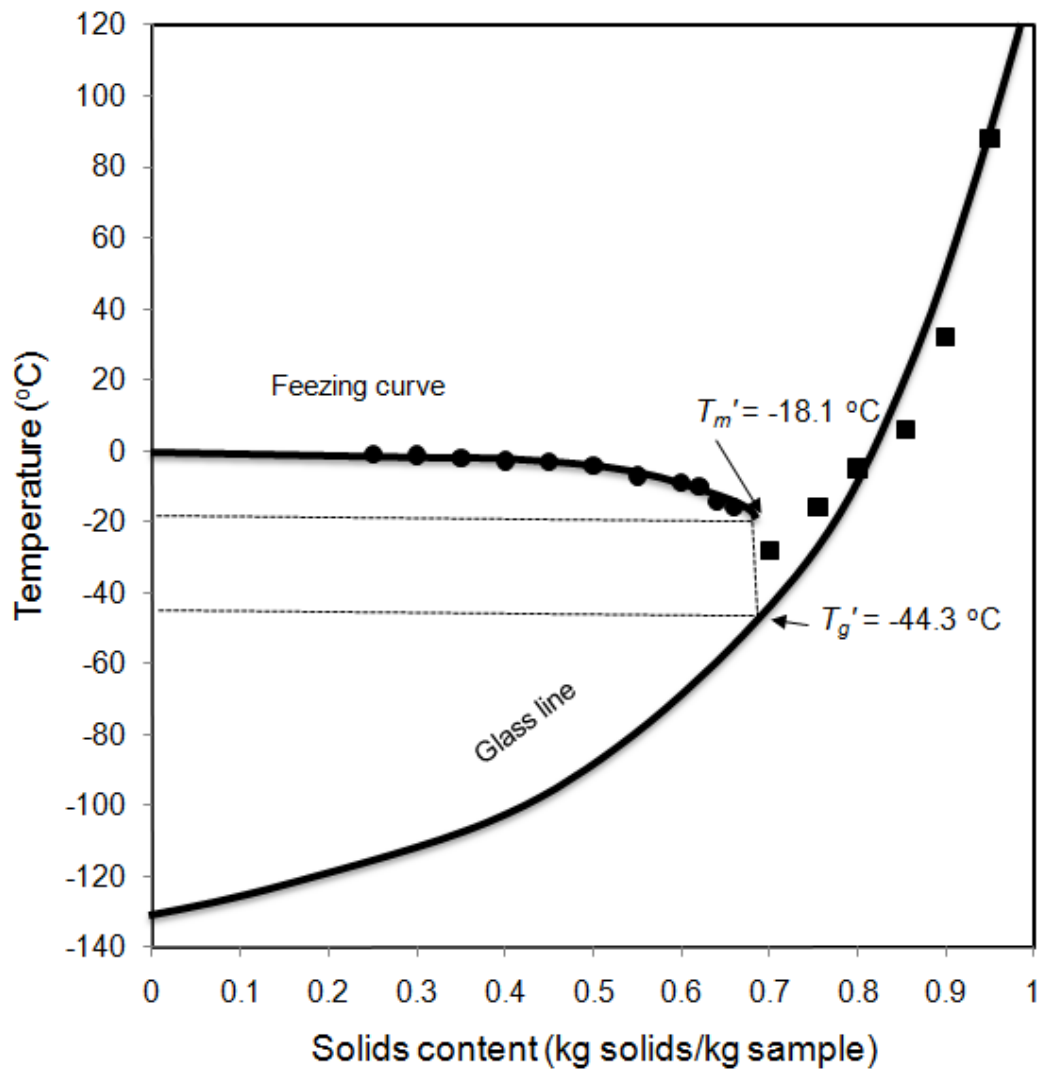


Figure 15

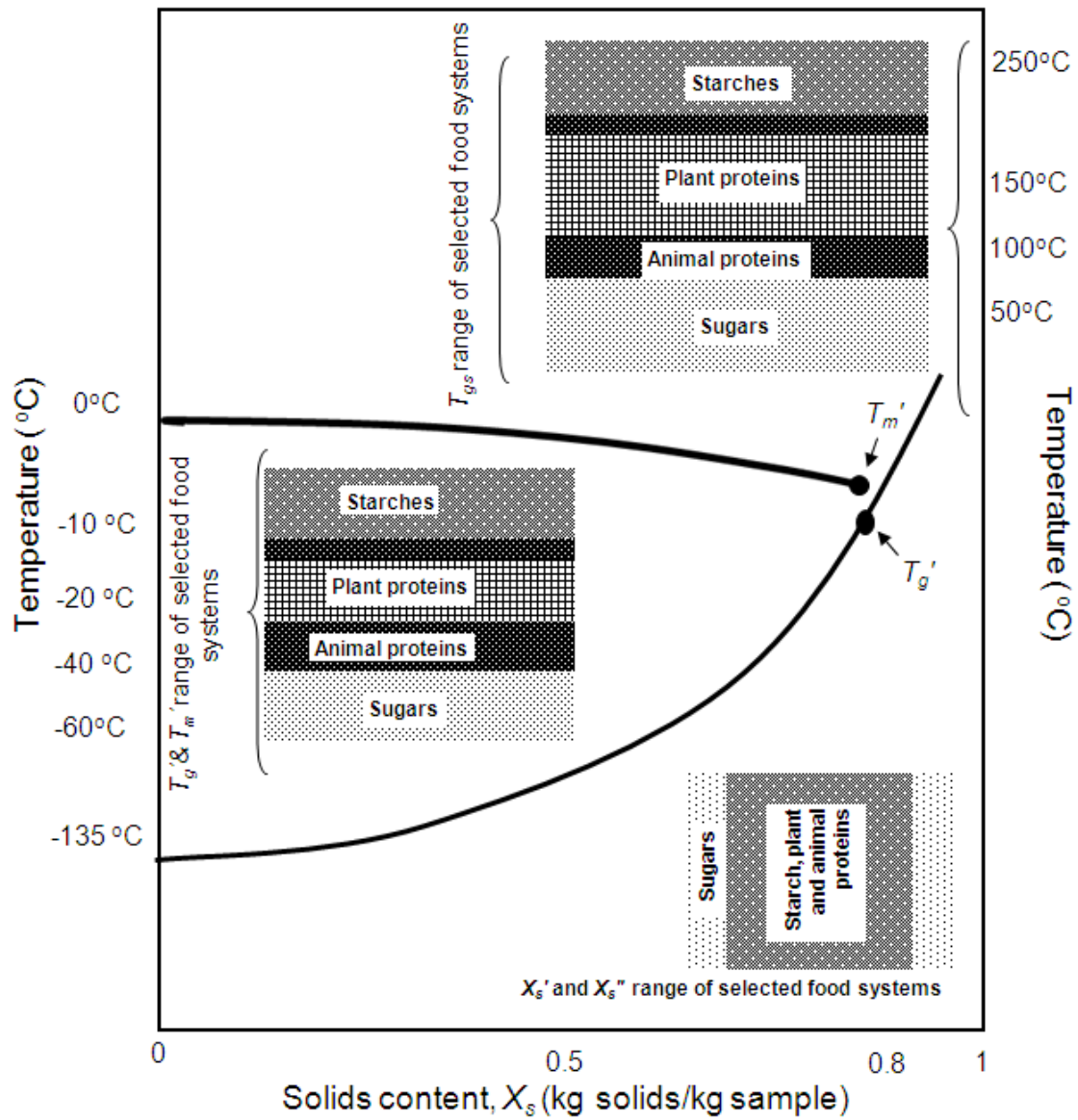


Figure 16