

Application of Glass Transition in Food Processing

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The phenomenon of glass transition has been employed to food products to study their stability. It can be applied as an integrated approach along with water activity and physical and chemical changes in food in processing and storage to determine the food stability. Also associated with the changes during agglomeration crystallization, caking, sticking, collapse, oxidation reactions, nonenzymatic browning, and microbial stability of food system. Various techniques such as Differential Scanning Calorimetry, Nuclear Magnetic Resonance, etc. have been developed to determine the glass transition temperature (T_g) of food system. Also, various theories have been applied to explain the concept of T_g and its relation to changes in food system. This review summarizes the understanding of concept of glass transition, its measurement, and application in food technology.

Keywords Glass transition, theories, food processing, DSC

INTRODUCTION

The phenomenon of glass transition is a concept originally developed for synthetic polymers, and has been applied to many food products to predict their stability. Although glassy materials are known for centuries, the scientific understanding is being evolved in past two decades (Ferry, 1991) and applied to characterize materials in various fields such as polymer science, food science, pharmaceuticals etc. A glassy material is a hard and fragile system with limited molecular mobility. According to Angell (1988), glass is any liquid or super-cooled liquid (10^{12} – 10^{13} Pa s) which effectively behaves like a solid that can support its own weight against gravity flow. White and Cakebread (1966) highlighted the importance of glassy state in determining food stability. Levine and Slade (1986) and Slade and Levine (1988) identified its merit in food processing and food stability during storage. They concluded that the phenomenon of glass transition could be applied as an integrated approach along with water activity (a_w), physical and chemical changes in food during processing and storage to

determine food stability. Agglomeration, crystallization, caking, sticking, collapse, oxidation reactions, nonenzymatic browning, and microbial stability of food systems also depend on glass transition temperature, T_g . Most of the review articles on glass transition focused on either theories or mathematical models developed to explain the phenomenon or its application in particular industry. Thus, objective of this review paper is to summarize the understanding of the phenomenon of glass transition, associated theories, its measurement techniques and instrumentation in food, polymer, and pharmaceutical sectors.

GLASS TRANSITION

Glass transition occurs when a super-cooled, malleable liquid/rubbery material is changed into a disordered solid glass upon cooling, or conversely when a brittle glass is changed upon heating into a super-cooled liquid/rubbery material (Roudaut et al., 2004). Basically it is a second-order time-temperature-dependent transition, which is characterized by discontinuity in physical, mechanical, electrical, thermal, and other properties of a material (Rahman, 1995). It is a kinetic process, and the metastable property of amorphous material and the rate of transition depend on temperature as well as moisture content (Bhandari and Howes, 1999). In a glassy

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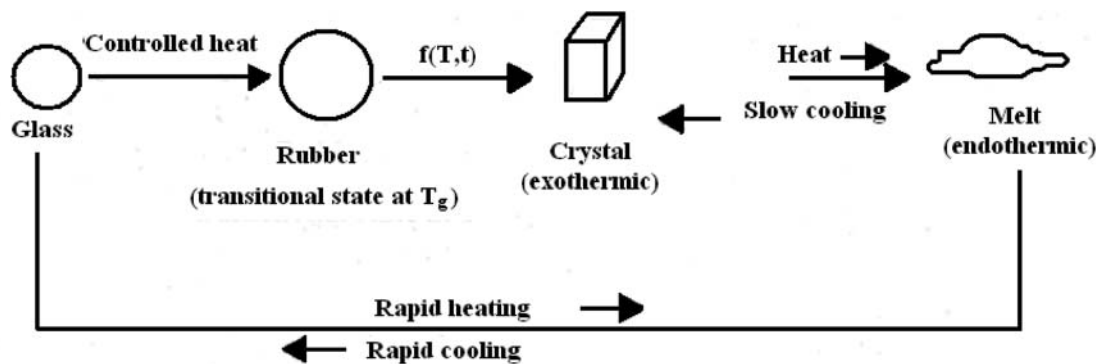


Figure 1 Summary of changes in the physical state of an amorphous glass through rubbery (translational) to crystalline state (Bhandari et al., 1997).

state, molecular movement is highly limited, which is necessary for an orderly alignment of molecules to crystallize (Flink, 1983). Thus, the temperature at which the amorphous system is converted from glassy to rubbery state is known as glass transition temperature (T_g). T_g is not unique for any substance and depends on the rate of cooling, molecular weight (M), water content, matrix composition etc. Figure 1 shows the various transitions an amorphous material undergoes with change in temperature. On heating, glass material undergoes transition to a rubbery phase leading to crystal formation. Further heating leads to the melting of the glassy material. The rapid cooling of the melt leads to the formation of disordered glass structure. The crystallization process is exothermic and melting is endothermic. However, this transition depends on temperature and time (Bhandari et al., 1997).

GLOBAL APPLICATION OF GLASS TRANSITION CONCEPT

The study of glass formation and transition can be employed in various researches, viz., environment, pharmaceutical industry, biology, and many other fields.

Environment

Glasses are important geological materials on earth produced due to the rapid cooling of magma and estimated as billion cubic meters of glass per year. Further, it has been argued that most of the universe water exists in a glassy state (Angell, 1985; 1995).

Pharmaceutical Industry

Glassy materials are extensively used for the preservation of therapeutically important molecules. For example, super-cooled water is used as a storage medium to preserve the biological activity of isolated components for their therapeutic and biochemical applications. Cooling of water at a rate of 10^6 K/s results in the formation of amorphous glassy super-cooled water. The T_g value of water is much colder and harder to determine but studies have estimated it to be around -108°C

(Giovambattista et al., 2004). Similarly, saccharide glasses are used to preserve biological structures (tissues, cells, enzymes) during storage and transportation (Ediger, 2000). During the process of enhancement of biopharmaceutical property of an existing drug through its physicochemical changes, T_g is an important tool for adjusting its physical changes. Pharmaceuticals in glassy state are known to be more rapidly absorbed in the human body than in crystalline form (Forster et al., 2001). A minimal energy is required for dissolution of randomly arranged molecules in amorphous materials. For example, indomethacin and nifedipine are poor water soluble drugs, which can be prepared as glass solutions by melt extrusion with amorphous polymer-polyvinyl pyrrolidone (PVP) to improve drug dissolution (Forster et al., 2001). During the glass formation in drugs, formation of extensive hydrogen bonding between drug and polymer leaves very few sites for reaction with other molecules, thus improves storage capability and physical stability (Paradkar et al., 2003).

Polymer Industry

Polymers are excellent materials where the knowledge of T_g , has a significant role in harnessing them for technological purposes. All synthetic polymers are solids that are at least partially amorphous. The end use and processing parameters decide the use of polymers either above or below T_g . For example, hard plastics which should not melt at room temperature and should be rigid, such as polystyrene and poly (methyl methacrylate) are used below their glass transitions (glassy state), while rubber elastomers such as polyisoprene and polyisobutylene which should have elastic properties at room temperature are used above their glass transitions (rubbery state). Thus, in polymers, knowledge of T_g is very important since it decides the mechanical properties of end products.

Biological Systems

It has been observed that macromolecules of biological interest, such as proteins and DNA, alter their individual behaviors around their glassy state. The proteins are known to

exhibit a dynamic (protein) glass transition, or sometimes referred to as the “slaved” glass transition, to emphasize the influence of solvent (e.g., water) in which they are usually embedded. The transition of various individual molecules in macromolecules with temperature in the biological system is analogous to the phenomenon of glass transition. For a protein molecule, motions of large segments of polymer and the local reorientation of units with very different characteristic times correspond to type α (relaxation processes/motions correspond to original T_g) and type β (relaxation processes/motion corresponds to sub T_g) relaxations similar to glass (Iben et al., 1989). During the phenomenon of glass transition, various short-range motions have been observed. Generally, the transitions are much more pronounced in denatured state than in native state. Glassy state materials have been observed in seed, prokaryotes, and pollens, and are found to be involved in protecting biological tissues from extremely dry conditions. Mainly the glass forming sugars, such as trehalose, or oligosaccharide, such as raffinose and stachyose, are the protectants in biological system. Sugars present in cells form glass matrix at low water conditions thus protecting large macromolecules like proteins from denaturation (Chang et al, 1996) and prevent the formation of molecular aggregates. The high viscosity of glass matrix lowers metabolic chemical reactions and thus increases the longevity of cells (Karmas et al., 1992; Roos 1995a).

THEORIES ASSOCIATED WITH GLASS LIQUID TRANSITION

There are many theories to describe the behavior of polymers and other materials near to their T_g range. Invariably, these theories have been applied to predict glass transition of foods and pharmaceuticals with some success. Table 1 summarizes various theories associated with the phenomenon of glass transition.

(i) Free Volume Theory

It was developed by Turnbull and Cohen (1959), and later revisited by Cohen and Grest (1979). Based on the concept of

free volume, glass transition is defined as that temperature at which free volume collapses sensibly to zero and the mobility is restricted keeping only movement allowed by the occupied volume (Moonan et al., 1985; Cohen and Grest, 1979). This theory is widely applied for its simplicity in approach and for the consideration that all relaxation processes have the same temperature dependence. The free volume theory explains the dependence of T_g on pressure, crosslink density, and molecular weight of the system. Above T_g range, free volume increases linearly with temperature (Abiad et al., 2009). When a polymer, above T_g is cooled, the decrease in free volume reaches to a point where there is insufficient space for long-range molecular motions (Sperling, 2006). Free volume theory has been used for strong/fragile classification of food material (Champion et al., 2000) and its utmost importance in extrusion, puffing, or flaking processes.

(ii) Kinetic Theory

It defines T_g as the temperature at which the relaxation time of the molecules present in the system is of the same order of magnitude as the time scale of the experiment. Kinetic theory is concerned with the rate of approach to equilibrium of the system, taking the respective motions of holes and molecules into account. Also, it examines the effect of heating/cooling and provides quantitative information about the heating capacities below and above T_g . Thus, decreasing the time frame of an experiment, i.e., the rate of either heating/cooling would reveal an increase in T_g . It explains the 6–7°C shift in glass transition per decade of time scale of experiments (Abiad et al., 2009).

(iii) Thermodynamic or Entropy Theory

Thermodynamic theory assumes that a glass is a stable state of matter (Adams and Gibbs, 1965) that can be achieved by a thermodynamic second-order transition observable by a significant change in the slope of energy or entropy versus temperature curves (Mansfield, 1993). Although this theory has not been directly applied to foods and pharmaceuticals, it has been successful in predicting various phenomena that may be

Table 1 Summary of basic theories associated with the glass transition phenomenon

Theories	Developed by	Application
Free volume theory	Turnbull and Cohen (1959)	Estimates T_g as a function of pressure, cross-link density, molecular weight, and composition. Allows the calculation of coefficients of expansion. Locates viscoelastic events associated with T_g .
Kinetic theory	-	Explains the variation of T_g as a function of heating/cooling rate.
Thermodynamic theory	Adams and Gibbs (1965)	Predicts T_g variation as a function of molecular weight, composition, plasticization, cross-link density.
Mode coupling theory	Sjogren (1989)	Predicts a critical temperature, T_c , at which the dynamic properties of the material, notably particle motion and relaxation, diverge.

associated to the behavior of these materials. These include variation in T_g as a function of molecular weight (Misra and Mattice, 1993), cross-link density, and plasticizer content. This theory can also be used to predict the T_g of binary polymer blends as a function of its components mass fractions and individual T_g values (del-Val et al., 1986; DiMarzio, 1990).

(iv) Mode Coupling Theory

The mode coupling theory is a kinetic description of glass dynamics and was developed by Sjogren (1989), explaining the transition at high temperature. It focuses on understanding the initial features of the slowing down of liquid like processes. With the lowering of temperature, the system passes through a critical point, which is responsible for dramatic increase in relaxation times (Ediger et al., 1996) It predicts the critical temperature (T_c) at which the dynamic properties of the material, notably particle motion and relaxation, diverge. This theory anticipates sharp transition in viscoelastic properties as well as a change in the relaxation behavior of the glass material near the predicted transition whereas at temperatures below the transition temperature, the theory anticipates a random freeze of liquid's configuration (Bengtzelius, 1984).

T_g Prediction Models

The glass transition temperature is affected by various properties of substances (interaction with solute, matrix, molecular weight) as well as their composition. Various models have been proposed and developed to predict T_g .

(i) Gordon–Taylor Equation

This prediction model is based on the assumption that the change in volume with temperature is linear and the volume contribution by each constituent in the mixture is the same and additive. It predicts the T_g value of composite mixture from the T_g values of individual pure components (Aguilera et al., 1993; Roos, 1995b; Seo et al., 2005). Usually, the model assumes that the T_g value of the mixture falls between the T_g values of individual components, and can be expressed as

$$T_g = \frac{x_1.T_{g1} + K.x_2.T_{g2}}{x_1 + K.x_2},$$

where T_{gm} : T_g of the mixture, x_i : weight fraction, and T_{gi} : T_g of the i th component, K : constant, which is a function of coefficient of expansion. This equation has been applied for polymer blends, such as sucrose-maltodextrin, and to solute–diluent systems, such as sucrose water and fructose water (Truong et al, 2002). It is also applied to predict the plasticizing effect of moisture content on T_g . The limitations of this model are that using it for ternary or higher mixtures requires a large

number of experiments and this model fails when a component in mixture has negligible effect on T_{gm} .

(ii) Couchman–Karasz Equations

This theory considers thermodynamic or entropy theory of glass transition and assumes that the entropy of mixing is a continuous function at the glass transition region. For an 'n' component, this theory can be expressed as:

$$T_{gm} = \frac{\sum_{i=1}^n w_i \Delta C_{pi} T_{gi}}{\sum_{i=1}^n w_i \Delta C_{pi}},$$

where T_{gi} : glass transition of the i th component in the mixture and x_i : mole fraction concentration of the i th component. The heat capacity (C_p) can be calculated by subtracting the heat capacities of the component at glassy and rubbery states respectively. This model has been applied for multi-component systems such as water, glucose, and sucrose (Kalichevsky et al., 1992b; Arvanitoyannins et al, 1993; Roos, 1995b). This equation can be further derived and applied for ternary, quaternary, and higher order systems as shown by Troung et al., 2002. Comparatively, this model requires less number of experimental values for predicting, as only T_g and ΔC_p of individual components are required. This prediction equation works well only for ideal mixing systems without any component variability.

(iii) William–Landel–Ferry (WLF) Kinetics

The change in viscosity follows the WLF kinetics,

$$\log_{10} \frac{\mu}{\mu_g} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)},$$

where μ : viscosity, μ_g : viscosity at T_g , T : temperature, and C_1 : 17.44 K and C_2 : 51.6 K are “universal” constants.

(iv) Mandelkern, Martin, and Quinn Equation

It is based on the WLF equation having an assumption that at T_g the ratio of free volume to volume reaches a critical constant value of 0.025 (William et al., 1955). The prediction equation can be expressed as

$$\frac{1}{T_g} = \frac{1}{x_1 + R.x_2} \times \left(\frac{x_1}{T_{g1}} + \frac{R.x_2}{T_{g2}} \right),$$

where R : $K \times \frac{T_{g1}}{T_{g2}}$, T_{gi} : glass transition of the i th component in the mixture, and x_i : mole fraction concentration of the i th component.

(v) Other models

(a) *Kwei's Prediction Model.* Kwei (1984) investigated various polymeric systems which showed S-shaped T_g

profiles. To account for this transition profile, an interaction component to the existing linear prediction model has been incorporated. Thus, it can be expressed as

$$T_{\text{mix}}^g = \frac{x_1 \cdot T_{g1} + k \cdot x_2 \cdot T_{g2}}{x_1 + k \cdot x_2} + q \cdot x_1 \cdot x_2,$$

where, T_{g_i} : glass transition of the i th component in the mixture, x_i : mole fraction concentration of the i th component, and k , q : fitting parameters (these depend on intermolecular interaction between the components of polymer mixtures) (Lin et al., 1989). This empirical model is mainly used for studying water solute interaction. Kingsley and Ileleji (2011) used this model to study the glass transition behavior of corn distillers dried grains with solubles (DDGS).

(b) *Pinal's prediction model.* Pinal (2008) added an additional term in the Couchman–Karasz equation to account for the effect of entropy mixture on T_g and expressed the prediction equation as

$$\ln(T_{\text{pred}}^{\text{gm}}) = \frac{x_1 \cdot \Delta C_{p1} \cdot \ln(T_{g1}) + x_2 \cdot \Delta C_{p2} \cdot \ln(T_{g2})}{x_1 \cdot \Delta C_{p1} + x_2 \cdot \Delta C_{p2}} - \frac{\Delta S_{\text{C}}^{\text{mix}}}{\Delta C_{p,m}},$$

where $\Delta C_{p,m}$: heat capacity difference between the liquid and crystalline form, and $\Delta S_{\text{C}}^{\text{mix}}$: configurational entropy of mixing that is accessible to liquid during experiment.

Factors Influencing T_g

Glass transition is influenced by heating/ cooling rate, pressure, molecular weight and water activity, composition and pH of the food material, etc.

(i) Heating/Cooling Rate

When a liquid is subjected to rapid/quench cooling, there is a formation of disordered state, i.e., the amorphous state, and show the phenomenon of glass transition. Slower cooling rate provides the molecules with enough time to form an ordered structure resulting in crystal formation. Also, in a polymer, many transitions may occur within a small temperature range difference. In order to decimate such transitions, heating/cooling rate should be properly maintained during thermal analysis. If the heating rate is too high, then the molecular mobility will be increased at once and will directly undergo the rubbery state without showing the transition temperature. It has been found that increase in cooling or heating rate would result in an increase in T_g (Table 2). Higher heating or cooling rate is generally associated with shorter experimental time scales, which would provide less time for potential motion of the molecules and consequently result in higher measurable glass

Table 2 Effect of heating rate on T_g (Blanchard et al., 1974)

Heating rate	T_g
(°C/min)	(°C)
5	100.0
10	106.0
20	108.0
40	109.0
80	111.0

transitions (Ding et al., 1999). Hsu et al. (2006) studied the influence of cooling rate on T_g of sucrose solution and rice starch gel and reported that T_g of sucrose was lower on rapid cooling as compared with slow cooling. For sucrose solution (70%), T_g was found to be -66.7°C and -64.6°C at rapid and slow cooling respectively. For sucrose solution (30%), T_g was -34.6°C and -33.3°C at rapid and slow cooling respectively. The T_g value for rice starch gel was -9°C and -7.5°C at rapid and slow cooling respectively. Yu and Christie (2001) reported that increasing the mass of pan and decreasing the heating rate will reduce peak temperature (Fig. 2). Sunooj et al., 2009 studied the effect of heating rate on T_g values for fresh as well as freeze-dried chicken and mutton samples. T_g values showed a linear increase with increase in rate of heating. However, for freeze-dried samples, T_g values changed marginally due to reduced moisture content.

(ii) Pressure

Based on the principles of thermodynamics, an increase in pressure of an amorphous system will decrease its entropy. This corresponds to increased T_g . As pressure increases, the free volume decreases and to maintain the molecular motion characteristic of the rubbery state, the temperature is increased, thus resulting in a higher T_g range (Ferry, 1960). However, large molecules such as proteins (denaturation) and starches (gelatinization) are significantly affected by pressure treatment rather than low molar

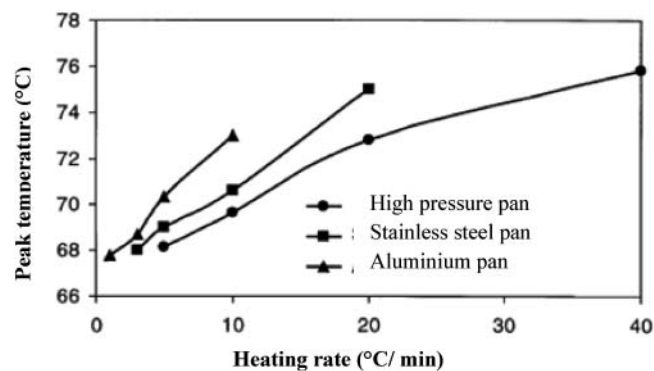


Figure 2 Effect of heating rate on peak temperature measured with different pans for 50% corn starch solution (Yu and Christie, 2001).

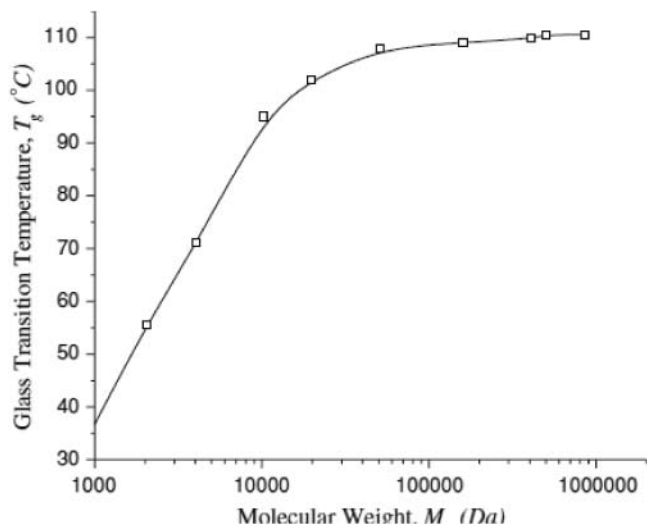


Figure 3 Effect of molecular weight on the T_g of polystyrene (Blanchard et al., 1974).

mass (M_w) compounds (Hayashi, 1992). Ahmed et al., 2009 studied the effect of high pressure treatment (350–650 MPa, 22–26°C, 15 min) on the thermal properties of three samples of amorphous polylactide and semi-crystalline polylactide (PLA) with M_w in the range of 3800–6200. They observed that amorphous polylactide showed higher T_g than semi-crystalline polylactide because of higher M_w . Overall, there was decrease in T_g with increase in pressure, which contradicts the above statements. The possible explanation for the decrease can be the synergistic effect of pressure and temperature.

(iii) Molecular Weight

The molecular weight of any food material strongly influences T_g values. The low molecular weight polymers (sucrose) and monomers (fructose/glucose) in their pure form have lower T_g than longer chain molecules. Figure 3 shows the effect of molecular weight on the T_g of polystyrene (Blanchard et al., 1974). According to Abiad et al. (2009), it is evident that increasing the molecular weight or the cross-link density for a given polymer will decrease its specific volume, resulting an increase in T_g (Fox and Flory, 1954). Fox and Flory (1950) indicated that T_g at a given molecular weight can be related to

glass temperature at infinite molecular weight ($T_{g\infty}$),

$$T_g = T_{g\infty} - \frac{K}{(\alpha_R - \alpha_G) \cdot M}$$

where K : constant depending on the material, and α_R and α_G : corresponding coefficients of expansion at rubbery and glassy states respectively. Also, Fox and Loshaek (1955) suggested a simple equation for linear polymers and predicted a linear decrease in T_g with the molecular weight of polymer,

$$T_g = T_{g\infty} - \frac{K}{M}$$

To and Flink (1978) validated this equation for glucose polymers with three or more glucose chains. Raudonus et al. (2000) studied the effect of addition of oligomeric and polymeric compounds on the T_g of isomalt using differential scanning calorimetry (DSC) at various water contents. They reported that the addition of 75% polydextrose and high molecular hydrogenated starch hydrolysate increased T_g to 69.4°C and 64.5°C respectively (Table 3). Busin et al., (1996) found a linear relationship between T_g (°C) and Dextrose Equivalent (DE) for maltodextrins over a range of DE (2 ± 100) with a satisfactory correlation coefficient:

$$T_g = -1.4DE + 449.5.$$

Also, Yu et al. (1994) studied T_g of mono-disperse polystyrene having variable molecular weights (4×10^3 – 4×10^5 Da), using the positron annihilation life time spectroscopy (PALS) method. Table 4 depicts T_g values determined by DSC as a function of molecular weight.

(iv) Water and Other Plasticizers

Addition of any additive in food can act as either plasticizer or anti-plasticizer. Plasticizer lowers substance's T_g and anti-plasticizer increases its T_g . Any miscible solvent or a low molecular weight additive incorporated in an amorphous system almost invariably will depress its T_g (Lechuga-Ballesteros et al., 2002). Effect of a plasticizer on T_g can be explained by two mechanisms: (i) the plasticizer molecules screen off the attractive forces between the material molecules, and (ii) the plasticizer molecules increase the space between the material

Table 3 Effect of molecular weight on the T_g of isomalt combinations (Raudonus et al., 2000)

Composition	T_g (°C)	Composition	T_g (°C)	Composition	T_g (°C)
Isomalt	63.6	Isomalt	63.6	Isomalt	63.6
25% Litesse III	53.0	25% HS 3375	49.6	25% HS 6075	56.2
50% Litesse III	59.0	50% HS 3375	49.2	50% HS 6075	59.5
75% Litesse III	69.4	75% HS 3375	49.2	75% HS 6075	64.5
Litesse III	90.8	HS 3375	54.6	HS 6075	75.0

Litesse III: polydextrose; HS 3375: hydrogenated hydrolyzed starch (low molecular weight); HS 6075: hydrogenated hydrolyzed starch (high molecular weight).

Table 4 Values of T_g determined by DSC as a function of molecular weight (Yu et al., 1994)

M_w (Da)	T_g (°C)
4,000	75
9200	90
25,000	96
400,000	102

molecules, both mechanisms providing a greater free volume and freedom for the molecules to move (Attenburrow, 1993). Water is considered to be the most effective plasticizer in food matrices that decreases T_g and mechanical resistance. The decrease in T_g is well depicted in Table 5, as well as in Fig. 4. (Roos and Karel, 1991; Brent et al. 1997; Moraru et al., 2002; Orford et al., 1989). Ohkuma et al. (2008) studied the effect of water on freeze-dried carp surimi-trehalose mixtures of varying moisture contents. Samples containing (2.5–16.2%, w/w) moisture had a clear T_g values. It was found that T_g decreased significantly with an increase in moisture content. This result is ascribed to the plasticizing effect of water (Fig. 5). It has been found that other low molecular compounds, such as sugar, glycerol, and sugar alcohols, also decrease T_g , as observed in Table 6. Chaudhary et al. (2011) studied the glass transition behavior of plasticized starch biopolymer system, i.e., plasticizers (glycerol and xylitol) having similar molecular size (e6.3 Å) but different molecular weights (glycerol – 92; xylitol – 152) were selected for studying the glass transition behavior (rubber like behavior) in multi-plasticized starch biopolymer with 70% amylopectin structure (Kalichevsky et al., 1993). In calorimetry measurements (bulk viscous flow), plasticized samples showed higher T_g than non-plasticized samples at low water activities, i.e., a typical anti-plasticization behavior. However, increased concentration of plasticizer to 15% and 20% by weight led to significant reduction in T_g . Thus, plasticizing effect can be described using the Gordon–Taylor equation as follows:

$$T_g = \frac{C_s T_{gs} + k C_w T_{gw}}{C_g + k C_w},$$

where C_s , C_w : mass fractions of substance and water, T_{gs} , T_{gw} : T_g values of substance and water respectively, and k : constant.

Table 5 Effect of water activity on the T_g of grapes (Sa and Sereno, 1994)

Water activity (a_w)	T_g values (°C)
0.12	–15.23
0.23	–23.01
0.33	–23.48
0.44	–34.93
0.53	–45.85
0.61	–59.08
0.76	–74.94

Table 6 Experimental T_g of 35% amylose starch at different water activities with only one plasticizer (glycerol) (Chang et al., 2006)

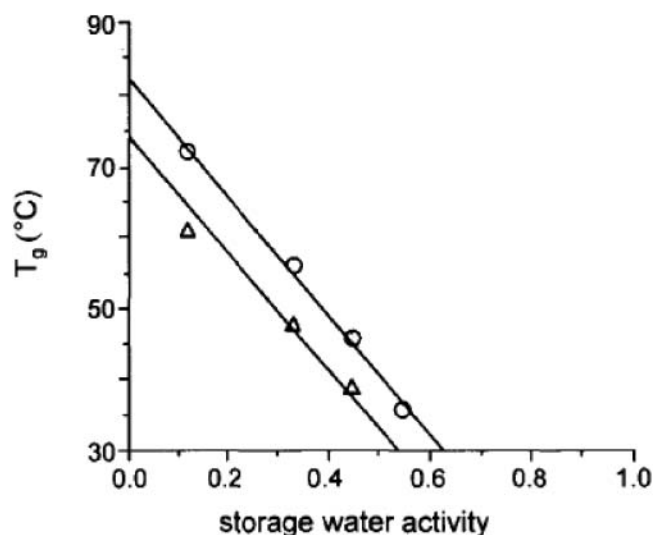
Water activity (a_w)	Moisture content (% w/w)	Glycerol concentration (% w/w)	T_g (°C)
0.11	6.41	0	165.2
0.11	5.80	10	117.5
0.11	5.78	20	86.9
0.32	8.89	0	117.1
0.32	7.86	10	86.5
0.32	9.61	20	68.8
0.56	10.62	0	91.2
0.56	9.83	10	71.2
0.56	11.23	20	37.8

Application of T_g in Food Processing and Related Phenomenon

The concept of glass/rubbery state is of practical importance when considering food stability. Increase in molecular mobility around T_g increases the diffusion of molecules, resulting in physical and chemical changes, which may have effect on food stability. Changes include caking, collapse, crystallization, agglomeration, oxidative reactions, etc. in food systems (Abbas et al., 2010).

Importance of T_g

Food is a heterogeneous system consisting of macromolecules such as carbohydrates, proteins, etc. These macromolecules undergo phase transition on change of moisture content and temperature, resulting changes in food properties. The

**Figure 4** Effect of water activity on the T_g of various infant formulas stored at 20°C as a function of water activity (Chuy and Labuza, 1994).

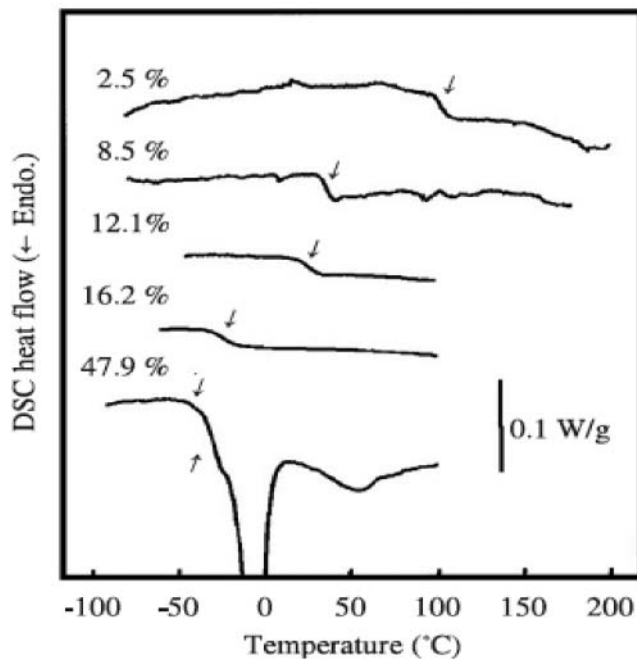


Figure 5 DSC thermograms for freeze-dried carp surimi-trehalose mixtures (80% trehalose in dry matter) of varying residual moisture (samples containing 2.5–16.5% (w/w) moisture content, and samples containing 47.9% (w/w) moisture content indicating T_{g1} and T_{g2} respectively).

glass transition occurs over a wide range of temperature owing to heterogeneity of food system (Ferry, 1980; Bosma et al., 1988). Food can be considered stable at a glassy state since below T_g , compounds involved in deterioration reactions diffuse and react slowly (Slade and Levine, 1991a). Also, the water in concentrated phase becomes kinetically immobilized and therefore do not support or participate in reactions (Rahman, 1999). The transition boundaries in food can be illustrated using state diagram. It explains complex changes in food under the influence of water content and temperature, and also assists in identifying the stability of food during storage as well as selecting a suitable condition of temperature and moisture content for processing. Figure 6 shows the state diagram indicating different states as a function of temperature and solid mass fraction. The freezing line (ABC) and solubility line (BD) are shown in relation to the glass transition line (EFS). Point F (X_s' and T_g') lower than T_m' (point C) represents the maximum freeze concentration condition. The water content at point F or point C is considered as unfreezable water. This unfreezable section of water remains unfrozen even at very low temperature. Point R is defined as T_g'' as the glass transition of solid matrix in the frozen sample, which is determined by DSC. In the region AHB, the phases presented are ice and solution. Below point B, first crystallization of solute occurs, thus HBCL region transforms to three states: ice, solution, and solute crystals. No free water exists on the right side of point C, and then the very concentrated solution is transformed to rubber state. Region ICFJ contains ice, rubber, and

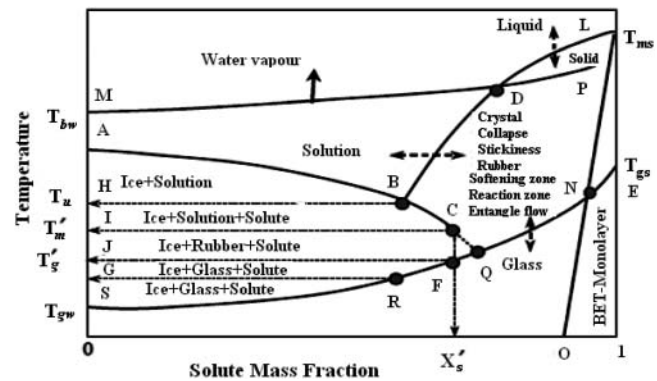


Figure 6 State diagram showing different regions and states of foods (T_{bw} : boiling point; T_u : eutectic point; T_m' : end point of freezing; T_g' : glass transition at end point of freezing; T_{gw} : glass transition of water; T_{ms} : melting point of dry solids; T_{gs} : glass transition of dry solids) (Rahman, 2006).

solute crystal. Point F is the T_g' value, below which point a portion of the rubber state is transformed to the glass state, thus region JFS contains glass, ice, and solute crystal. Region BQEL is important in food processing and preservation as this region shows many characteristics such as crystallization, stickiness, and collapse. Line BDL is the melting line and is important when products reach high temperatures during processing, such as frying, baking, roasting, and extrusion cooking. Line MDP is the boiling line for water evaporation from liquid and solid phase (Rahman, 2006).

Changes in Physical Properties during Glass Transition

In food systems, many of physical properties change with temperature, especially above T_g (Fig. 7). There is an increase in free molecular volume, C_p , entropy, and decrease in viscosity and rigidity at a temperature above T_g . Free volume is the volume unoccupied by the “solid matter” of molecules, and is available for their free movements (Flink, 1983). In glass phase, free volume is below the critical volume restricting the translation motion. Above T_g , free volume increases, resulting in increased molecular mobility. This is the basis for free molecular theory of glass transition given by Turnbull and Cohen (1959), and later revisited by Cohen and Grest (1979). During glass transition there exist continuous changes in heating capacity. It might be due to the need of additional energy to generate an increase in volume so that a larger motion of molecules is allowed (Wunderlich, 2005). Roos and Karel (1991) reported an increase in ΔC_p (J/g solids °C) over the glass transition region, as the molecular weight of solute decreases, the potential reduction in average polymer molecular weight might partly account for increase in ΔC_p . The viscosity of glass ($\sim 10^{12}$ Pa s) is reduced to 10^6 – 10^8 Pa s during its rubbery state when the temperature of glass is increased to T_g . (Downton et al., 1982).

Application of T_g in Food-related Processes

(i) Agglomeration

Agglomeration is a process in which primary particles attach together to form a bigger porous secondary particles (conglomerates). During agglomeration, there is liquid bridge formation among particles due to change in the properties of product's various components. Agglomeration may be desirable or undesirable. Controlled agglomeration is used to improve the property of food powders, product appearance, and handling. For instant food powders, agglomeration is of great significance, as this will determine their solubility time and rehydration properties. In case of amorphous substances, agglomeration depends on parameters such as moisture content and temperature of the product; the compression force and its application time with which the particles are pressed together influences the mechanical properties (Palzer, 2005). The mechanical properties that influence agglomeration are found to be related with T_g . In General, T_g of a material is decreased by water content and increases the adhesive forces under a controlled contact period in which the agglomeration takes place. As the product temperature exceeds T_g , amorphous materials enter the rubbery state and the reduced viscosity induces flow, deformation, and bonding. Agglomeration is stabilized when the glassy state of the final product is obtained at or below T_g by drying or cooling. If the contact period is long at temperature higher than T_g , it will result in caking as undesired agglomeration. Therefore, the concept of glass transition can be applied to optimize the desired agglomeration process.

(ii) Caking

Caking is a phenomenon in which the low moisture powders form lump followed by agglomeration and sticky product due to various temperatures and humidity conditions resulting in loss of properties and functionality of powders. There is decrease in the viscosity of food material, resulting in inter-bridging between particles, finally leading to cohesiveness and caking. Decrease in viscosity has been explained by the phenomenon of glass transition. The amorphous components of food, especially low molecular components, on exposure to higher temperature or humidity conditions undergo glass-rubbery transition. Lloyd et al., 1996, found that the caking of spray-dried lactose was related to the onset temperature of T_g . Further, it was found that the packing density of compacted amorphous lactose powder increased the above onset temperature of T_g , confirming the viscous flow of product above T_g . Low molecular weight protein hydrolyzates, presumably amino acids, were found to exhibit high hygroscopicity and contribute to caking during storage of spray-dried fermented soy sauce powders (Hamano and Aoyama, 1974). Thus, to prevent caking, high molecular weight compounds can be added to increase the T_g of food, and this leads to the development of

anti-caking agents, which are generally high molecular weight compounds.

(iii) Collapse

Structure collapse of the product during air/freeze drying, storage of dried products, is responsible for reduction in volume and porosity, which results in the loss of desirable appearance, volatile substances, and poor rehydration ability. In freeze drying there is a formation of porous product, and if the temperature of the dehydrating porous product is above T_g , the viscosity of the solid material may not be enough to support the structure, and "collapse" or shrinkage occurs (Tsourouffis et al. 1976; To and Flink, 1978). To maintain the original volume, the product temperature should not be above T_g . For various food liquids during freeze drying, the collapse temperature may vary between 5°C and 60°C (Bellows and King, 1973), depending upon their composition. Foods with higher sugar contents (fruit juices) will have lower collapse temperature. Tsourouffis et al. (1976) showed that collapse temperatures can be raised by the addition of high molecular weight materials. But recent studies have shown that T_g alone do not dictate collapse during drying. Other concepts such as surface tension, pore pressure, environment pressure, structure, and mechanisms of moisture transport play important roles in explaining the formation of pores. Some other factors could be strength of the solid matrix (i.e., ice formation, case hardening, surface cracks formation, permeability of water through crust, change in tertiary and quaternary structure of polymers; presence or absence of crystalline, amorphous, and viscoelastic nature of solids; matrix reinforcement; and residence time). However, some of these factors are related to glass transition (Rahman, 2001).

(iv) Crystallization

Crystallization is a very important process related to the quality of food products. Depending on the product, the absence/presence of crystals, as well as their size and shape, are critical factors for the desired texture properties and the free flowing characteristics and dissolution of powders. Moreover, crystallization may promote release of substances entrapped in glass, for instance water, which will increase the water content of the remaining amorphous phase. Crystallization occurs at the temperature above T_g as there is increase in mobility and arrangement of molecules into ordered crystalline structure following the WLF kinetics. Sugar crystallization in foods has been shown to be a consequence of changes in molecular mobility occurring above T_g (Roos and Karel, 1990). Crystallization of lactose impairs the solubility of dairy powders, and accelerates damaging chemical changes, although controlled crystallization can be used to reduce the hygroscopicity and caking tendency of whey and other dairy powders. Thus, crystallization process temperature (close to T_g) is by molecular diffusion, indicating the influence of water content on T_g . Crystallization process rejects impurities, including

volatiles (Mazzobre et al., 1993). Senoussi et al. (1995) found loss of diacetyl as a function of rate of crystallization of lactose during storage. In addition, during the storage of lactose at 20°C above T_g , it was found that the amorphous product went through immediate crystallization, and practically all diacetyl was lost after six days. In cotton candy and certain hard candies, the enhanced mobility due to decreased T_g often leads to crystallization of sucrose unless sufficient crystallization inhibitors are present in the formulation. Graining, or sugar recrystallization, causes substantial change in hard candy confections (Lees, 1965). As sugar crystals are formed, the water content of the liquid phase surrounding the crystals increases due to the exclusionary process of forming of crystal lattice. This increased local moisture content causes a change in moisture dynamics. Moisture continues to penetrate into the candy matrix ahead of the crystallizing front. In the crystallizing region, however, the increased water activity causes moisture to migrate back out into the air, resulting in a net loss of weight.

(vi) Oxidation Reactions and Nonenzymatic Browning

In condition of increased moisture content, T_g is reduced and molecular mobility is increased. As a result, the oxygen mobility and diffusion rate are increased, increasing the oxidation and resulting in off flavor and odor generation. Oxidation phenomena occur in low moisture food systems, such as fat or ascorbic acid oxidation (Rahman, 2004). The oxidation of unsaturated lipids entrapped in sugar-based matrices is affected by physical changes such as collapse or crystallization occurring above glass transition (Shimada et al., 1991; Labrousse et al., 1992). The encapsulated oil was released as a consequence of the crystallization of amorphous lactose. The released oil underwent rapid oxidation, while encapsulated oil remained un-oxidized. The rate of browning in the food systems analyzed fruit and food models were very low in glassy state, but at temperatures above T_g , in addition to decreasing viscosity and increasing reaction rate, crystallization and collapse induce Maillard reaction. Karel et al. (1993) and Karmas et al. (1992) indicated that phase transitions with physical aspects of the matrix are the main factors affecting the rates of nonenzymatic browning reactions. Nonenzymatic browning was found to be very slow below T_g . Bell et al. (1998) studied the glycine loss and Maillard browning as functions of T_g . At water activity of 0.54, pH of 7, storage temperature of 25°C, and $T - T_g$ close to 0, the rate constant was very low but increased with increase in $T - T_g$ value. Bell (1996) studied the kinetics of nonenzymatic browning pigment formation in a model PVP (different molecular weight) matrix. As the system changed from glassy to rubbery state, nonenzymatic reaction rate increased by seven-fold.

(v) Microbial Stability

Microbial stability in general depends on water activity with higher microbiological safety at lower a_w . But this concept has some limitations or factors that can alter this general

theory: (i) Water activity is defined at equilibrium whereas food systems may not be in a state of equilibrium, (ii) the critical limits of water activity may also be shifted to higher or lower levels by other factors such as pH, salt content, antimicrobial agents, heat treatment, and temperature, (iii) nature of solute used also plays an important role, (iv) it does not indicate the state of the water present and how it is bound to the substrate (Scott, 1953; Rahman and Labuza, 1999; Slade and Levine, 1991b), and hence considering the above limitation, T_g can be a better concept to explain microbial stability. Slade and Levine (1987) introduced the concept of using water dynamics or glass-rubber transition instead of water activity to predict the microbial stability of concentrated and intermediate-moisture foods. Sapru and Labuza (1993) found that spores at T_g have high heat resistance, and above T_g they are easy to inactivate. At a given temperature, the inactivation rate decreases with the increase of T_g of spores. Kou et al., (1999) observed the germination of *Aspergillus niger* spores in starch samples for water content/temperature conditions just above T_g , but not in samples below T_g . Due to lack of in-depth studies, this concept has not been widely used to understand the microbial stability.

Measurement Techniques of T_g

Several techniques are available for the determination of T_g . It is usually quantified by measuring various physical properties as a function of temperature. These measurements include specific volume, deformation, conductivity, elasticity, and thermal properties (e.g., C_p). The glass transition range is then identified as the temperature where these properties change significantly. These methods can be classified as calorimetric, thermo-mechanical, volumetric, and spectroscopic methods (Table 7). Depending on the method employed, T_g of a food sample may vary and is closely associated to how sensitive is the measured property to changes in temperature, specifically around the material glass transition region (Brittain and Bruce, 2006).

(i) Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermal analysis technique that investigates changes in C_p of materials as a function of temperature. Most of the transitions defined in the state diagram are commonly measured by DSC using appropriate protocol. A sample of known mass is heated or cooled and the change in C_p is tracked with the changes in the heat flow. The heat flow is measured as the energy required to maintain a zero temperature difference between the sample and an inert reference material as the two specimens are subject to identical temperature schemes in a cooled or heated environment (Ma et al. 1990; Madani et al., 2007). DSC is widely used in food, pharmaceutical, and polymer industries to measure heat flow and temperature-dependent specific heat as well as phase transitions. DSC can be used to determine T_g , in addition to cold

Table 7 Summary of the techniques used for glass transition measurement (Abiad et al., 2009)

S. No.	Techniques	Property measured
1.	Differential scanning calorimetry (DSC)	Heat flow rate
2.	Modulated temperature DSC (MDSC)	Temperature-dependent specific heat
3.	Thermo-mechanical analysis (TMA)	Dimensional deformation (volume, density, or linear displacement)
4.	Dilatometry (DIL)	
5.	Dynamic mechanical analysis (DMA)	Viscoelastic properties (storage/loss moduli)
6.	Dielectric relaxation spectroscopy (DRS)	Relaxation, magnitude, and time dependence of electrical polarization
7.	Nuclear magnetic resonance (NMR)	Spin-spin and spin lattice relaxation times
8.	Positron annihilation lifetime spectroscopy (PALS)	Local free volume hole properties Relaxation and lifetime of positron and positronium
9.	Inverse gas chromatography (IGC)	Gas retention time or volume
10.	Thermal mechanical compression test (TMCT)	Linear displacement and strain Force dissipation
11.	Oscillatory squeezing flow (OSF)	Stiffness and viscoelastic properties
12.	Thermally stimulated depolarization current (TSDC)	Current flow
13.	Atomic force microscopy (AFM)	Change in resonance frequency

crystallization, crystallization, phase changes, melting, cure kinetics, and other reactions such as oxidative stability. It is a thermo-analytical technique in which the difference for heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined C_p over a range of temperatures to be scanned. This technique was developed by Watson and O'Neill (1964) and introduced commercially in 1963 at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. A DSC test is considered as a closed thermodynamic process that permits no matter exchange but allows energy to be added or removed from the system (Wunderlich, 2005). As these events take place at a relatively constant pressure, the total heat transferred, measured by the areas under the peaks, is directly proportional to the change in enthalpy (ΔH) of the sample (Wunderlich, 2005; Sahin et al., 2006). DSC reports phase transitions in the sample as peaks, which are enthalpies absorbed (endothermic) or released (exothermic) during the transition. Endothermic peaks are observed in glass-rubber transitions, melting, denaturation, gelatinization, and evaporation whereas exothermic peaks or enthalpies are associated to freezing, crystallization, and oxidation processes.

There are two types of DSC measurement, usually identified as power-compensation DSC or heat flow DSC and heat-flux DSC. In the former, sample and the reference materials are kept at the same temperature by using the individualized heating elements, and the observable parameter is recorded as the difference in input between them. In the later, the DSC monitors the heat difference between the sample and reference materials. Table 8 summarizes the difference between these two methods. Table 9 shows different attributes which could be detected by DSC and its implication in industries.

(ii) *Improved Versions of DSC*

To increase the efficiency, sensitivity, and functionality of DSC, many improvements have been made to the conventional DSC. It includes (a) modulated temperature DSC, (b) high pressure DSC, (c) fast scan DSC, and (d) UV DSC.

(a) *Modulated temperature DSC (MDSC)*. Modulated temperature DSC is an improved version of DSC with increased resolution and sensitivity to detect weak transitions or when two transitions occur within the same temperature range. It is achieved through the application of two simultaneous heating profiles: (i) linear underlying rate and (ii) sinusoidal modulated rate, which can be expressed as

$$T = T_0 + q.t + B.\sin(\omega t),$$

where T_0 : initial temperature, q : heating rate, B : amplitude of temperature modulation, and ω : angular frequency (Reading, 1993; Reading et al., 1994). The additional sinusoidal modulated rate provides information about the reversing and nonreversing components of heat flow response. The nonreversing component of heat signal is associated with kinetically controlled events that are dependent on both temperature and time. MDSC is particularly useful for the study of reversible (related to C_p) thermal reactions, and is less useful for nonreversing (kinetically controlled) reactions. Glass transitions, heating capacity, melting, and enantiotropic phase transitions

Table 8 Difference between heat flow and heat flux DSC

Parameters	Heat flow	Heat flux
Fast heating(250°C/min plus)	Yes	No
Modulated techniques	Yes	Yes
Accuracy of C_p values	High	Moderate
ΔH accuracy	High	Moderate
Ease of cleaning	Very	Moderate
Isothermal performance	Excellent	Affected by sample

Table 9 Various attributes detected by DSC and their implication in industry

Industry	Transitions	Purpose
Pharmaceuticals	T_g	Collapse/storage temperature Amorphous content
	C_p	Processing conditions
Polymers	T_m	Polymorphic forms, purity
	T_g	Indicator of material properties Effect of additives
	T_m	Polymer processing, heat history
	Exotherm	Reaction rate, curing of materials
Food	C_p	Energy needed to process
	T_c	Recrystallization times, kinetics
	T_g	Storage temperature, properties
	T_m	Processing temperature

are some of the reversible thermal events. Vaporization, decomposition, cold crystallization, relaxation phenomena, and monotropic phase transitions are some of the examples of nonreversible processes. The ability of MDSC to differentiate between reversible and nonreversible thermal events can yield improved separation of overlapping transitions. In measuring T_g , MDSC demonstrates a higher sensitivity than the conventional DSC. Rather than measuring T_g as a simple shift in the baseline, MDSC measures T_g via the analysis of amplitude of heat flow oscillation (Reading, 1993; Reading et al., 1994; Hill et al., 1998).

(b) *High pressure DSC.* In food research, novel nonthermal processes such as high pressure processing, pulse electric field, irradiation, etc. have been developed. During high pressure processing, food components undergo various transitions that can be studied using high pressure (HP) DSC. High pressure DSC is used for other reasons also such as (i) an oxidative stability test may take too long at atmospheric pressures to be convenient (an antioxidant package in motor oil), (ii) reactions producing water/methanol as a by-product, leading to foaming that could be suppressed by higher pressure, (iii) reaction kinetics affected by pressure and needs controlled pressure for its reactions, and (iv) transitions such as T_g and boiling point are responsive to pressure (Höhne and Blankenhorn, 1994). A maximum gas pressure of 100 MPa was reported for the investigation of polymorphic changes in fatty compounds, modification of T_g for food with amorphous phase (sugar, starch, dough, frozen foods), or oxidative stability of oil at high oxygen pressure (Le Parlour et al., 2004).

(c) *UV-DSC/Photo-DSC.* In this method, samples are exposed to UV light from sources such as mercury vapor lamps, LEDs, etc. over a range of frequencies and intensities during the test run. The sample weight is optimized for each individual sample type depending on UV reaction kinetics and the energy released during the reaction. A mechanical refrigerator act as a cooling accessory to effectively remove the heat energy generated. As a general rule, cooling block temperature

should be at least 30°C lower than the isothermal temperature at which the reaction is carried out. The T_g measurement is based on the change in heat flow signal with the UV exposure. Generally heating scan is run before and after UV exposure for the experimental sample and T_g is deduced. It has been observed that T_g continuously diminishes with the continual UV exposure. Two important parameters taken under consideration while performing UV degradation or curing reactions are the light intensity and the isothermal temperature of experiment. Increase in these two parameters generally decreases the UV reaction time. UV-DSC is also used to study the decomposition of materials under UV radiation, understand the effects on the storage of pharmaceuticals, on antioxidant packages in polymers and rubbers, on food properties, or on dyes in sunlight. It is also possible to use kinetics to model degradation by UV light. Because of high intensities of UV available, an accelerated testing is possible (Perkin Elmer)

(d) *Fast scan DSC or hyper DSC.* It applies very high heating rates to a sample to increase the sensitivity of DSC or to trap kinetic behavior. Fast scan heating rates range from 100–300°C/min whereas hyper DSC heating rates range from 300–750°C/min using the small furnace mass. When heating rates of 100–750°C/min are applied, the response of DSC to weak transitions is enhanced and it is possible to see very low levels of amorphous materials in pharmaceuticals, to measure small amounts of natural products, to freeze the curing of thermosetting compounds, and to inhibit the cool crystallization of polymers as well as the thermal degradation of organic materials.

(iii) (a) *Thermo-mechanical Analysis (TMA), and (b) Dilatometry*

Thermo-mechanical analysis measures the thermal expansion (linear thermal deformation) as a function of temperature under a non-oscillatory load such as compression, tension, flexure, or torsion (Ma et al., 1990) to locate the T_g of various materials. In TMA, a cylindrical or oblong specimen measuring 2–6 mm in diameter or length and usually 2–10 mm in height is subjected to slight loading (0.1–5 g) through a vertically adjustable quartz glass probe. The probe is integrated into an inductive position sensor and the system is heated at a slow rate. If the specimen expands or contracts, it moves the probe. A thermocouple close to the specimen measures the temperature. TMA technique may be operated with different modes, i.e., penetration mode using probes of different geometries and measures the relaxation/deformation as a function of compression, tensile, flexural, or torsion force. However, dilatometry measures the dimensional changes of samples (shrinkage/expansion) as a function of temperature. Since these changes may be either linear or volumetric, it focuses on direct measurement of volume, density, and linear displacement. Although it is similar to TMA except that in this method no external load is applied.

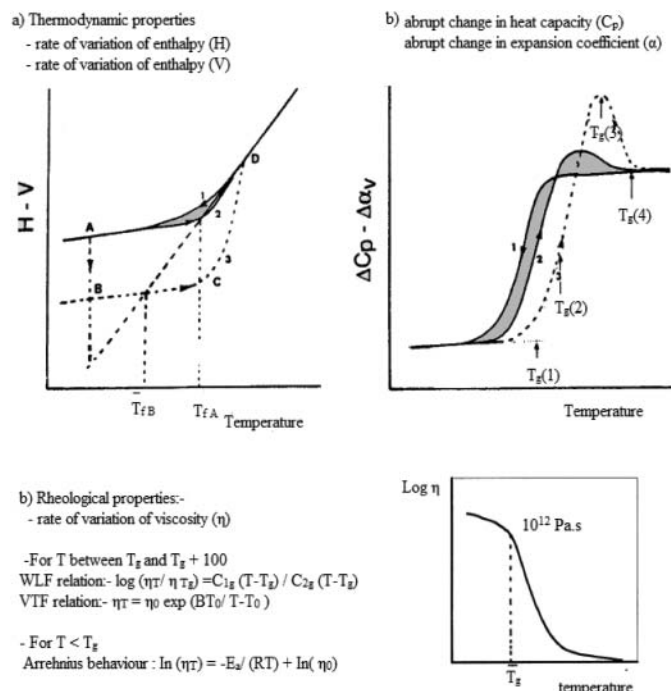


Figure 7 Summaries of the changes in physical properties that occur during glass liquid transition (Champion et al., 2000).

(iv) Dynamic Mechanical Analysis or Dynamic Mechanical Thermal Analysis (DMA)

In DMA, a small deformation is applied to the sample in a cyclic manner and its response to stress, temperature, frequency, and other values is studied. DMA works by applying sinusoidally oscillating deformation to the sample relating to its stiffness. The sample can be subjected by either controlled stress or strain. The stiffness is calculated by the relationship between stress and strain. The time shift between stress and strain is a measure of the friction generated on polymer molecules when it is deformed. The time shift is used to calculate the viscoelastic properties of the material such as the loss modulus and storage modulus. DMA also measures damping in the form of $\tan \delta$. It explains the energy dissipation of the sample under cyclic load, giving information about the energy absorbed by the sample. In this technique the modulus change value will explain T_g . It is seen as a large drop in the storage modulus. To check that the transition is the glass transition, multi-frequency test can be run and the activation energy is calculated (Fig. 8). The activation energy for T_g is roughly 300–400 kJ mol⁻¹.

(v) Dielectric Relaxation Spectroscopy (DRS)

It is also known as the impedance spectroscopy and measures the dielectric properties of sample as a function of frequency. It is capable of measuring the molecular mobility as

well as the structural characteristic of a sample material over a wide range of temperature and frequency (10⁻⁶–10¹⁵ Hz) (Volkov and Prokhorov, 2003). Dielectric spectroscopy measures the relaxation behavior of material as it is subjected to a temperature ramp over a given polarizing frequency range. Consequently, for amorphous materials, two different relaxation processes can be determined: (i) the principal a-relaxation process, which is associated with glass–rubber transition in the amorphous region, and (ii) the secondary b-relaxation process, which is associated with intramolecular oscillations of small dipolar groups. The dielectric response can be expressed in various forms, viz., relaxation times, complex dielectric permittivity (ϵ^*) with real (ϵ'), and imaginary (ϵ'') components, dielectric loss factor ($\tan \delta = \epsilon''/\epsilon'$); complex dielectric modulus ($M^* = 1/\epsilon^*$) or absorption conductivity (σ). All these parameters are mutually related and equivalent in the sense of information (Volkov and Prokhorov, 2003). Figure 9 shows variation of $\tan \delta$ as a function of temperature for amorphous dry D-mannose and a mixture containing 10% water (w/w). As illustrated, these results facilitate the clear localization of T_g of the material at any temperature indicated by its maximum $\tan \delta$ (Noel et al., 2000).

(vi) Phase Transition Analyzer (PTA)

Phase transition analyzer uses a combination of time, temperature, pressure, and moisture to measure the controlling T_g and T_m (melting temperature) of a biopolymer sample (Strahm et al., 2000; Strahm and Plattner, 2000). The controlling T_g and T_m can be described as the temperatures at which sufficient amount of sample is softened to allow particle compaction (T_g) or melted to allow for flow (T_m). It consists of two sealed chambers, top and bottom, separated by an interchangeable capillary die. The two chambers house electric heaters and contain a hollow cavity that allows a cooling fluid to be used. The pistons, mounted together through sidebars, are held in a fixed position during testing. An air cylinder, mounted to the bottom of PTA, maintains a constant pressure on the sample. A linear displacement transducer measures the deformation, compaction, and flow relative to initial sample height. This procedure has an importance in extrusion technology.

(vii) Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance is a spectroscopic technique based on the magnetic properties of atomic nuclei, and is often used to monitor the motional properties of molecules by detecting the relaxation characteristics of the NMR active nuclei, such as ¹H, ²H, ³H, ¹³C, ¹⁷O, ²³Na, and ³¹P. Since segmental motion is a fundamental factor in the glass transition of polymers, NMR can be used to detect T_g (Zeleznaek and Hosney, 1987; Perez, 1994). In NMR, spin–lattice relaxation

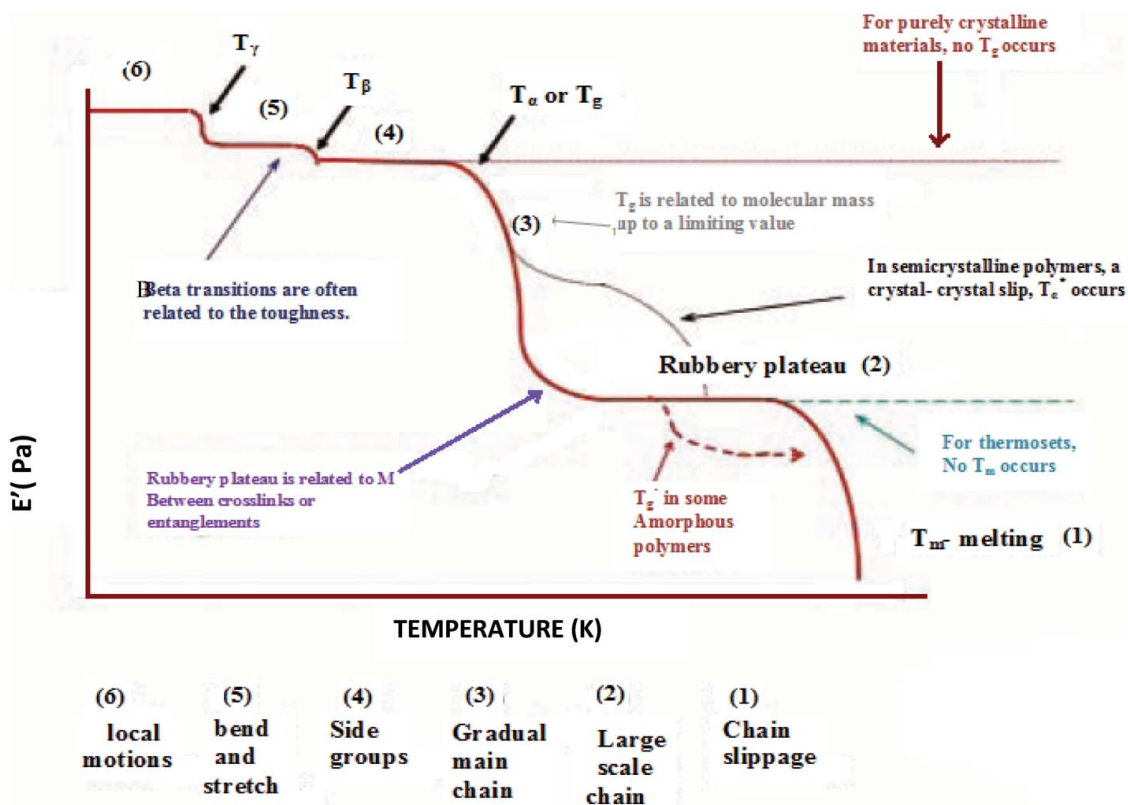


Figure 8 Various short-range motions during glass transition that can be studied using DMA.

time (T_1) and spin-spin relaxation time (T_2) are studied. Spin-spin relaxation time is related to glass transition and T_1 is related to molecular mobile classes. NMR, which is capable of measuring the motional properties of molecules, may have strong potential in the study of glass transition. Kalichevsky et al. (1992b), Ablett et al. (1993) and Kalichevsky et al.

(1992a, 1992c, 1992d) studied the spin-spin relaxation characteristics during glass transition in amylopectin, gluten, gluten with corn oil, caprylin or hydroxycaproic acid, soluble glutenin, gliadin, gluten with sucrose, glucose or fructose, maltotriose, maltoheptaose, pullulan, and gelatin gels. It was found that the behavior of the spin-spin relaxation time of the "rigid" component was related to glass transition.

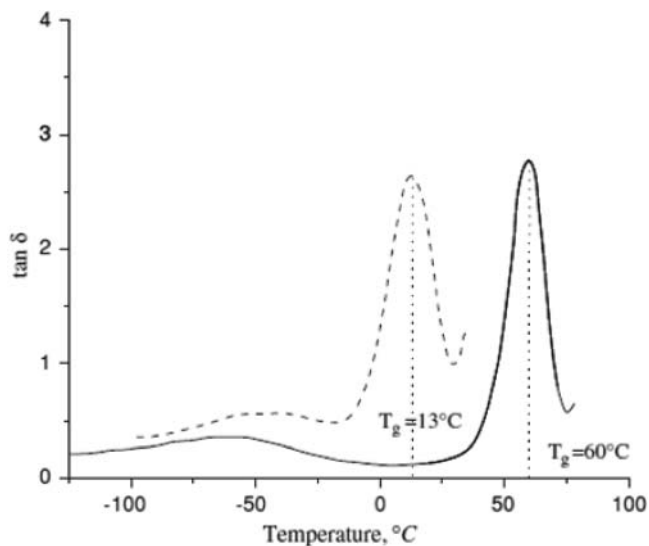


Figure 9 Variation of $\tan \delta$ with temperature at 1 kHz for dry amorphous D-mannose (---) and its 10% w/w water mixture (—) (Noel et al., 2000).

(viii) Positron Annihilation Lifetime Spectroscopy (PALS)

Positron Annihilation Lifetime Spectroscopy is a micro-probe that can directly determine local free-volume properties in polymeric materials. It gives information about the dimensions, distributions, and concentrations of voids within the material. This is obtained by monitoring the lifetime of positrons and positroniums (Ps) in a given material. A positron is an antiparticle or antimatter of an electron having a charge of +1 whereas Ps is a neutral bound atom consisting of an electron and a positron. Annihilation is the phenomenon in which the electron and positron meet and vanish into other forms of energy. The lifetime of positrons in matter is a function of electronic environment. In other words, the measured lifetimes are those of a thermal positron in the material under consideration. There are two types of positronium: (i) the ortho-Positroniums, o-Ps, where the spins of two particles are parallel, and (ii) the para-Positroniums, p-Ps, where the spins

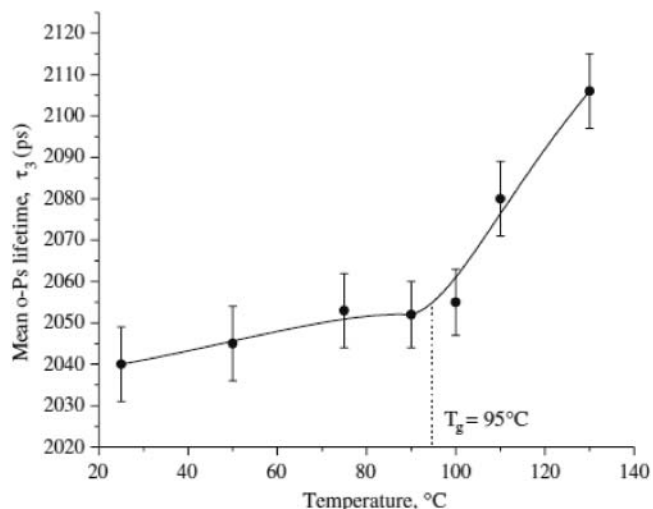


Figure 10 Mean o-Ps lifetimes for polystyrene as a function of temperature. T_g values agreed with that determined by DSC (Liu et al., 1993).

are anti-parallel. The lifetimes of o-P and p-P in vacuum are 142 nanosecond and 125 picosecond respectively. The o-P is mainly the positronium of interest and is monitored to obtain information about holes and the free volume. Figure 10 illustrates a typical τ_3 -temperature plot for polystyrene (Liu et al., 1993).

CONCLUSIONS

From the review study, it is agreed that T_g plays an important role in the stability of food. Various factors that influence T_g as reviewed indicate the need for more detailed study on the effect of process parameters, viz., pH, pressure, and heterogenous characteristics of food materials. The review also summarizes various techniques employed to measure T_g , but most of these have not been used extensively in food sector, implicating the heterogeneity of food ingredients and process sequences employed in food industry. The understanding of mobility of individual components according to their molecular size, physico-chemical characteristics, distribution of water and lipids, and their profiles responsible for phase transition to the observed macroscopic behavior is to be explained and correlated.

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