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APPLICATION OF GLASS TRANSITION IN FOOD PROCESSING

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ABSTRACT

Glass transition phenomenon has been employed to food products to study their stability. It can be applied as an integrated approach along with water activity, 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, non enzymatic browning and microbial stability of food system. Various techniques like differential scanning calorimetry (DSC), NMR etc have been developed to determine the glass transition temperature (T_g) of the food system. Also various theories have been given to explain the concept of T_g and its relation to changes in food system. This review summarizes the understanding of glass transition concept, its measurement and application in food technology.

Keywords: Glass transition, theories, food processing, DSC

Introduction

The glass transition phenomenon is a concept originally developed for synthetic polymers, which has been applied to many food products to predict their stability. Though glassy materials are known for centuries, the scientific understanding being evolved in past two decades (Ferry, 1991) and applied to characterize materials in various fields like 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 glass transition phenomenon can be applied as an integrated approach along with water activity, physical and chemical changes in food during processing and storage to determine the food stability. Agglomeration, crystallization, caking, sticking, collapse, oxidation reactions, non enzymatic browning, and microbial stability of food systems also depend on T_g . Most of the review articles on glass transition focussed either on 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 glass transition phenomenon, 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 a discontinuity in physical, mechanical, electrical, thermal, and other properties of a material (Rahman, 1995). It is a kinetic process and metastable property of amorphous material and the rate of transition depend on the temperature as well as moisture content (Bhandari, 1999). In glassy state, molecular movement is highly limited, which is necessary for an orderly alignment of molecules to crystallise (Flink, 1983). Thus the temperature at which the amorphous system gets converted from glassy to rubbery state is called as glass transition temperature (T_g). T_g is not unique for any substance and depends on the rate of cooling, molecular weight, water content, matrix composition etc. Fig. 1 shows the various transitions an amorphous material undergoes with the temperature change. On heating, glass material undergoes transition to a rubbery phase leading to crystal formation. Further heating leads to 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 the temperature and time (Bhandari *et al*, 1997a).

Global application of glass transition concept

Glass formation and transition study can be employed in various research viz. environments, pharmaceutical, industry, biology and many other fields.

Environment

Glasses are the 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 the glassy state (Angell, 1995).

Pharmaceutical industry

Glassy materials are extensively used for 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 its therapeutic or biochemical applications. Cooling of water at the rate on the order of 10^6K/s results in formation of amorphous glassy supercooled water. The glass transition temperature of water is much colder and harder to determine but studies has 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, glass transition temperature is important tool in 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 poorly water soluble drugs, which can be prepared as glass solutions by melt extrusion with amorphous polymer-polyvinyl pyrrolidone (PVP) to improve the 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 the storage capability and physical stability (Paradkar *et al*, 2003).

Polymer industry

Polymers are the excellent material where the knowledge of T_g , has a significant role in harnessing them for technological uses. All synthetic polymers are solids that are at least

partially amorphous. The end use and processing parameters decides 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 like polystyrene and poly (methyl methacrylate) are used below their glass transitions (glassy state), while rubber elastomers like 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, DNA alter their individual behaviours 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 the solvent (e.g. water) in which the proteins are usually embedded. The transition of various individual molecules in macromolecules with temperature in the biological system is analogous to the glass transition phenomenon. For a protein molecule, motions of large segments of the polymer and the local reorientation of units with very different characteristic times corresponds to type α (relaxation processes/ motions corresponding 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 glass transition phenomenon, various short range motions have been observed. Generally, the transitions are much more pronounced in denatured state than the native state. Glassy state materials has been observed in seed, prokaryotes, pollen and are found to be involved in protecting biological tissue from extremely dry conditions. Mainly the glass forming sugars like trehalose or oligosaccharide like raffinose and stachyose are the protectants in

biological system. Sugars present in cells form glass matrix at low water conditions thus protecting the large macromolecules like proteins from denaturation (Chang *et al*, 1996) and prevent formation of molecular aggregates. The high viscosity of glass matrix lowers the metabolic chemical reactions and thus increases the longevity of cells (Karmas *et al*, 1992; Roos 1995)

Theories associated with glass liquid transition

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

(i) Free volume theory

It was developed by Turnbull and Cohen (1959), and later revisited by Grest and Cohen (1979). Based on the free volume concept, 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). 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 glass transition temperature 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 during extrusion, puffing or flaking process.

(ii) Kinetic theory

It defines the T_g as the temperature at which the relaxation times of the molecules present in system are of same order of magnitude with 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 the holes and molecules into account. Also, it examines the effect of heating/cooling and provides quantitative information about the heat capacities below and above the glass transition temperature. Thus, decreasing the time frame of an experiment, i.e., the rate of either heating/cooling would reveal an increase in the T_g . It explains the 6-7°C shifts in the glass transition per decade of time scale of the experiments (Abiad, 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 the 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 associated to the behavior of these materials. These include the variation of T_g as a function of molecular weight (Misra *et al*, 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 (del Val., 1986; DiMarzio, 1990)

(iv) Mode coupling theory

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 the liquid like processes. With the lowering temperature, the system passes through a critical point which is responsible for dramatic increase in relaxation times (Ediger, 1996). It predicts a critical temperature (T_c) at which the dynamic properties of the material, notably particle motion and relaxation, diverge. This theory anticipates a sharp transition in the viscoelastic properties as well as a change in the relaxation behaviour of the glass material near the predicted transition, whereas at temperatures below the transition temperature, the theory anticipates a random freeze of the liquid's configuration (Bengtzelius, 1984).

T_g prediction models

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

(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 same and additive. It predicts the T_g value of composite mixture from the T_g values individual pure components (Aguilera *et al*, 1993; Roos, 1995; Seo *et al*, 2004). Usually, the model assumes that T_g value of the mixture falls between the T_g of individual component 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 that 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 the T_g . The limitation 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_g .

(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 can be calculated by subtracting the heat capacities of the component at glassy and rubbery state respectively. This model has been applied for multi component systems such as water, glucose and sucrose (Roos, 1995; Arvanitoyannins *et al*, 1993; kalichevsky *et al*, 1992). This equation can be further derived and applied for ternary, quaternary and higher order systems as shown by Truong *et al*, 2002. Comparatively, this model requires less number of experimental values for predicting as only the 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 William-Landel-Ferry (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 Williams-Landel-Ferry (WLF) equation having an assumption that at the T_g , the ratio of free volume to volume reaches a critical constant value of 0.025 (William *et al*, 1995). The prediction equation can be expressed as

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

Where, R : $K \cdot \frac{T_{g1}}{T_{g2}}$

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

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

Where, T_{gi} : glass transition of the i^{th} component in the mixture and x_i : mole fraction concentration of the i^{th} component, k , q : fitting parameters (that depends on the 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 behaviour of corn distillers dried grains with soluble.

(b) Pinal's prediction model

Pinal (2008) added an additional term in the Couchman-Karas equation to account for the effect of entropy mixture on the T_g and expressed the prediction equation as

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

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

Factors influencing T_g

Glass transition is influenced by heating and 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 amorphous state and show the glass transition phenomenon. Slower cooling rate provide 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 the increase in cooling or heating rate would result in an increase in T_g (Table 2). Higher heating or cooling rates are 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 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 the T_g of sucrose was lower on rapid cooling as compared to slow cooling. For sucrose solution (70%), T_g was found to be -66.7°C and -64.6°C for rapid and slow cooling respectively. For solution (30%), T_g was -34.6°C and -33.3°C for rapid and slow cooling respectively. The T_g of rice starch gel was -9°C and -7.5°C for rapid and slow cooling, respectively. Yu *et al*, 2001 reported that increasing the mass of pan and decreasing the heating rate will reduce the 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 the increase in rate of heating. However, for freeze-dried samples, T_g values changed marginally due to reduced moisture content.

(ii) Pressure

Based on principles of thermodynamics, an increase in pressure on an amorphous system will decrease its entropy. This corresponds to increased glass transition temperature. 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 glass transition temperature range (Ferry, 1960). However, the large molecules like proteins (denaturation) and starches (gelatinization) are significantly affected by pressure treatment rather than the low molar mass

compounds (Hayashi, 1992). Ahmed *et al*, 2006 studied the effect of high pressure treatment (350- 650 MPa, 22-26 °C, 15 min) on the thermal properties of three samples of amorphous and semi-crystalline polylactides (PLA) with molar mass (M_w) in the range of 3800-6200. He observed that amorphous polylactide showed higher T_g than the semi crystalline due to the higher molar mass. But overall there is decrease in glass transition temperature with increasing pressure which contradicts the above statements. The possible explanation for the decrease can be synergistic effect of pressure and temperature.

(iii) Molecular weight

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

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

Where, K: constant dependent on the material, and α_R , α_G : corresponding coefficient 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 the glass transition temperature with the molecular weight of the 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 the isomalt using differential scanning calorimeter at various water contents. They reported that the addition of 75% polydextrose and high molecular hydrogenated starch hydrolysate increased the 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 the T_g determined by differential scanning calorimetry as a function of molecular weight.

(iv) Water and other plasticizers

Addition of any additives in food can either act as plasticizer or antiplasticizer. Plasticizer lowers the T_g of the substance and antiplasticizer increases the T_g . Any miscible solvent or a low molecular weight additive incorporated in an amorphous system almost invariably will depress its glass transition temperature (Lechuga *et al*, 2002). The effect of a plasticizer on the 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 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 the T_g and mechanical resistance (Brent *et al* 1997; Moraru *et al*.,

2002; Roos & Karel, 1991). Ohkuma *et al* (2008) studied the effect of water on the freeze-dried carp surimi-trehalose mixtures of varying moisture content. Samples containing (2.5-16.2%, w/w) moisture had a clear T_g values. It was found that the T_g decreased significantly with an increase in the moisture content. This result is ascribed to the plasticizing effect of water (Fig. 5). It has been found that the other low molecular compounds such as sugar, glycerol, and sugar alcohols also decreases the T_g . Chaudhary *et al*, 2011 studied the glass transition behaviour 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 behaviour (rubber like behaviour) in multi-plasticized starch biopolymer with 70% amylopectin structure. In the calorimetry measurements (bulk viscous flow) of plasticized samples showed higher T_g than non-plasticized samples at low water activities i.e a typical antiplasticization behaviour. However, increased concentration of plasticizer to 15% and 20% by weight led to significant reduction in T_g temperature. Thus plasticising effect can be described using Gordon-Taylor equation as follow

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

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

Application of T_g in food processing and related phenomenon

The concept of glass/ rubbery state is of practical importance when considering the food stability. The 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. Change includes caking, collapse, crystallization, agglomeration, oxidative reactions etc in food systems.

Importance of T_g

Food is a heterogeneous system consisting of macromolecules like carbohydrates, proteins etc. These macromolecules undergo phase transition on change of moisture content and temperature resulting the change in the food properties. The glass transition occurs over a wide range of temperature, owing to heterogeneity of the food system (Ferry, 1980; Bosma *et al*, 1988). Food can be considered stable at the glassy state since below glass transition temperature compounds involved in deterioration reactions diffuse and react slowly (Slade & Levine, 1991). 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 the complex changes of 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. Fig. 6 shows the state diagram indicating the different states as a function of temperature and solids mass fraction. The freezing line (ABC) and solubility line (BD) are shown in relation to the glass transition line (EFS). The point F (X_s' and T_g') lower than T_m' (point C) represent the maximum freeze concentration condition. The water content at point F or C is considered as the 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 the solid matrix in the frozen sample, which is determined by differential scanning calorimetry (DSC). In the region AHB, the phases present are ice and solution. Below point B, first crystallization of solute occurs, thus HBCL region transforms to the three states: ice, solution and solute crystals. No free water exists in the right side of point C and then the very concentrated solution is transformed to rubber state. The region

ICFJ contains ice, rubber and solute crystal. Point F is the T_g' , below which point a portion of the rubber state is transformed to the glass state, thus region JFS contains glass, ice and solute crystal. The region BQEL is important in food processing and preservation as this region shows many characteristics such as crystallization, stickiness and collapse. The line BDL is the melting line that 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 the liquid and solid phases (Rahman, 2006).

Changes in physical properties during glass transition

In food systems, many of physical properties changes with the temperature, especially above T_g . There is an increase in free molecular volume, heat capacity (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 Grest and Cohen (1979). During glass transition there exist continuous changes in the heat 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 $^{\circ}\text{C}$) over the glass transition region as the molecular weight of the solute decreases, the potential reduction in average polymer molecular weight might partly account for the ΔC_p increase. The viscosity of a glass ($\sim 10^{12}$ Pa s) is reduced to 10^6 - 10^8 Pa s during its rubbery state when the temperature of the 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 particle (conglomerates) are formed. During agglomeration, there is liquid bridge formation among the particles due to change in the properties of various components in the product. Agglomeration may be desirable or undesirable. Controlled agglomeration is used to improve the property of food powders, product appearance and handling. For the 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 the parameters such as the moisture content and temperature of the product, the compression force and its application time with which the particles are pressed together that 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. The 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. So the glass transition concept can be applied to optimise the desired agglomeration process.

(ii) Caking

Caking is a phenomenon in which the low moisture powders forms lump followed by agglomeration and sticky product due to various temperatures and humidity conditions resulting in loss of properties and functionality of the powders. There is decrease in the viscosity of the food material resulting in interbridging between the particles and finally leading to cohesiveness and caking. The decrease in the viscosity has been explained by the glass transition phenomenon. The amorphous components of food especially low molecular components on exposure to higher temperature or humidity conditions undergo the glass- rubber 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 above onset temperature of T_g , confirming the viscous flow of the product above T_g . Low molecular weight protein hydrolyzates presumably the 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 in order to increase the T_g of the food and this led to 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 the reduction in volume and porosity, which results in the loss of desirable appearance, volatile substances and with 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 (To and Flink, 1978, Tsourouflis *et al* 1976). 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 content(fruit juices), will have lower collapse temperature and Tsourouflis *et al.* (1976) showed that the collapse temperatures can be raised by the addition of high molecular weight materials. But recent studies showed that the glass transition temperature alone do not dictate the collapse during drying. Other concepts such as surface tension, pore pressure, environment pressure, structure and mechanisms of moisture transport play important role in explaining the formation of pore. Some other factor 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 the release of substances entrapped in the glass, for instance water, which will increase the water content of the remaining amorphous phase. Crystallization occurs at 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 powders 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 . Crystallisation process rejects impurities including volatiles. Senoussi *et al.* (1995) found a loss of diacetyl as a function of rate of crystallisation of lactose during storage. Also during the storage of the lactose at 20°C above T_g , it was found that the amorphous product went through immediate crystallisation and practically all diacetyl was lost after 6 days. In cotton candy and certain hard candies, the enhanced mobility due to decreased T_g often leads to crystallization of the 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 form, the water content of the liquid phase surrounding the crystal increases in water content due to the exclusionary process of forming the 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 in weight.

(vi) Oxidation reactions and Non enzymatic 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 flavour and odour generation. Oxidation phenomena occur in low moisture food systems, such as fat or ascorbic acid oxidation. The oxidation of unsaturated lipids entrapped in

sugar based matrices is affected by physical changes such as collapse or crystallization occurring above glass transition (Labrousse *et al*, 1992; Shimada *et al*, 1991). 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 was very low in the glassy state, but at temperatures above T_g , in addition to decreasing viscosity and increasing reaction rate, crystallization and collapse induces 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 non-enzymatic browning reactions. Non-enzymatic browning was found to be very slow below glass transition temperature. Bell *et al* (1998) studied the glycine loss and maillard browning as a function of T_g . At water activity of 0.54, pH of 7, and storage temperature of 25°C and $T-T_g$ close to 0, the rate constants was very low but with the increase in $T-T_g$, it increased. Bell (1996) studied the kinetics of non enzymatic browning pigment formation in a model polyvinyl pyrrolidone (PVP)(different molecular weight) matrix. As the system changed from glassy to rubbery state, non- enzymatic reaction rate increased seven fold.

(v) Microbial Stability

Microbial stability in general depends on water activity (a_w) 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 , anti-microbial 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 (Rahman & Labuza, 1999; Scott, 1953) 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, still 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. heat capacity). 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 the food sample may vary and they are closely associated to how sensitive is the measured property to changes in temperature, specifically around the material glass transition region.

(i) Differential scanning calorimetry (DSC)

DSC is a thermal analysis technique that investigates the changes in heat capacity (C_p) of materials as a function of temperature. Most of the transitions defined in the state diagram are

commonly measured by DSC method using appropriate protocol. A sample of known mass is heated or cooled and the change in heat capacity 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 C-Y *et al.* 1990; Madani *et al.*, 2007). DSC is widely used in food, pharmaceutical, and polymer industries to measure the heat flow and temperature-dependent specific heat as well as phase transitions. DSC can be used to determine the T_g , in addition to cold crystallization, crystallization, phase changes, melting, cure kinetics, and other reactions such as oxidative stability. It is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the 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 heat capacity over the range of temperatures to be scanned. This technique was developed by Watson and O'Neill (1960) and introduced commercially at the Pittsburgh Conference (1963) 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 of enthalpy (ΔH) of the sample (Sahin *et al.*, 2006; Wunderlich, 2005). DSC reports the 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 the using the individualized heating elements and the observable parameter 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 summarize the difference between these two methods. Table 9 shows the different attributes which could be detected by DSC and its implication in industries.

(ii) Improvised versions of DSC

To increase the efficiency, sensitivity and functionality of DSC, many improvements have been done 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)*

MDSC 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

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

Where, T_0 : initial temperature, q : heating rate, B : amplitude of temperature modulation, and ω : frequency (Reading, 1993; Reading *et al*, 1994). The additional sinusoidal modulated rate provides information about the reversing and nonreversing components of the heat flow response. The non reversing component of the 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 the heat capacity) thermal reactions, and is less useful for non-reversing (kinetically controlled) reactions. The glass transitions, heat capacity, melting, and enantiotropic phase transitions are some of the reversible thermal events. The vaporization, decomposition, cold crystallization, relaxation phenomena, and monotropic phase transitions are some of the examples of non reversible process. The ability of MDSC to differentiate between reversible and non-reversible thermal events can yield improved separation of overlapping transitions. In measuring the glass transition temperature, MDSC demonstrates a higher sensitivity than the conventional DSC. Rather than measuring the T_g as a simple shift in the baseline, MDSC measures T_g via the analysis of amplitude of heat flow oscillation (Hill *et al*, 1998; Reading, 1993; Reading *et al*, 1994)

(b) High pressure DSC

In food research novel non thermal process like high pressure processing, pulse electric field, irradiation etc, has been developed. During high pressure processing, food components undergo various transitions that can be studied using the High Pressure DSC. High Pressure (HP) DSC is used for other reasons like (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 like the T_g and boiling point are responsive to pressure. A maximum gas pressure of 100 MPa was reported for investigation of polymorphic changes in the fatty compounds, modification of glass transition temperature 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 vapour lamps, LEDs, etc over a range of frequencies and intensities during the test run. The sample weight is optimised for each individual sample type depending on UV reaction kinetics and the energy released during the reaction. A mechanical refrigerator act as the 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 the T_g is deduced. It has been observed that T_g is continuously diminished 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 the degradation by UV light. Because

of the high intensities of UV available, an accelerated testing is possible (Perkin Elmer-
www.perkinelmer.com.)

(d) Fast scan DSC or Hyper DSC

It applies very high heating rates to a sample to increase the sensitivity of a DSC or to trap kinetic behaviour. Fast scan heating rates range from 100-300 °C/min, where as 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, measure small amounts of natural products, freeze the curing of thermosetting compounds, and inhibit the cool crystallization of polymers as well as the thermal degradation of organic materials.

(iii) (a) Thermo mechanical analysis (TMA) and (b) dilatometry

TMA measures the thermal expansion (linear thermal deformation) as a function of temperature under a nonoscillatory load like viz. compression, tension, flexure, or torsion (Ma C-Y *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. But, 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 the volume, density, and linear displacement. Though it is similar to TMA except that in this method there is no external load is applied.

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

In DMA, a small deformation is applied to sample in a cyclic manner and its response to stress, temperature, frequency and other values are 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 the stress and the strain. The time shift between the 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 about 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 a T_g is roughly 300-400 kJmol⁻¹.

(v) Dielectric Relaxation Spectroscopy (DRS)

It is also known as the impedance spectroscopy and it measures the dielectric properties of the 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 temperature and frequency (10^{-6} - 10^{15} Hz) range (Volkov *et al*, 2003). Dielectric spectroscopy measures the relaxation behaviour of the material as it is subject 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 the 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 *et al*, 2003). Figure 9 shows the variation of $\tan \delta$ as a function of temperature for amorphous dry D-mannose and for 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 and Strahm and Plattner, 2000). The controlling T_g and T_m can be described as the temperature at which sufficient amount of a sample is softened to allow for 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 the 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)

NMR 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 , ^{13}C , ^{17}O , ^{23}Na and ^{31}P . Since segmental motion is a fundamental factor in the glass transition of polymers, NMR can be used to detect T_g (Zeleznaĳ and Hoseney, 1987; Perez, 1994). In NMR, spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) are studied. T_2 is related to the glass transition and T_1 related to molecular mobile classes. The NMR, which is capable of measuring the motional properties of molecules, may have strong potential in the study of glass transition. Kalichevsky *et al.* (1992) and Ablett *et al.* (1993) studied the spin-spin relaxation characteristics during the 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 behaviour of the spin-spin relaxation time of the ‘rigid’ component was related to the glass transition.

(viii) Positron Annihilation Lifetime Spectroscopy (PALS)

PALS is a microprobe that can determine directly the 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 the 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 the 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-Positronium, o-Ps, where the spins of the two particles are parallel, and (ii) the para- Positronium, p-Ps, where the spins are antiparallel. The lifetime of o-Ps and p-Ps are 142 nanosecond and 125 picosecond in vacuum, respectively. The o-Ps is mainly the positronium of interest and is monitored to obtain information about holes and the free volume. Fig. 10 illustrated a typical τ_3 –temperature plot for polystyrene (Liu *et al*, 1993).

Conclusion

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 indicates the need for more detailed study on the effect of process parameters viz., pH, pressure and heterogeneous characteristics of the food materials on T_g . The review also summarizes various techniques employed to measure the T_g but most of them 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 its profile responsible for phase transition to the observed macroscopic behaviour to be explained and correlated and so on.

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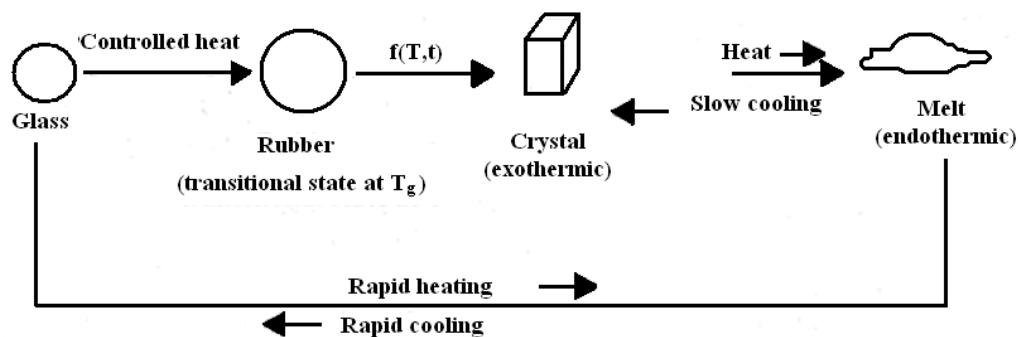


Fig.1. Summary of Changes in physical state of an amorphous glass through rubbery (translational) to crystalline state (Bhandari *et al*, 1997a).

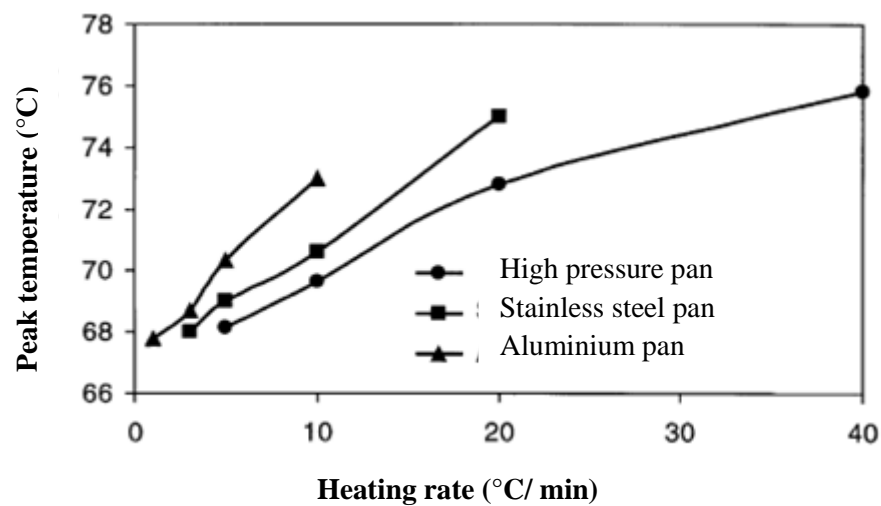


Fig. 2. Effect of heating rate on peak temperature measured with different pans for 50% corn starch solution (Yu *et al*, 2001).

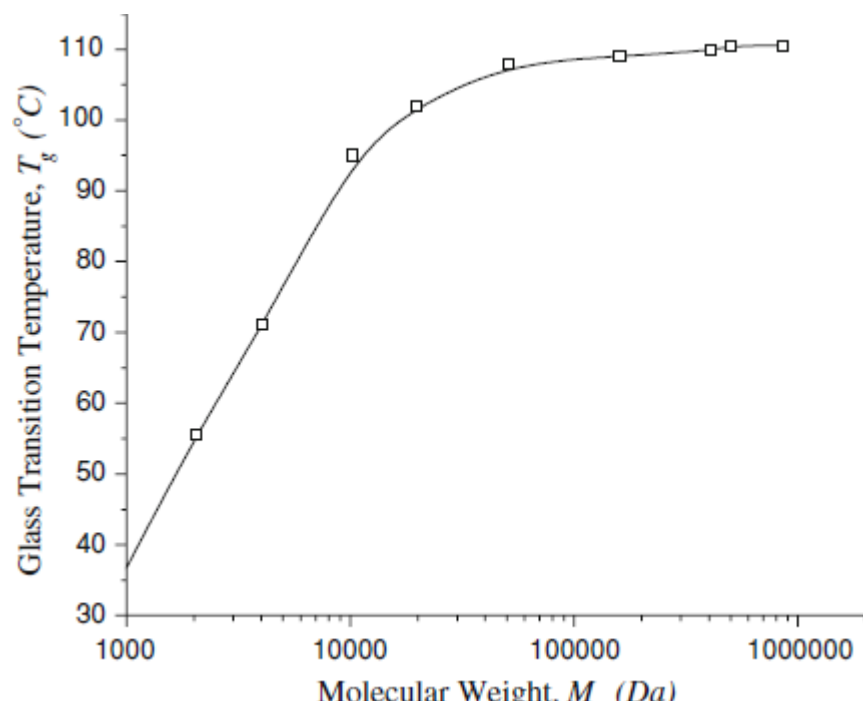


Fig. 3. Effect of molecular weight on the T_g of polystyrene (Blanchard *et al*, 1974).

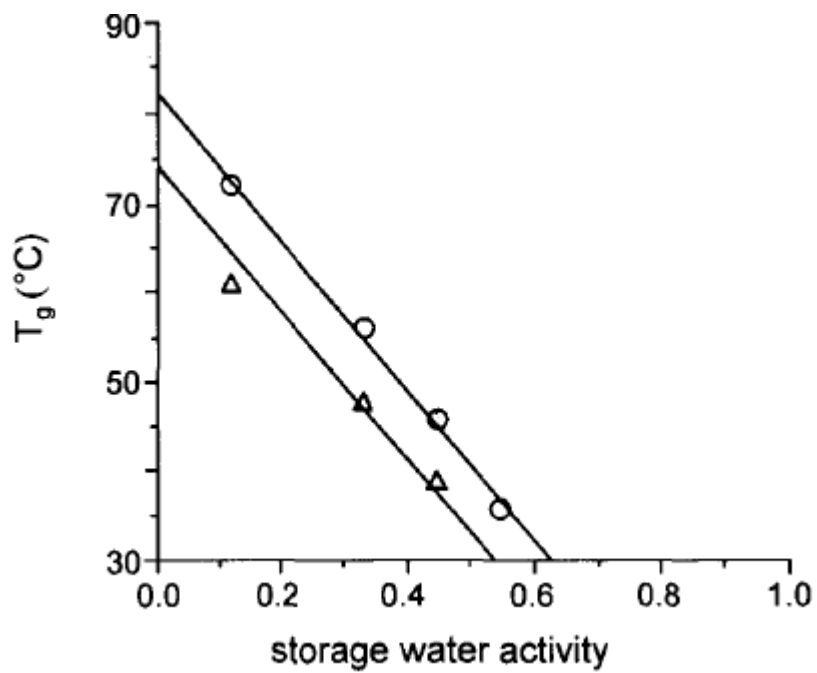


Fig. 4. Effect of water activity on T_g of various infant formulas stored at 20°C as a function of water activity (Chuy and Labuza, 1994).

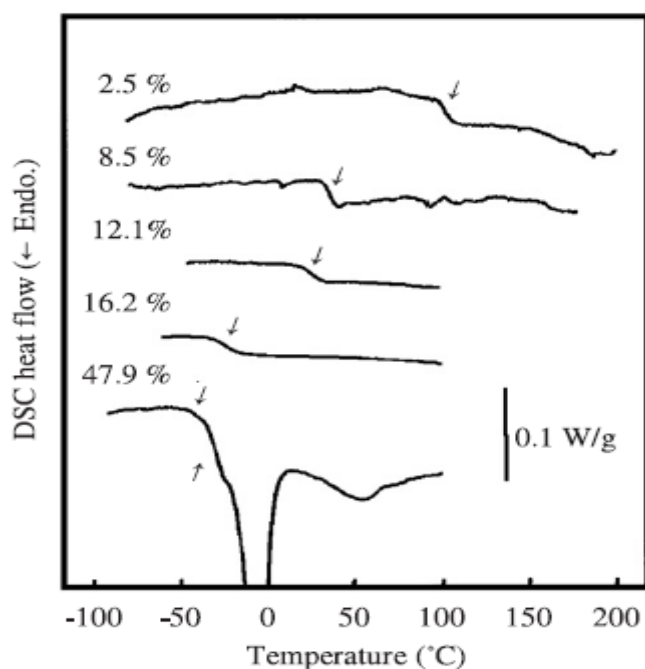


Fig. 5. DSC thermograms for freeze-dried carp surimi-trehalose mixtures (80% trehalose in dry matter) of varying residual moisture. (↓= samples containing 2.5-16.5% (w/w) moisture content, ↑ & ↓ and = samples containing 47.9% (w/w) moisture content indicating T'_{g1} and T'_{g2} respectively.)

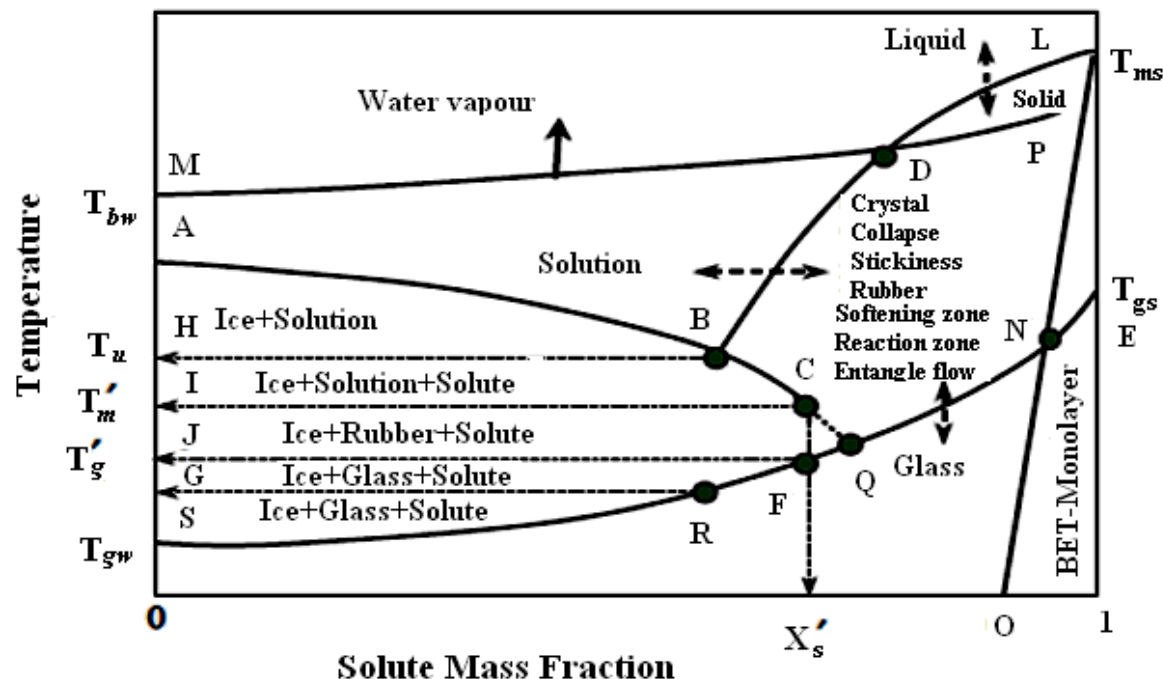
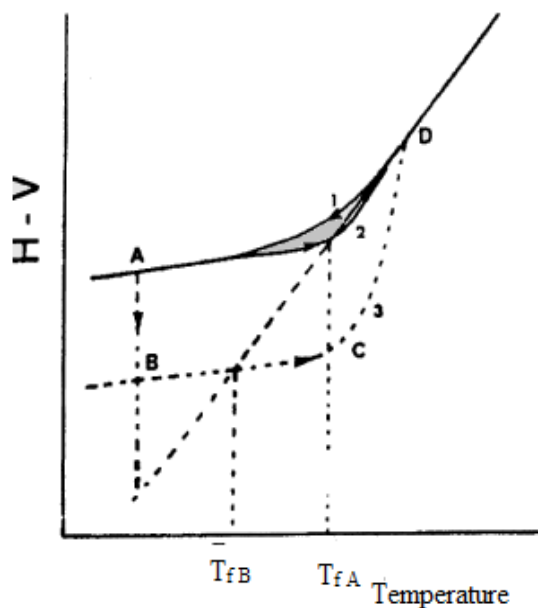


Fig. 6. State diagram showing different regions and state of foods (T_{bw} , boiling point; T_u , eutectic point; T_m' , end point of freezing; T_g' , glass transition at end point of freezing; T_{gw} , glass transition of water; T_{ms} , melting point of dry solids; T_{gs} , glass transition of dry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

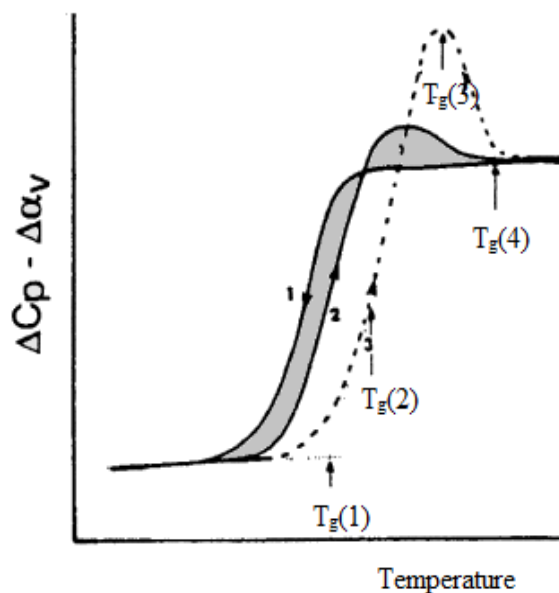
a) Thermodynamic properties

- rate of variation of enthalpy (H)
- rate of variation of enthalpy (V)



b) abrupt change in heat capacity (C_p)

- abrupt change in expansion coefficient (α)



b) Rheological properties:-

- rate of variation of viscosity (η)

- For T between T_g and $T_g + 100$

WLF relation:- $\log (\eta_T / \eta_{T_g}) = C_{1g} (T - T_g) / C_{2g} (T - T_g)$

VTF relation:- $\eta_T = \eta_0 \exp (BT_0 / (T - T_0))$

- For $T < T_g$

Arrhenius behaviour : $\ln (\eta_T) = -E_a / (RT) + \ln (\eta_0)$

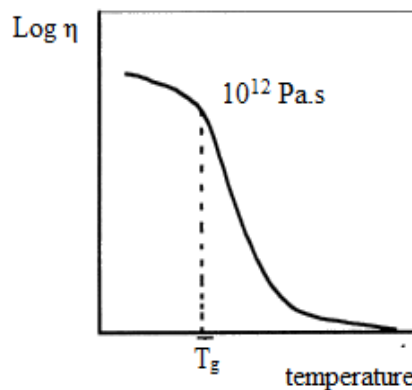


Fig. 7. Summaries the changes in physical properties occur during glass liquid transition (Champion *et al*, 2000).

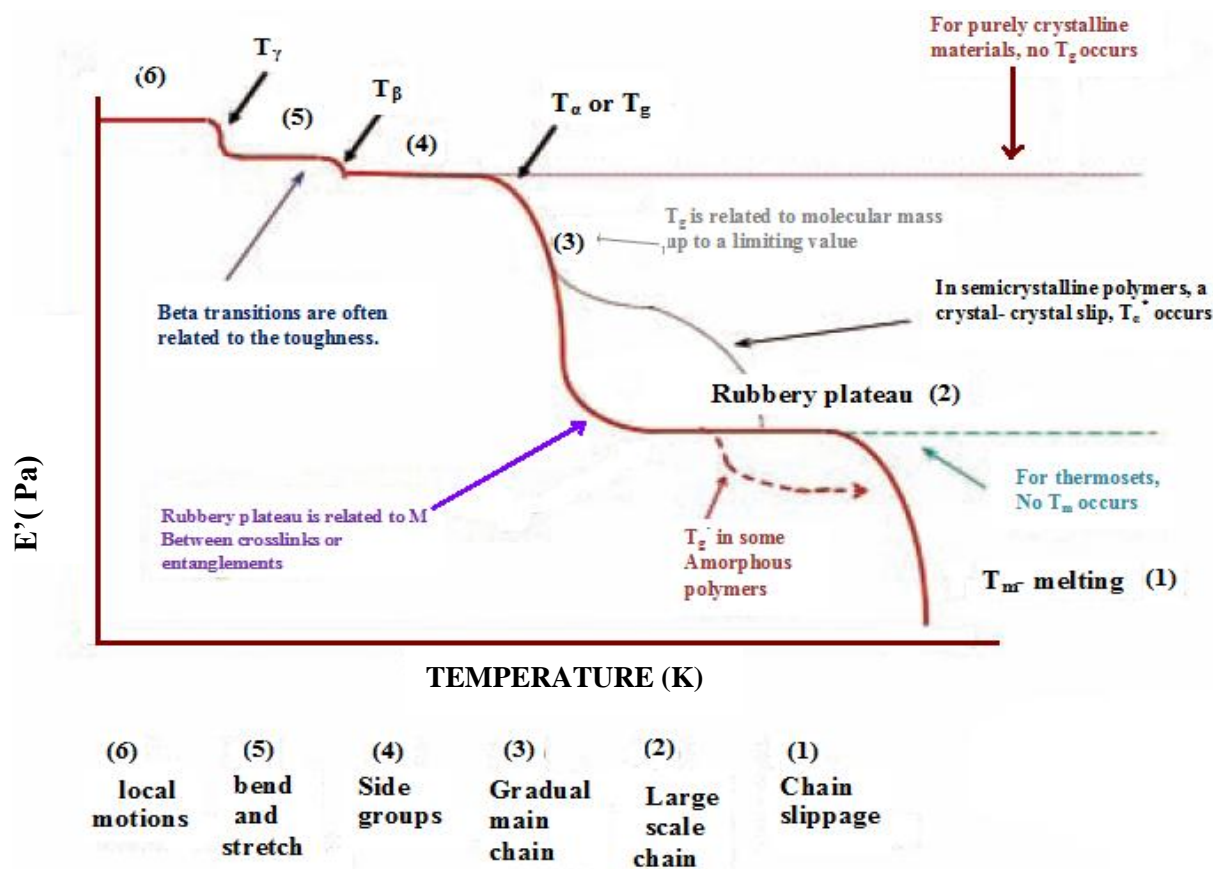


Fig. 8. Various short range motions during glass transition that can be studied using DMA.

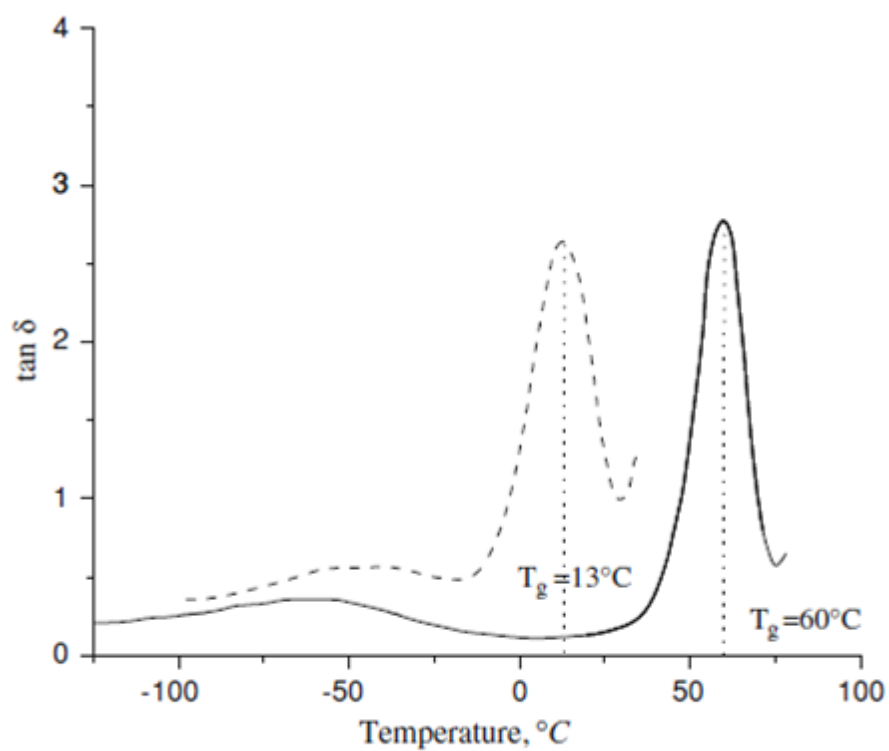


Fig. 9. Variation of $\tan \delta$ with temperature at 1 kHz for dry amorphous D-mannose (—) and its 10% w/w water mixture (---) (Noel *et al*, 2000).

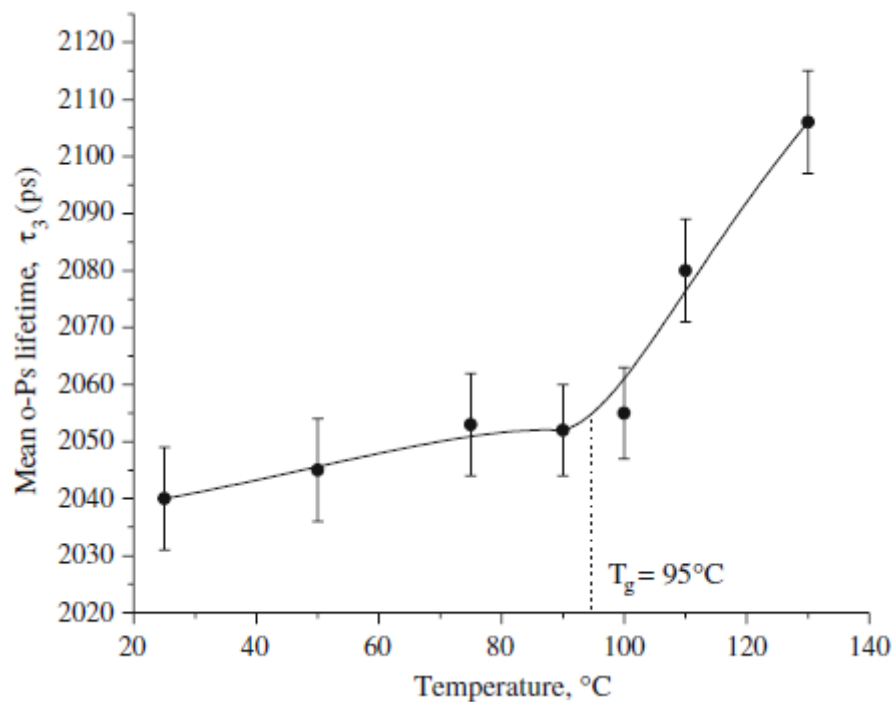


Fig. 10. Mean o-Ps lifetimes for polystyrene as a function of temperature T_g values agreed with that determined by DSC (Liu *et al*, 1993).

Theory	Developed by	Application
Free volume theory	Turnbull and Cohen (1959)	Estimate T_g as a function of pressure, cross-link density, molecular weight, 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)	Predict 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.

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

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

Table 2. Effect of heating rate on the glass transition temperature (Blanchard *et al*, 1974).

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

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

(Litesse III- polydextrose, HS 3375- hydrogenated hydrolysed starch (low molecular weight), HS 6075- hydrogenated hydrolysed starch (high molecular weight))

M _w (Da)	T _g (°C)
4,000	75
9,200	90
25,000	96
400,000	102

Table 4. Values of T_g determined by DSC as a function of molecular weight (Yu *et al*, 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 5. Effect of water activity on T_g of the grapes (Sa *et al*, 1994)

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

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

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,
4	Dilatometry (DIL)	density or linear displacement)
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

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

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

Table 8. Difference between heat flow and heat flux DSC.

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

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