ELSEVIER

Trends in Food Science & Technology 17 (2006) 129–141

TRENDS IN FOOD SCIENCE & TECHNOLOGY

Viewpoint

State diagram of foods: Its potential use in food processing and product stability

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State diagram is a map of the different states of a food as a function of water or solids content and temperature. The main advantage of drawing map is in identifying different states of a food, such as freezing point and glass transition, which helps in understanding the complex changes when food's water content and temperature are changed. It also assists in identifying food's stability during storage as well as selecting suitable conditions of temperature and moisture content for processing. This paper provides an overview and critical assessment on the basic concepts of the state diagram with their terminologies, selected measurement techniques, and their use. Glass transition alone could not be considered as generic rules for food stability criteria since numbers of instances, such as pore formation, diffusion, microbial stability, non-enzymatic browning, other factors or mechanisms play important role. However, it is definitely one of the factors affecting the stability, and a future challenge to combine the glass concept with other mechanisms or factors.

Introduction

In the literature new concepts and hypotheses are being developed and proposed in the areas of food properties in order to bring food science from empiricism to the strong scientific foundation (Rahman, 2005). In the middle of the 20th century scientists began to discover the existence of a relationship between the water contained in a food and its relative tendency to spoil (Scott, 1953). In 1980s Labuza and his group generated significant data on food stability as a function of water activity. They also began to realize that the active water could be much more important to the stability of a food than total amount of water present. Thus, it is possible to develop generalized rules or limits for the stability of foods using water activity. For example, there is a critical water activity below no microorganisms can grow is about 0.6 values of water activity. A food product is most stable at its monolayer moisture content, which vary with the chemical composition and structure. This was the main reason why food scientists started to emphasis water activity rather than total water content. Since then, the scientific community has explored the great significance of water activity in determining the physical characteristics, processes, shelf life, and sensory properties of foods. It is now used to predict the end point of drying, process design and control, ingredient selection, product stability and packaging selection.

Recently, the limitations of water activity are pointed and alternatives are proposed. These limitations are: (i) water activity is defined at equilibrium, whereas foods 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, anti-microbial agents, heat treatment, and temperature, (iii) nature of the 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 (Chirife, 1994; Hardman, 1986; Rahman & Labuza, 1999; Scott, 1953). Glass transition concept was put forwarded considering the limitations of water activity.

Glassy materials have been known for centuries but it is only in the last 70 years or so that scientific understanding of these systems has evolved (Ferry, 1991). A glassy material is hard and fragile. Angell (1988) described a glass as any liquid or super-cooled liquid whose viscosity is between 10^{12} and 10^{13} Pa s thus effectively behaving like a solid, which is able to support its own weight against flow due to gravity. To put this viscosity into context, a supercooled liquid with a viscosity of 10^{14} Pa s would flow 10^{-14} m/s in the glassy state compared to the flow rate of a typical liquid is in the order of 10 m/s. In other words, a glass is a liquid that flows about 30 μm in a century (Buitink & Leprince,

0924-2244/$ - see front matter
doi:10.1016/j.tifs.2005.09.009

2004). This is evidenced by the fact that ancient stained glass windows are thicker at their base due to flow under gravity (Kasapis, 2005).

The early papers of the glass transition in food and biological systems appeared in the literature in the 1960s (Luyet & Rasmussen, 1968; Rey, 1958; White & Cakebread, 1966). Perhaps, White and Cakebread (1966) was the first, who highlighted the importance of the glassy state of foods in determining its stability. The significant applications of the glass transition concept in the 1980s are emerged in food processing when Levine and Slade (1986); Slade and Levine (1988) identified its merits in huge variety. In 1990s Roos, Karel, and other groups generated significant data on the glass transition and components of state diagram for numbers of food components. The hypothesis has recently been stated that this transition greatly influences food stability, as the water in the concentrated phase becomes kinetically immobilized and therefore does not support or participate in reactions (Rahman, 1999; Slade & Levine, 1991a).

The rules of glass-transition concept are: (i) the food is most stable at and below its glass transition, and (ii) higher the $T-T_g$ (i.e above glass transition), higher the deterioration or reaction rates. Similarly, mechanical and transport properties could also be related with glass transition. It is very interesting to see that this concept has been so widely tested in foods. In many instances glass transition concept does not work alone, thus it is now being recommended to use both the water activity and glass transition concepts in assessing process-ability, deterioration, food stability, and shelf-life predictions (Roos, 1995a,b). Recently the concept of state diagram based on glass transition and freezing curve is proposed. Food industry is currently using water activity concept in determining food stability. The scientific evidence showed that glass transition concept could be added to their existing criterion on water activity. This should give better confidence to the food industry in determining the food stability. Food industry could locate their products in the state diagram as a function of solids content and temperature. Based on the location they could determine the stability of their product. The objective of this work is to explore in depth concepts of state diagram and glass transition.

Glass transition and glassy state

Glass transition is a nature of 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). The process is considered to be second order thermodynamic transition in which the material undergoes a change in state but not in phase. It is more meaningful to define as the nature second-order change in the properties since each measurement technique is based on monitoring change in a specific property, and since change or break in properties are achieved within a certain temperature range rather than a specific temperature. A perfect second-order transition occurs at a specific temperature (Allen, 1993; Kasapis, 2005).

State diagram and its components

State diagram

State diagram is the map of different states of a food as a function of water or solids content and temperature (Rahman, 2004). The main advantages of drawing a map are to help in understanding the complex changes when food's water content and temperature are changed. It also assists in identifying food's stability during storage as well as selecting a suitable condition of temperature and moisture content for processing. Fig. 1 shows state diagram indicating different states as a function of temperature and solids mass fraction.

Components of state diagram

Earlier state diagram was constructed with only freezing curve and glass transition line. Recently, attempts are being made to add other structural changes with glass line, freezing curve, and solubility line in the state diagram. Numbers of micro-regions and new terminologies are being included in constructing the state diagram. The presented state diagram shown in Fig. 1 is updated from Rahman (2004). In Fig. 1 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) is a characteristic transition (maximal-freeze-concentration condition) in the state diagram defined as the intersection of the vertical line from T_m' to the glass line EFS. The water content at point F or C is considered as the un-freezeable

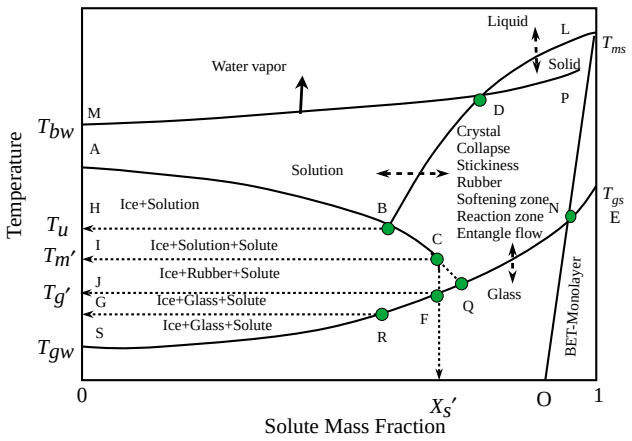

Fig. 1. State diagram showing different regions and state of foods (T_{bw}, boiling point; T_u, eutectic point; T_m', end point of freezing; T_g', glass transition at end point of freezing; T_{gw}, glass transition of water; T_{ms}, melting point of dry solids; T_{gs}, glass transition of dry solids.

water ($1-X_s'$). Un-freezable water mass fraction is the amount of water remaining unfrozen even at very low temperature. It includes both un-crystallized free water and bound water attached to the solids matrix. The point Q is defined as T_g'' and X_s'' as the intersection of the freezing curve to the glass line by maintaining the similar curvature. Point R is defined as T_g''' as the glass transition of the solids matrix in the frozen sample, which is determined by DSC. This is due to the formation of same solid matrix associated un-freezable water and transformation of all free water into ice although the sample contains different level of total water before the start of DSC scanning (Rahman, Sablani, Al-Habsi, Al-Maskri, & Al-Belushi, 2005a).

Different zones or regions are marked in the state diagram showing different characteristics. The line BDL is the melting line which is important when products goes high temperature during processing, such as frying, baking, roasting, extrusion cooking. In case of multi-component mixture such as food a clear melting is difficult to observe at high temperature due the reactions between components. In this case Rahman (2004) defined it as decomposition temperature. Line MDP is the boiling line for water evaporation from the liquid (line MD) and solid phases (line DP). This line does not intersect the *y*-axis at the right. The line LNO is drawn from the BET monolayer stability as a function of temperature, which are discussed later. The region of drying and freezing process can be easily visualized in the diagram, and product stability could be assessed based on moisture content and temperature.

State of water in foods

Different states of water, such as bound, free, capillary, mobile, non-solvent, and un-freezable water are defined in the literature (Rahman, 1995). The state of water can be measured with different techniques or methods. The water sorption isotherm is based on the three types of water: monolayer, multiplayer and mobile or free water (Rockland, 1969). The BET-monolayer is estimated from water sorption isotherm and commonly presented in the literature. It could be mentioned that only BET-monolayer has strong theoretical basis and should be used in stability determination (Rahman, 2005; Rahman & Labuza, 1999). Un-freezable water content can be estimated comparing DSC endotherms of samples having freezable water from the plot of meting enthalpy as a function of water content (Roos, 1987). This procedure was used for model crackers (Given, 1991), strawberry (Roos, 1987), dates (Rahman, 2004), sucrose (Ablett, Clark, Izzard, & Lillford, 1992; Ablett, Izzard, & Lillford, 1992), cabbage (Paakkonen & Plit (1991a)) and garlic (Rahman *et al*., 2005a). From state diagram shown in Fig. 1, un-freezable water can be estimated from point C and F. Comparison of determining un-freezable water using different methods was presented for dates (Rahman, 2004) and garlic (Rahman *et al*., 2005a). It is always found that BET-monolayer values are much lower that the un-freezable water (Duckworth & Smith, 1963).

It is important to explore more in depth information on the characteristics, such as mobility, and factors affecting its nature below and above glassy state in order to apply the glassy concept. It was found that water remained high in mobility below glassy state (Bell *et al*., 2002; Li, Dickinson, & Chinachoti, 1998). Thus glassy state could not be appropriate term to imply or to predict the molecular dynamics of water and its influence on food stability. Other characteristics were measured by Hatakeyama, Quinn, and Hatakeyama, 1996 and Paakkonen and Plit, 1991b. Techniques used to determine the state of water are: dielectric spectroscopy, Fourier transformation infrared spectroscopy (FTIR), X-ray scattering, nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), electrical resistance and self-diffusion methods. Although many techniques are being used to determine the mobility and state of water and solutes available for chemical reactions, but their interpretation is far from straightforward (Hardman, 1986).

Measurement methods

Most of the transitions defined in the state diagram are commonly measured by DSC method using appropriate protocol. The thermo-mechanical analysis (TMA) and oscillation methods are less commonly used, however these methods are more sensitive. In this paper mainly these two methods are discussed in the following sections.

Differential scanning calorimetry (DSC)

The glass transition temperature is difficult to determine in real food systems due to their complexity and/or heterogeneity (Champion, Le Meste, & Simatos, 2000). DSC detects the change in heat capacity occurring over glass transition temperature range. In 1990s modulated DSC (MDSC) was commercialized in order to increase the sensitivity and resolution of thermal analysis, provide the heat capacity and heat flow in a single experiment (Kasapis, 2005; Verdonck, Schaap, & Thomas, 1999). It is common to use mainly heating DSC curve to study the characteristic transitions, and usually heating rate at 5 °C/min are used. However, heating rate affects the values of glass transition. The experimental conditions, such as cooling rate, sample size, and annealing conditions used should be always reported with glass transition values. Calorimetric or spectroscopic techniques have some limitations in terms of sample size and shape, and water content control. In some cases, for example in case of starch it is less sensitive.

The typical DSC curves shown in Figs. 2–4 are based on the level of moisture contents and types of the samples. Fig. 2 shows DSC graphs for low moisture content (i.e. high

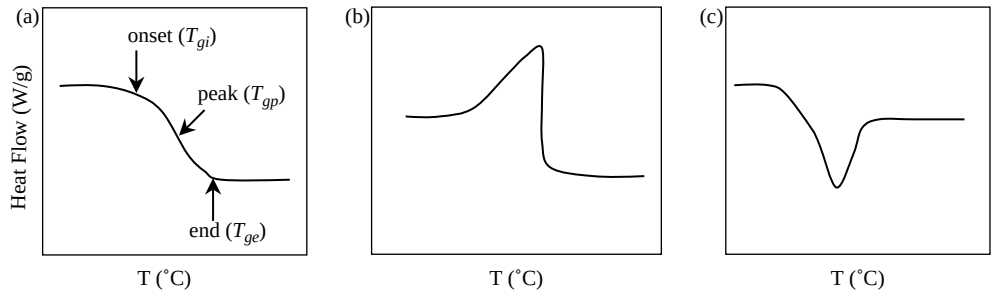

Fig. 2. Typical DSC thermograms for glass transition of samples containing un-freezable water.

solids) when there is no freezable water in the sample. In case of samples with un-freezable water the DSC curve is shown in Fig. 2 indicating no ice formation during cooling or ice melting during heating. Many foods or food components showed an exothermic (Fig. 2B) or endothermic (Fig. 2C) peak. The endothermic overshoot may be deliberately used to help in detecting the glass transition, with materials for which the heat capacity jump is particularly small and smeared out over a broad temperature range. There is no consensus for the definition of the glass transition point on a DSC curve among the various points that may be chosen as onset (T_{gi}), mid (T_{gp}), and end (T_{ge}). Earlier data presented in the literature mainly presented the mid or peak point, however, recent trend is to present onset, mid, and end points.

Fig. 3 shows DSC cooling and heating curves for samples containing freezable water. If moisture content is high and cooling rate is relatively slow, freezing of water is observed during cooling as shown F in Fig. 3A. If the sample contains relatively low freezable water and cooling rate is relatively fast, freezing exotherm does not appear as shown in Fig. 3B. The location of T_g''' and T_m' are shown in Fig. 3. In many samples an exothermic peak E (Fig. 3B) is observed after glass transition and melting endotherm in the heating DSC curve. In order to determine T_m' optimum annealing need to be done in order to maximize the ice formation at a temperature between T_g''' and apparent T_m' (without annealing). It is common to perform annealing at $T_m'-1$. Because of kinetic constraints, solutions with high initial solutes (60–80%) may require several days or even weeks of annealing at $T_g' < T < T_m'$ until the maximally freeze-concentrated state is achieved (Karel *et al.*, 1994). The observed exothermic enthalpy relaxation peak during re-warming, between the glass transition and the melting endotherm may disappear after annealing or rescanning (Baroni, Sereno, & Hubinger, 2003; Rahman, 2004). This process, generally called devitrification, corresponds to ice crystallization. Freezable water that had remained unfrozen due to hindered crystallization during a fast cooling, which crystallizes during warming.

In many cases two glass transitions are observed as shown in Fig. 4 even with annealing (Fonseca, Obert, Beal, & Marin, 2001; Rahman, 2004). In extreme case, second glass transition could be observed with melting endotherm (Fig. 4B). Different hypothesis are proposed for two or more glass transitions. The two transitions occurred, one due to the backbone of a large polymer or less mobile component, and other due to the less mobile or side chains (Rahman, 2004). Another reasons could be due to the incompatibility of different solutes in the mixture (Li & Chen, 2001; Morales-Diaz & Kokini, 1998). Other proposed concept for solution even with single solute is: it is the result of formation of a solute-crystal-rich, un-equilibrated phase trapped around or within the rapidly nucleated ice crystals, and/or solute inclusion within the ice crystals itself (Goff, Caldwell, Stanley, & Maurice, 2002). Li and Chen (2001) used these two glass transitions to identify the degree of compatibility of rice starch-hydrocolloid mixtures.

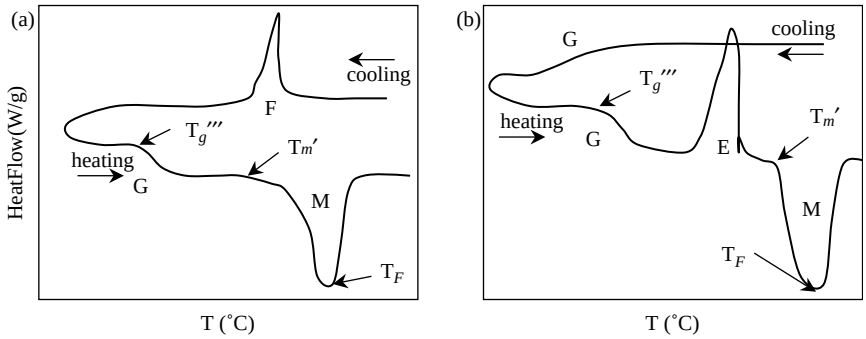

Fig. 3. Typical DSC thermograms showing glass transition, freezing and melting endotherms for sample containing freezable water.

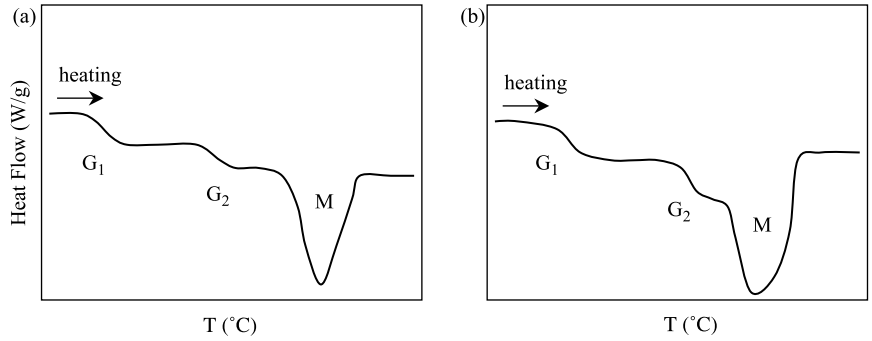

Fig. 4. Typical DSC thermograms showing two glass transitions and melting endotherm for sample containing freezable water.

Dynamic mechanical thermal analysis (DMTA)

Other useful and sometimes more sensitive methods include thermo-mechanical analysis (TMA), dynamic mechanical analysis (DMA), dynamic mechanical thermal analysis (DMTA), and dynamic oscillation method. In this method structural properties are examined with G' and G'' as a function of temperature at a constant frequency or time of measurement. Typical curves are shown in Fig. 5. Again it is necessary to specify how the transition temperature (T_r) is defined from the experimental curves. The temperature is commonly taken from the maximum of the loss factor (tanδ), which is more easily determined. The maximum of the loss modulus (E'' or G$''$) is much better for transition determined from point of view of its physical meaning (Champion *et al*., 2000). Moreover, no tan δ peak is expected with small molecular weight systems. In Fig. 5A it was proposed that the rheological glass transition was the point between the glass transition and the glassy state (Kasapis, Al-Marhobi, & Sworn, 2001). The transition from T_g (DSC glass) and T_r (mechanical or rheological glass) should not be considered as fully equivalent. Shalaev and Kanev (1994) mentioned that mechanical glass transition occurs above DSC glass due to sample's ability to keep its form. In DSC and DMTA the sample is submitted to stresses of different physical nature (change of temperature in DSC, shearing or compression in DMTA). The experimental time may also be different (depending on cooling-heating rates and annealing in DSC, on measurement frequency in DMTA). Blond (1994); Kasapis, Al-Marhoobi, and Mitchell (2003) studied the comparisons of glass transition from DSC and mechanical methods. A different coupling of the imposed perturbations with the structural units (with particular relaxation times) may be responsible for discrepancies in the data obtained with different techniques. In Fig. 5B the cross over between G$'$ and G$''$ is not observed. In general it could recommend to present T_{ri}, T_{re}, T_{rc}, and T_{rp} in comparable to glass transition by DSC. However, the question remained unanswered why transition from different methods vary?

Freezing point

Cooling curve is one of the most simple and popular methods to measure the freezing point of foods (Rahman, 1995; Rahman *et al*., 2002b). Cooling curve method was used to measure the freezing point of milk (Chen & Chen, 1996; Chen, Chen, & Free, 1996), coffee extract (Barnett, 1973), dates (Kasapis, Rahman, Guizani, & Al-Aamri, 2000), and tuna flesh (Rahman *et al*., 2003). Typical melting endotherms for melting of ice are shown in Fig. 6. The ice melting or freezing point is commonly characterized from the endothermic peak during melting (Goff, Caldwell, Stanley, & Maurice, 1993; Rahman, 2004). This method provides very accurate determination for a sharp peak. In case of wider peak (Fig. 6C) it is

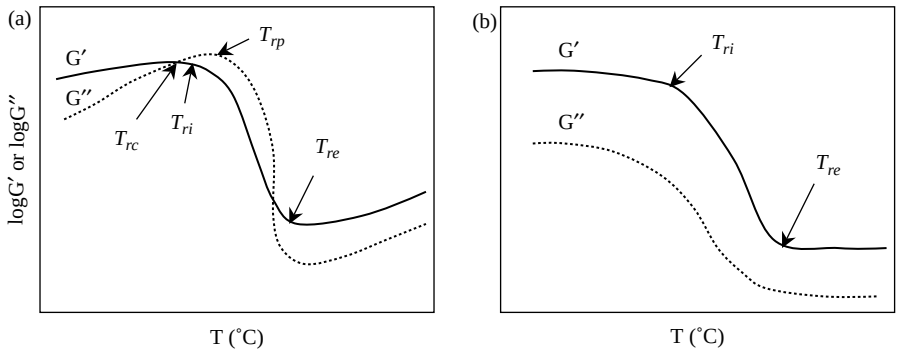

Fig. 5. The typical plots of log G' or log G'' showing the glass transition.

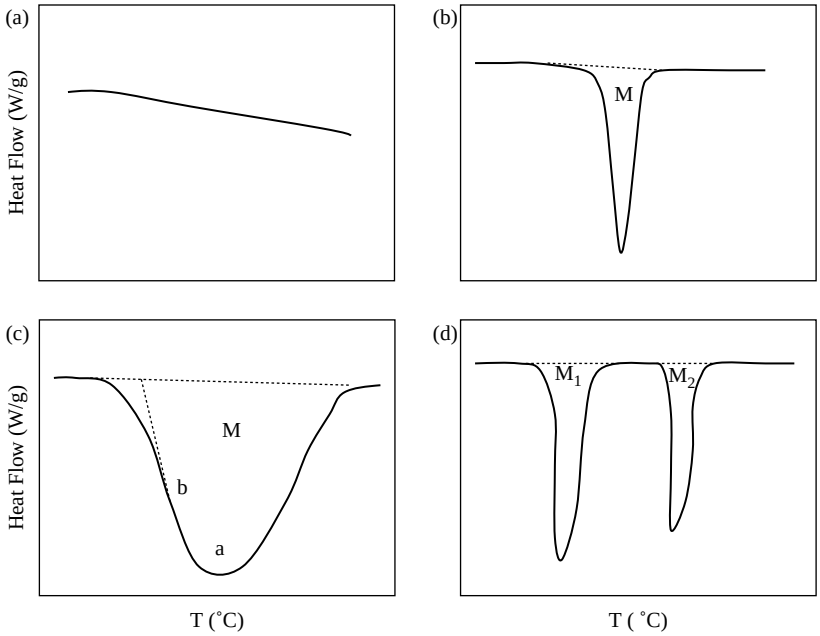

Fig. 6. Typical thrmogram for sample containing un-freezable water and different types of melting endotherms of ice.

difficult to determine from the peak. The wider peak appears due to the wide variation on the state of water in foods. In this case maximum slope of the endotherm (point b in Fig. 6B) or the extra-plotted peak onset temperature of the ice melting (Fonseca *et al*., 2001; Goff *et al*., 1993). When the sample contains mainly free water, it shows a sharp endothermic peak on melting at melting similar to pure water (Fig. 6B). Multi-peak natures of the DSC curves are found for the metastable states of water in gum from *acacia Senegal* (Phillips, Takigami, & Takigami, 1996) and gellan (Hatakeyama *et al*., 1996) (Fig. 6D). The sample containing non-freezing water shows no first-order transition (Fig. 6A).

Theoretical progresses in glassy state

Kasapis (2005) provided evolution of the science of the glassy phenomena, which cuts across several domain of science. Champion *et al*. (2000) reviewed different proposed theories for understanding the glass transition. These are free volume theory, entropy-controlled co-operative motions, mode coupling theory, frustration-limited domains, and hierarchical correlated molecular motions. Among all the theories, the free volume theory and relaxation phenomena are beginning to contribute in explaining some changes in foods below glass temperature. The more compact molecular organization and the strengthening of interactions result in changes in mechanical and also in transport properties. Its relevance is being increasingly recognized with cereal products (Borde, Bizot, Vigier, Emery, & Buleon, 1999; Champion *et al*., 2000). Kasapis (2005) is anticipated that much attention will be focused in the area of the coupling theory in the future.

Applications of glassy state in foods

The applications of glass transition and state diagram concept are provided in the following section.

Diffusion process

The glass transition affects diffusion-controlled chemical reactions through the decrease of diffusion coefficient (Slade & Levine, 1991b; Karel & Saguy, 1991). The decease in diffusivity is due to the changes in viscosity and mobility. The diffusion time of a water molecule over 1 Å distance should be more than 10^6 years at room temperature in a glassy matrix based on the Stoke–Einstein relation (Champion *et al*., 2000). The time scale for the loss of stability in food at low water content is not so large. There was no important drop below the glass although there was a change in slope above or below glass transition when diffusivity was plotted as a function of temperature (Ablett, Darke, Izzard, & Lillford, 1993; Karel *et al*., 1994). The decoupling started at $T_g/T > 0.86$ and the discrepancy increases as temperature reached close to glass transition (Champion, Hervet, Blond, Le Meste, & Simatos, 1997).

The diffusion coefficient of water in low-moisture food polymers decreased with the decrease of moisture content without any break in the glass transition when plotted diffusivity versus water content. The diffusivity depends mainly on moisture content and exhibits a low sensitivity to the nature of surrounding polymer (Bruin & Luyben, 1980). The plot of water diffusivity and viscosity of maltose-eater mixture showed extremely divergent when $T_g/T > 0.8$ instead parallel to each other (Parker & Ring, 1995). In this case solute diffusion, macroscopic viscosity did not significantly reduce the diffusion of small molecules

(Contreras-Lopez, Champion, Hervet, Blond, & Le Meste, 1999; Le Meste *et al*., 1999; Martin, Ablett, Sutton, & Sahagian, 1999). This decoupling evidence (between viscosity of the diffusion medium and diffusion of small molecule) indicated that the decrease of diffusivity near or below glass is not solely due to the decrease of viscosity. Other factors affecting diffusivity are the porosity, porous structure, size (solute and matrix) of molecules, nano-defects, and structural collapse of foods.

Texture and structure

Glassy state usually provides the crispy texture of dried foods. A sharp decreasing trend was observed when compressive failure stress of frozen or dried sample is plotted as a function of temperature (Roudaut, Maglione, & Le Meste, 1999). This change was defined as brittle–ductile transition. It is not generally true that brittle–ductile appears at the glass transition although in certain cases the brittle–ductile transition coincided with the glass transition temperature (Parker & Smith, 1993). There was a remarkable difference between the brittle–ductile and glass transitions temperature in case of fish meat (Watanabe, Tang, Suzuki, & Mihori, 1996) and gelatinized starch (Nicholls, Appleqvist, Davies, & Ingman, 1995). The reasons could be due to number of extrinsic factors including strain rate, temperature, stress state, specimen geometry, and presence of notches and flaws.

Crystallization

Temperatures above glass allow molecular mobility and the rearranging of molecules to the crystalline state (Levine & Slade, 1986). Increasing $T-T_g$ causes an increasing rate of crystallization with increasing crystallinity (Jouppila & Roos, 1997). The crystallization time of amorphous lactose can be predicted using WLF equation (Roos & Karel, 1992). Crystallization under low $T-T_g$ conditions appears to produce smaller and less perfect crystallites than those produced under high $T-T_g$ conditions, due to lower molecular mobility. However, glass transition is not necessarily the best inhibitor of isomalt crystallization (McFetridge, Rades, & Lim, 2004).

Stickiness

Initiation of viscous flow, caking, and stickiness depends on the glass transition temperature. In case of spray dried lactose, caking and collapse was increased with the increase of $T-T_g$ (Lloyd, Chen, & Hargreaves, 1996). The sticky point of an amorphous sucrose and fructose was found 10 °C higher than glass transition (Roos & Karel, 1991).

Grain damage by drying

Considerable differences between the values of thermal expansion coefficients β_{glass} and β_{rubber} in the two zones were observed (Perdon, 1999). A hypothesis based on glass transitions inside rice kernels was proposed to explain rice fissure formation and heat rice yield during the drying process (Cnossen, Siebenmorgen, Yang, & Bautista, 2000; Perdon, Siebenmorgen, & Mauromoustakos, 2000; Siebenmorgen *et al*., 2000; Yang, Jia, Siebenmorgen, Pan, & Cnossen, 2003a; Yang, Jia, Howell, 2003b).

Pore formation in foods

The glass transition theory is one of the concepts that have been proposed to explain the process of shrinkage, collapse, fissuring, and cracking during drying (Cnossen & Siebenmorgen, 2000; Karathanos, Kanellopoulos, & Belessiotis, 1993; Karathanos, Angelea, & Karel, 1996; Krokida *et al*., 1998; Rahman, 2001). The *hypothesis* indicates that a significant shrinkage can be noticed during processing only if the temperature of the drying is higher than the glass transition of the material at that particular moisture content (Achanta & Okos, 1996). The methods of freeze-drying and hot air drying can be compared based on this theory. Recent experimental results dictate that the concept of glass transition is not valid for freeze-drying of all types of biological materials indicating the need of the incorporation of other concepts (Sablani & Rahman, 2002), thus an unified approach need to be used. Other instances when glass concept is not valid are also reported (Ali, Hanna, & Chinnaswamy, 1996; Del Valle, Cuadros, & Aguilera, 1998; Rahman, Al-Zakwani, I. & Guizani, 2005b; Rahman, Al-Amri, & Al-Bulushi, 2002a; Ratti, 1994; Krokida & Maroulis, 2000; Wang & Brennan, 1995). The mechanism proposed for the deviation was case hardening, and internal pressure development (Achanta & Okos, 1996; Rahman *et al*., 2005b; Ratti, 1994). In case of casehardening the permeability and integrity of the crust play a role in maintaining the internal pressure inside the geometric boundary. Internal pressure always tries to puff the product by creating a force to the crust. Glass transition concept cannot explain the effect of crust and internal pressure. After analyzing experimental results from literature, Rahman (2001) identified that the glass transition theory does not hold true for all products or processes. Other concepts, such as surface tension, pore pressure, structure, environment pressure, and mechanisms of moisture transport also play important roles in explaining the formation of pores. Rahman (2001) hypothesized that as capillary force is the main force responsible for collapse, so counterbalancing this force causes formation of pores and lower shrinkage. The counterbalancing forces are due to generation of internal pressure due to vaporization of water or other solvents, variations in moisture transport mechanism, and pressure outside the material. Other factors could be strength of solid matrix (i.e. ice formation, case hardening, surface cracks formation, permeability of water thru crust, change in tertiary and quaternary structure of polymers, presence or absence of crystalline, amorphous, and

viscoelastic nature of solids, matrix reinforcement, residence time). Some of these factors are related to the glass transition.

Microbial stability

The microbial stability of food has long been estimated by its water activity. The rule is: (i) lower the water activity, the microbiologically stable the food and (ii) foods are most stable at its BET-monolayer moisture content. The water activity at the monolayer water content is also called the *critical water activity*. The above concept has limitations as discussed earlier. Franks (1991); Slade and Levine (1987) maintained that water activity could serve as a useful, but not sole indicator of microbial safety. Slade and Levine's (1987) hypothesis was that water dynamics or glass–rubber transition may be applied instead of water activity to predict the microbial stability of concentrated and intermediate-moisture foods. Sapru and Labuza (1993) studied the inactivation of bacterial spores and their glass transition temperature. Spores at glass transition have high heat resistance, and above glass they are easy to inactivate. At a given temperature, the inactivation rate decreases with the increase of glass transition temperatures of spores. Chirife and Buera (1994) maintained that glass–rubber transition would not be useful in predicting with confidence the microbial stability of foods. They analyzed data from the literature and concluded that water activity and glass transition are two different entities. The mobility factors (i.e. glass transition) in addition to water activity are not useful for a better definition of microbial stability of foods. Water activity is a solvent property and glass is a property related to the structure of food. Thus, both properties are needed for understanding food-water relationships at different conditions (Chirife & Buera, 1994; Taylor, 1995; Van den Berg, 1991). Macroscopic heterogeneities in a food material can induce the presence of areas with a higher mobility (Champion *et al*., 2000). Chirife, Buera, & Gonzalez (1999) showed mold growth may be possible below glass transition if non-glassy micro-regions exist. Champion *et al*. (2000) stressed for further studies to investigate effects of non-homogeneous water distribution and/or phase separation on reaction rates. Hills, Manning, Ridge, and Brocklehurst (1996) first studied by NMR relaxation and electrical conductivity to actually distinguish the effect of local rather than global water activity on microbial stress in porous media. They found that the microbial stress does not correlate with the global water activity measured for the whole assemble but rather with the local water activity actually surrounding the cells.

Desiccation-tolerant organisms

Desiccation-tolerant organisms (anhydrobiotes), such as seed and pollen are capable of surviving the removal of their cellular water. The lifespan of seeds can be remarkably long, ranging from decades to centuries (Kivilaan & Bandurski, 1981; Priestley, Cullinan, & Wolf, 1985; Steiner & Ruckenbauer, 1995) and even millennia (Shen-Miller, Mudgett, Schopf, Clarke, & Berger, 1995). In late 1980s, Burke (1986) forwarded the hypothesis that cytoplasm of seeds could enter into a glassy state. He suggested that in dry anhydrous organisms, glasses could be formed from cell solutes like sugars that were known to provide protection from denatured of large molecules and formation of molecular aggregates, and high viscosity may stop all chemical reactions that require molecular diffusion. Thus, the glass concept turned out to be an interesting hypothesis to account for the survival in the dry state. More recently, in addition to the measurement of glass transition temperature, efforts focused on the assessment of additional physical properties, such as molecular density, local viscosity, and molecular properties of the glass (Buitink & Leprince, 2004).

Oxidation

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, Roos, & Karel, 1992; Shimada, Roos, & Karel, 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.

Non-enzymatic Browning

Karel, Buera, and Roos (1993); Karmas, Buera, and Karel (1992); Buera and Karel (1993) indicated that phase transitions with physical aspects of the matrix are factors affecting the rates of non-enzymatic browning reactions. Non-enzymatic browning below glass transition was very slow. The systems were used vegetables, dairy products and model food systems with amino acids and sugars in a PVP matrix. Many other investigations showed only glass transition cannot explain the process, since the reaction was also affected by several other factors, such as structural changes, water content (i.e. water activity) independently of its plasticizing effect, pH, and types of solutes in the matrix (Bell, 1996; Bell & Hageman, 1994; Bell, Touma, White, & Chen, 1998; Buera & Karel, 1993; Karel *et al*., 1994; O'Brien, 1996; Roos & Himberg, 1994).

Enzymatic reaction

Several enzymatic reactions can occur at low water contents (Drapon, 1972; Silver & Karel, 1981) or in the frozen state (Fennema, 1975; 1978; Simatos & Blond, 1991; 1993; Franks & Hatley, 1992) such as those catalysed by alkaline phosphatase, lipoxygenase, lipase or invertase. The effect of temperature on the reaction rate depends on the

relative value of the diffusion of the reactants and the activity of the enzyme in such concentrated media. Champion *et al*. (2000) pointed that there is risk of proposing a unified theoretical model to predict the reactions in such concentrated materials. Torreggiani *et al*. (1999) found no clear relationship between the anthocyanin loss and $(T-T_g')$ of strawberry juices. Other important factors such as the pH of the unfrozen phase and types of solutes could influence anthocyanin pigment stability.

Denaturation of protein

The properties and functionality of the protein depend on whether it exists in the native or denatured state and maintaining protein structure and functionality is important in food science. Reaction rates at constant water activity but different glass transition values were not significantly different (Bell & Labuza, 1991; Bell & Hageman, 1994). The temperature of denaturtion decreased with increasing moisture content to some plateau, where further increases in moisture no longer influenced the denaturation temperature (Bell & Hageman, 1996). Thermal stability of protein correlated with glass transition temperatures (Bell & Hageman, 1996). They hypothesized that in dry state, the additives were acting as plasticizers, enhancing the mobility and thus the unfolding of the globular proteins.

Hydrolysis

The effect of glass transition on different chemical reactions is not as clear as in the cases with physical changes. This is due to the multiple roles of water in foods, such as plasticizer, reactant or product of chemical reactions, and pH (Buera, Chirife, & Karel, 1995). One of the chemical reactions that proposed to occur only in the rubbery phase (i.e. above glass transition) is sucrose inversion in acid containing amorphous powders (Levine & Slade, 1989). Glass transition is not a key factor determining the rate of sucrose hydrolysis (Buera *et al*., 1995). The major effect on the rate of hydrolysis was related to changes in pH, which is moisture dependent. Knowledge of the actual pH of a system, and the possible changes that may occur during concentration or drying are necessary for better understanding of chemical changes in low and intermediate moisture foods. Sucrose hydrolysis in an acid-containing (low pH 3.1) amorphous starch powder (native or pre-gelatinized) occurred to a significant extent in the glassy state (Schebor, Buera, Chirife, & Karel, 1995). The mobility effects are not controlling the extent of reaction. Hydrolysis (31–85% remaining sucrose) observed at different water content and temperature below glass. Little reaction occurred at moisture contents below the so-called BET monolayer. Temperature was a critical factor controlling sucrose inversion.

Enzyme and vitamins inactivation

The stability of enzymes and vitamins in low water systems was analyzed based on glass concept. The stability could not be explained by glass concept. The other factors are the types of solutes in the matrix, water activity and temperature (Bell & White, 2000; Cardona, Schebor, Buera, Karel, & Chirife, 1997; Champion *et al*., 2000; Mazzobre, Buera, & Chirife, 1997; Schebor, Buera, & Chirife, 1996).

Future challenges

First phase of the data generation and applications of the glassy concept has been done. The second phase of the characterizing the glassy state and molecular mobility has started in recent works. The third phase of coupling glassy concept with other concepts remained a challenge for us. It is very important to develop accepted standard measurement protocol, and how different methods are varied. Scattered results are presented in the literature for comparing between rheological/mechanical and DSC methods of glass transition. Much more need to be done in order to make meaningful comparisons.

Variation of data from different sources as well as different measurement techniques could be one of the major limitations when data need to be used. For example, Labuza and Roe (in press) compiled glass transition temperature of dry trehalose from 15 literature sources and found that it varied from 75 to 120 °C. In case of multi-component mixture such as food it is more complicated due to the compositional variation even for same material, for example fruits composition varies with variety, maturity level, growing locations, and seasons. Although different reasons are proposed for such variations, it is difficult for the food scientists and engineers to use it in real applications when the variation in temperature is 45 °C say for trehalose.

Recently, many papers presented data on the water activity as well as glass transition as a function of water content. However, it was not identified where is the link between them in order to determine stability. Karel *et al*. (1994) attempted to relate water activity and glass transition by plotting equilibrium water content and glass transition as a function of water activity. By drawing a vertical line on the graph stability criterion could be determined from isotherm curve and glass transition line. At any temperature (say 25 °C) stability moisture content from glass transition line was much higher than the stability moisture from the isotherm. The question is how to use both? At present it is a real challenge to link them. As a first attempt I have plotted BET-monolayer value as LO line in the state diagram shown in Fig. 1. It intersects at point N with the glass line ES, which shows that at least in one location (point N) glass and water activity concepts provide the same stability criterion. This approach form more micro-regions, which could give different stability in the state diagram. More studies regarding the stability need to be done on the left (above and below glass) and right sides (above and below) of the line LO. A successful combination of water activity and glass transition could open more in depth knowledge on stability criteria. In addition how other factors, such as pH,

preservatives could be linked with these concepts. We are far away to develop a unified theoretical basis.

Heterogeneity in chemical composition and structure in food is giving another hurdle to apply in foods beyond the pure components. Various physical and chemical reactions can still occur in the glassy state, suggesting glass transition cannot be considered as an absolute threshold temperature for stability. Sub-glass relaxations and physical ageing are phenomena showing that the molecular mobility below glass transition cannot be neglected (Champion *et al*., 2000). Above the glass transition, a simple WLF model based on viscosity is not sufficient to account for the effect of temperature and water content on kinetics of transformations or on mechanical properties. More characteristics of glass formed in different food matrix, such as translation/rotational diffusion, viscosity for flow, mechanical spectroscopy, fragility, αβ-cross over temperature, and distribution of relaxation times could be explored in order to explain the different level of stability in glassy foods. These characteristic parameters specific to food products, and their variation will allow the glass concept to be even more efficient in rationalizing formulation and process control of foods (Champion *et al*., 2000).

It is evident from the review that the variation of stability below glass transition not following the rule indicating only glass transition temperature for developing the stability rule could not be enough. The types or characteristics of glassy state form in different types of foods with variations of composition and water content should be used to characterize the stability criterion. In addition the effect of temperature below T_m', T_g'', T_g', and T_g''' should also be explored. Sample having freezable water are more complex and four temperatures are defined as $T_m' > T_g'' > T_g' > T_g'''$ (Rahman *et al*. 2005a). There are only few references available including all four characteristic temperatures with their moisture content. It is important to know how these temperatures affect the stability of foods. It would be interesting to explore what are differences in stability exist in product with in these different ranges.

Conclusion

Overviews of the basic concepts of the state diagram based on glass transition concept with their terminologies, measurement techniques, and their applications in food stability are reviewed in this work. All measurement methods need to be standardized. In all systems and processes the glass transition concept alone are not valid, thus both water activity and glass transition concepts need to be used. How to combine both concepts (glass transition and water activity) with other factors is a challenge? Studies on the characteristics of glassy state formed in different types of foods with varied composition and water content could explore why in many instances glass transition concept failed to determine the stability.

Acknowledgement

The author would like to acknowledge the support of Sultan Qaboos University towards the research works on developing state diagram for foods.

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