

## **THERMAL ANALYSIS, STATE TRANSITIONS AND FOOD QUALITY**

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### **Abstract**

Thermal properties of food systems are important in understanding relationships between food properties and changes in food quality. Concentrated food systems (low-moisture and frozen foods) are seldom in an equilibrium state and they tend to form amorphous, non-crystalline structures. Several glass transition-related changes in such foods affect stability, e.g., stickiness and caking of powders, crispness of snack foods and breakfast cereals, crystallisation of amorphous sugars, recrystallisation of gelatinised starch, ice formation and recrystallisation in frozen foods and rates of non-enzymatic browning and enzymatic reactions. Relationships between glass transition, water plasticisation and relaxation times can be shown in state diagrams. State diagrams are useful as stability or quality maps and in the control of rates of changes in food processing and storage.

**Keywords:** food properties, glass transition, state diagram, thermal analysis

### **Introduction**

Food systems are complex mixtures of carbohydrates, proteins, lipids, a variety of minor components and water. The use of differential scanning calorimetry (DSC) to observe protein denaturation or gelatinisation of starch has been well established and thermal analytical techniques are extensively used to study the melting and crystallisation behaviour of lipids, which exhibit complex polymorphic forms and recrystallisation phenomena. Carbohydrates and proteins in food systems are generally miscible with water and show both first-order phase transitions (e.g., melting; crystallisation) and state transitions (e.g., denaturation; gelatinisation; glass transition) [1–3]. All thermal properties of food systems are important in understanding relationships between food properties and changes in food quality. Hence, dielectric analysis (DEA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have become common and important thermal analytical methods in physicochemical characterisation of food components and foods [4–8].

Carbohydrates and proteins in concentrated food systems are seldom in an equilibrium state and they tend to form amorphous, non-crystalline structures [1–3]. Well-

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known examples of foods with amorphous or partially amorphous components are baked products, extruded foods, dehydrated foods and frozen foods [3]. In these systems, removal of water as part of the manufacturing process results in the formation of a non-crystalline, amorphous state of carbohydrates and proteins. These materials show various time-dependent changes that affect product stability and shelf life and their thermal properties resemble those of non-crystalline synthetic polymers [3, 9, 10]. Hence, various thermal analytical techniques are crucial in obtaining information of glass transitions and glass transition related transformations in food systems.

The glass transition of amorphous food systems has been found to control changes in food structure and texture and it has been suggested to affect diffusion and thereby rates of chemical and enzymatic reactions [1–3, 11–14]. In general, amorphous structures are fairly stable in the solid, glassy state at temperatures below the glass transition [2]. At temperatures around and above the transition, the solid state is transformed to a supercooled liquid state with time-dependent flow [3, 15]. For example, dehydrated, glassy foods have a solid and brittle behaviour while the materials may flow or become soggy above the glass transition. Apparently, such changes will have significant effects on the sensory properties of the materials [10, 16].

There are several glass transition-related changes in foods that affect food quality. These changes include stickiness and caking of powders and sugar containing products, collapse in freeze-drying and collapse of dehydrated structures, crispness of snack foods and breakfast cereals, crystallisation of amorphous sugars, recrystallisation of gelatinised starch, ice formation and recrystallisation in frozen foods and to some extent non-enzymatic browning and enzymatic reactions [1–3]. However, these reactions may become obvious also as a result of glass transition-related changes in mechanical properties or crystallisation [14,17].

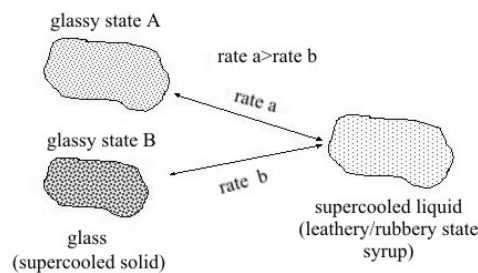
The importance of thermal analytical techniques to the physicochemical analysis of food systems and foods has increased significantly as it was realised that the physicochemical properties in particular of frozen and low moisture, concentrated systems are related to the physical, non-equilibrium state of the materials [1, 3, 18, 19]. The use of thermal analytical techniques and the information obtained is useful in controlling food quality changes in processing and in food storage. The relationships of the physicochemical, time-dependent changes in foods, state transitions and food quality are emphasised in the present article.

## **The non-equilibrium state and state transitions**

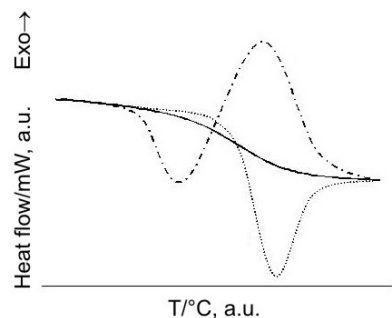
Phase transitions are traditionally classified according to thermodynamic changes occurring at transition temperatures [3, 9]. First-order transitions are those at which the first derivatives of the thermodynamic functions suffer discontinuity, i.e., at a first-order transition temperature there is a discontinuity in heat capacity and thermal expansion coefficient. Typical first-order transitions are those occurring between the three basic states of materials, i.e., gaseous, liquid and solid states. At a second-order transition temperature, there is a step change in properties suffering discontinuity in a first-order transition. For example, amorphous materials exhibit a change in heat ca-

capacity over a glass transition, and therefore this change in state has some thermodynamic properties typical of a second-order phase change. However, the glass transition is a property of a non-equilibrium system and the transition cannot be classified as a pure phase transition, and should be rather considered as a state transition.

Amorphous or partially amorphous structures in foods are formed in food processing when water is removed, for example, in baking, concentration, dehydration, freezing and extrusion [1, 3, 10, 15, 18, 20]. These supercooled, amorphous, non-equilibrium materials exhibit time-dependent changes as they approach an equilibrium state, e.g., the crystalline state. Furthermore, depending on the rate of solvent removal or cooling into the solid state, glasses with different properties can be obtained (Fig. 1). The glass transition occurs over a temperature range, although it is often referred to with a single temperature value. Glass transition may be present in either low-moisture and dehydrated foods or frozen foods in which a concentrated solute phase is formed as ice is separated from the material. Pure food components, such as amorphous sugars, often show a single, clear glass transition that can be observed using dielectric, mechanical and thermal analytical or various spectroscopic techniques [4, 7, 21]. However, in several real food systems, components may be only partially amorphous (carbohydrates, e.g., starch and sugars; proteins) and many food components are only partially miscible or immiscible forming single or several phases in a food microstructure [22, 23].



**Fig. 1** A schematic representation of effects of cooling rate on glass properties. A high cooling rate produces a glass with a relatively high free volume and enthalpy



**Fig. 2** Enthalpy relaxation of amorphous materials at the glass transition. An exotherm is apparent for glasses with a relatively high free volume and enthalpy while an endotherm is observed when heat is required by the material to undergo the transition to the supercooled liquid state

Glass transition occurs in both cooling and heating and also in removal or sorption of a plasticiser or a solvent or both. As a state transition and because of the non-equilibrium nature of the amorphous phase, the glass transition is time-dependent. Thus, methods using different experimental time scales (e.g., frequency) give different temperature locations for the glass transition. Furthermore, depending on the rate of glass formation and possible changes with time in the glassy state (ageing) various relaxations may be associated with an observed glass transition (Fig. 2).

### Glass transitions and water plasticization

The glass transition occurs at 100–150°C below the component melting temperature, which has been confirmed to apply to sugars [24]. The glass transition, however, occurs over a temperature range, which can be relatively narrow, for example the glass transition of amorphous sugars occurs over a range of 10–20°C, and also extremely broad, for example, the glass transition of food polymers may cover a range of 50°C or more [3, 25, 26]. There is also a possibility that single foods exhibit numerous glass transitions depending on composition and extent of phase separation. An anhydrous food may, at least theoretically have a glass transition of monosaccharide components below room temperature and a glass transition of proteins at above 200°C. For example, sugars and casein are only partially miscible [27].

Foods can be considered as systems where water has the main interaction with carbohydrate and protein components while properties of lipids are relatively little affected by water, i.e., these components exist in separate phases [3]. The transition temperatures of carbohydrates and proteins are affected by water and it is often observed that an increase in water content results in a decrease in transition temperatures [2].

In amorphous carbohydrates and proteins, water acts as a plasticizer, i.e., the free volume of the materials increases with increasing water content resulting in a decrease in the glass transition temperature. Therefore, changes in amorphous food properties may result either from glass transition occurring because of increasing temperature (thermal plasticization) or increasing water content (water plasticization). For example, the glass transition of dehydrated food solids often decreases as a

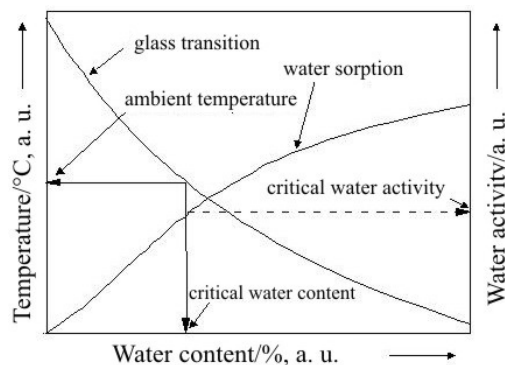


Fig. 3 Critical water content and water activity of amorphous biological materials

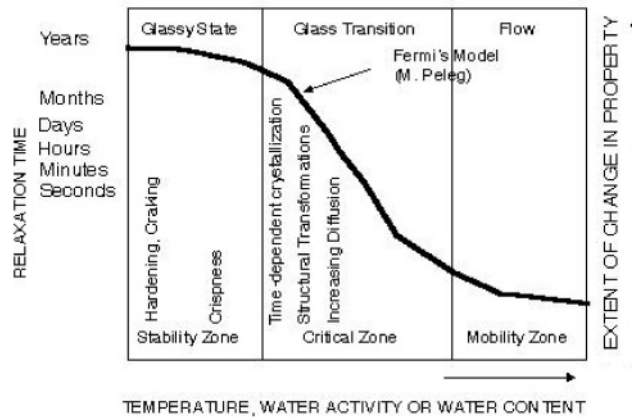
result of water sorption and their properties may change from glass-like materials to rubbery systems or viscous liquids isothermally if water sorption is sufficient to cause glass transition [2, 3].

The effect of water on the glass transition can be predicted, for example, using the Gordon–Taylor equation [3, 28]. We have combined the use of water sorption data and glass transition data to establish diagrams showing critical values for water content and water activity that result in glass transition at storage temperature (Fig. 3). Such diagrams can be established using, for example, the Gordon–Taylor equation to model water plasticization and the Guggenheim–Anderson–De Boer (GAB) equation to model water sorption [3].

The critical water content and water activity diagrams together with state diagrams are important in explaining changes in time-dependent mechanical and flow properties that are governed by glass transition and water plasticization [3].

### Glass transition and stability

The effect of glass transition on the mechanical properties of food materials has been well established. Many of these changes result from the rapid changes in viscosity and modulus that take place over and above the glass transition temperature range [29]. These changes in viscosity and flow properties affect stickiness and caking of powders, crispness of amorphous solids, and crystallization of amorphous solids and recrystallization of ice in frozen systems [3, 19]. One of the underlying causes in these changes is the reduced relaxation time of mechanical changes as described in Fig. 4.



**Fig. 4** Effect of temperature, water activity or water content on relaxation times and relative rates of mechanical changes of amorphous biological materials

In addition to the changes in mechanical properties associated with the glass transition, it has been suggested that the glass transition may affect rates of diffusion-controlled reactions in amorphous food systems. However, direct relationships between reaction rates and glass transition cannot be established, because reaction rates are affected by a number of additional and independent factors. These include

the independent effects of temperature, pH and reactant and product concentrations [11, 12, 17, 23, 30]. The reactant and amorphous food matrix molecules may also form separate phases and exhibit water partitioning and water migration affecting local reaction environments within a food microstructure [23]. It may, however, be assumed that in a homogeneous food system, in agreement with homogeneous synthetic polymers, molecular mobility in the glassy state is limited to molecular rotations and vibrations, but in the supercooled liquid state translational mobility appears. Unfortunately, foods are extremely heterogeneous systems and may exhibit molecular mobility well below a measured, 'macroscopic' or 'average' glass transition temperature. Studies on effects of glass transitions in food systems on reaction rates have observed that the glass transition may affect diffusion and indirectly reaction rates, particularly rates of non-enzymatic browning in concentrated model systems [11, 23]. Consequently, reaction rates often increase substantially at temperatures above the glass transition, but reactions may occur below a measured, macroscopic glass transition of a food system depending on other factors affecting reaction rates, such as reactant concentration, pH, temperature and water content.

An important consequence of glass transition in food systems is time-dependent component crystallization, e.g., lactose crystallization in dairy powders and amylopectin crystallization in gelatinised starch [19, 31–34]. Such time-dependent crystallization is most often observed in storage of foods and pharmaceuticals when the storage relative humidity exceeds a critical value and the material or its structural component may undergo the glass transition. At such conditions the rate of crystallization becomes a function of water sorption that controls the water content-dependent temperature difference to the glass transition,  $T - T_g$  [19]. In frozen food systems, both a solute, such as lactose in ice-cream, or the solvent crystallization may be affected by the glass transition of solids and unfrozen water [18, 20, 35]. It seems, for example, that the rate of ice recrystallization is affected by the glass transition of the mixture of non-frozen water and solutes. This is also observed in DSC measurements of rapidly cooled carbohydrate solids that show a devitrification (ice formation) exotherm above the glass transition [3].

## Conclusions

Thermal analytical techniques provide macroscopic information of phase and state transitions in food and biological systems, but they do not give information of heterogeneities in food microstructure. It seems that several complementary techniques are needed to understand time-dependent properties of amorphous foods. Knowledge of local microstructure, transformations and water relations as well as phase separation and their effects on rates of changes and stability is required to understand properties and kinetics in amorphous systems.

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