DEVELOPMENT OF BANANA FLAKE PRODUCT: EFFECTS OF WATER ACTIVITY AND GLASS TRANSITION ON QUALITY AND PRODUCT STABILITY

INTRODUCTION

Banana ranks fourth among the developing world's most important food crops, after rice, wheat and maize. Local consumption accounts for 90 % of production, mainly in the poorest countries of Africa, Latin America and Asia. In some areas, it is the principle food crop. Banana and its close relative, the plantain, which are part of genus *Musa*, are nutritious and delicious staple foods throughout most of the developing world. In addition, they are significant sources of export income. Despite its status as one of the world's most important commodities, the fruit is considered merely a snack food in industrialized nations. Banana is widely grown and becomes an important economic plant in Thailand. There are many species but the popular are *Musa* (AAA group) ' Kluai Hom Thong', *Musa* (AA group) ' Kluai Khai' and *Musa* (ABB group) , ' Kluai Numwa'. Banana is easily digestible and a rich source of carbohydrates, phosphorus, calcium, potassium, and vitamin C Banana can be processed to various products such as banana puree, banana flour, banana powder, banana chips, banana jam, banana juice, banana figs and banana flake. The products from banana have many problems about quality of banana between process and after process.

This project focuses on the production of banana flake using a drum dryer. However, banana flake obtained from drum drying is known to exhibit a poor quality since it rapidly absorbs moisture and becomes sticky. The quality of banana flake depends partly on changes occured during processing and storage. Some of these changes involve modification of physical structure. Other changes are due to chemical reactions, but these are also affected by physical structure, primarily due to effects on diffusivities of reactants and reaction products. Quality loss of banana flake for example loss of crispness and browning occur after absorbing moisture. Deteriorative changes result from reactions between compounds within banana flake and increasing

water content. At increasing water contents, the materials also have higher water activity (a_w) and several reactions in low-moisture food systems have been shown to exhibit higher rates above specific water contents and water activity. One of the product properties that has been found to be linked to structural changes during processing and storage is the glass transition temperature (T_g). Water activity (a_w), glass transition temperature (T_g), dehydration mechanisms and theories, and chemical and physical changes should be recognized as key elements for any food dehydration operation. Glass transition temperature and water activity are important tools to predict available water in food and the physical state of solid foods. The purpose of this study is to relate water activity and glass transition concept to quality and stability of the banana flake.

OBJECTIVE

1. To determine the moisture sorption isotherm of banana powder at various water content and water activity.

2. To investigate the effect of water content/ water activity on Glass Transition Temperature (T_g) of banana powder.

3. To correlate Glass Transition Temperature and water activity of banana powder, applying the appropriate mathematical models.

4. To develop banana flake product.

5. To investigate the effects of storage temperature on qualities of banana flake.

LITERATURE REVIEWS

1. Banana

" Banana" is a general term embracing a number of species or hybrids in the genus *Musa* of family Musaceae. Banana and plantain (*Musa* spp.) are major stable food for millions of people in the tropical world. The banana production of the world has been estimated to be 80.6 Mt annually. Genetic improvement in cultivated bananas is difficult due to the absence of sexual reproduction mechanisms. In vitro protocols have been standardized to allow commercially viable propagation of desired clones of *Musa*, and the plant tissue culture techniques are being used to select *Musa* variants. The tissue variability could be very beneficial to the banana breeder. With tissue culture technique, it might be possible to isolate improved variants of standard cultivars with resistance to pest and diseases. This variability has been reported in different banana cultivars through physical and chemical mutagenesis. Traditionally, the classification of bananas was mainly based on their morphological characterization such as fruit color or weight of bunch (Xu *et al*., 2006).

Banana is one of the important economic plants and grown countrywide in Thailand. There are many species but the popular are *Musa* (AAA group) 'Kluai Hom Thong, *Musa* (AA group) 'Kluai Khai' and *Musa* (ABB group), 'Kluai Numwa'. Banana can be processed in to various products such as banana puree, banana flour, banana powder, banana chips, banana jam, banana figs, banana juice and banana flake (Silayoi, 2002).

Though banana supply is quite abundant, its loss can reach 40% due mostly to inadequate storage facility during peak harvest times and industrial processing (Filho, 1994). Drying is one of industrial processing for banana.

2. Drying

Drying is a process in which water is removed to halt or slow down the growth of spoilage microorganisms as well as the occurrence of chemical reactions. Drying of fruits and vegetables demands special attention, as these are considered important source of vitamins and minerals essential for mankind. Dried fruits and vegetables have gained commercial scale and has become an important sector of the agricultural industry. Losses of fruit and vegetables in developing countries are estimated to be about 30-40% of the production (Karim and Hawlader, 2005).

Banana used for drying must comply with certain specifications, such as degree of maturity and the use of healthy fruit, since the drying process will not improve the initial quality. Another important factor that interferes with the quality of drying product is the drying temperature, since this controls the final product's moisture content and consequently its microbiological stability during storage. The drying temperature also affects the product's color and texture, as well documented in the literature since it promotes browning by caramelization and the maillard reaction, and a drying out of the product surface (Leite *et al*., 2005).

Drying is a complicated process involving simultaneous heat and mass transfer. Fruit and vegetables have certain morphological features quite distinct from other natural materials that greatly influence their behaviour during drying and preservation. Fruits are generally characterized by high initial moisture content, high temperature sensitivity (i.e. color, flavor, texture and nutritional value are subjected to thermal deterioration), and shrinkage of materials during drying. The required amount of thermal energy to dry a particular product depends on many factors, such as, initial moisture content, desired final moisture content, temperature and relative humidity of drying air, and air flow rate (Karim and Hawlader, 2005).

A major criterion to describe the quality of the dried foods is that when it is reconstituted by the addition of water, they are very close to or essentially indistinguishable from the original food material used in their preparation.

The speed of reconstitution and the appearance of the product are both important features that need to be adequately considered in selecting a drying process. Drying makes it possible not only to stabilize the product by reducing its moisture content and water activity, but also to create new ranges of products. A large number of studies have been carried out to study how the process affects the quality of the dried banana, i.e. freeze-drying, osmotic dehydration, and vacuum drying (Boudhrioua *et al*., 2002).

The selection of dryer should be based on the entire manufacturing process. Raw materials, intermediate product, and final product specifications and characteristics (i.e., final moisture content) need to be clearly defined. Preprocessing steps may be considered to partially remove water prior to final drying step (i.e., osmotic dehydration prior to freeze drying). The final assessment for selecting a dryer should include, but not be limited to, the production capacity, initial moisture content of the product, particle size distribution, drying characteristics of the product, maximum allowable product temperature, explosion characteristics (i.e., spray or fluid bed dryings), moisture sorption isotherms and physical data of material (Humberto *et al.*, 2001).

Mao (1975) studied on drying of banana puree by drum dryer. He found that drum rotation rates greater than 2rev/min and drum temperature less than 142 °C gave the best results. Drum clearance influenced the texture and moisture content of the product. The emulsifiers, monostearin and lecithin gave excellent film formation on drum, rehydration properties, and texture of the rehydrated puree. Egg yolk gave excellent texture of both the dried and the reconstituted product.

Radhakrishnaiah *et al*. (1979) reported that a slurry of either groundnut or soy flour with banana pulp, sugar and corn starch was homogenized and drum-dried; the presence of corn starch improved flaking. They found that optimum drying conditions were at a steam pressure of 45 lb/in^2 gauge and a drum rotation speed of 3.5 rev/min. The texture of dried product was crisp, free-flowing, sweet with a characteristic of

banana flours. The product may be consumed as flakes or as a gruel after reconstitution in water.

Wanachat et al. (1999) studied on banana (Kluai Numwa) flake production by drum dryer . They found that the optimum drying condition was 145 °C, at 1 rpm and a drum clearance of 1 mm. Banana fake product (100 g) contained 90.91 g of carbohydrate, 2.47 g. of protein, 0.58 g of lipid, 0.16 g of Ca, 2.08 mg of P, 0.35 g of fiber, 2.35 g of ash and 1.10 g of water.

Most food products with reduced water content are partially or completely amorphous in nature. Amorphous or partially amorphous structures in foods are formed in various processes such as baking, concentration, drum-drying, freeze-drying, spray-drying and extrusion that allow a sufficiently short time for the removal of water or the control of concentrated solids (Roos *et al*., 1998). Water content reduction may be another interesting alternative to prolong product shelf-life, and this method is utilized for other fruits. In this sense, the fruit may be processed to be consumed as a dried product (powder or snack) (Karanthanos *et al*., 1995). The control and optimization of operating parameters during manipulation and processing of products may be considered essential in achieving a viable and efficient operation. One might expect that the optimal operating conditions depend on the type of product being processed. Various changes in physical, chemical, and/or biological characteristics of foodstuffs occur during processing, storage and distribution (Karel *et al*., 1993). Food dehydration is not limited to the selection of a dryer. The physicochemical concepts associated with food dehydration need to be understood for an appropriate assessment of the drying phenomena in any food product. Water activity (a_w), glass transition temperature (T_g), dehydration mechanisms and theories, and chemical and physical changes should be recognized as key elements for any food dehydration operation (Humberto *et al*., 2001). One of the product properties that has been found to be linked to structural changes during thermal processing is the glass transition temperature (T_g).

3. Glass Transition

Glass transition temperature (T_g) can be defined as the temperature at which an amorphous system changes from the glassy to the rubbery state Glass transition in amorphous materials over a range of temperatures. It is in the nature of a second-order phase transition which occurs without a release or absorbing of latent heat. It happens during heating or wetting conditions accompanied by an increase of the molecular mobility and free volume. (Roos and Karel, 1991a; Slade and Levine, 1991 and Rahman, 1995).

A state diagram (Figure 1) shows the physical state as a function of concentration. The freezing line (AB) and solubility line (BC) are shown in relation to the glass transition line (DEF). The glass forms at a characteristic glass transition temperature (point E) lower than the eutectic temperature (point B) and the water content at point E is unfreezable water. Glass transition temperature decrease from the T_{gs} of pure amorphous material to a theoretical T_{gw} of pure water at -135°C. T'_g and $X's$ are two parameters which reflect the physical state of the non-crystallizing solute (Roos and Karel, 1991a; Rahman, 1999)

Glass Transition Measurement Techniques

Complementary methods have been employed to measure glass transitions in food ingredients and products and/or aspects of molecular mobility and diffusely related to the effects of glass transitions in aqueous food glasses and rubbers (Louise and Harry, 1993).

1. Differential Scanning Calorimetry (DSC)
2. Dynamic Mechanical Thermal Analysis (DMTA)
3. Electron Spin Resonance (ESR.)
4. Nuclear Magnetic Resonance (NMR)
5. Thermal Mechanical Analysis (TMA)
6. Thermodielectrical Analysis (TDEA) .
7. Thermal Gravimetric Analysis (TGA)

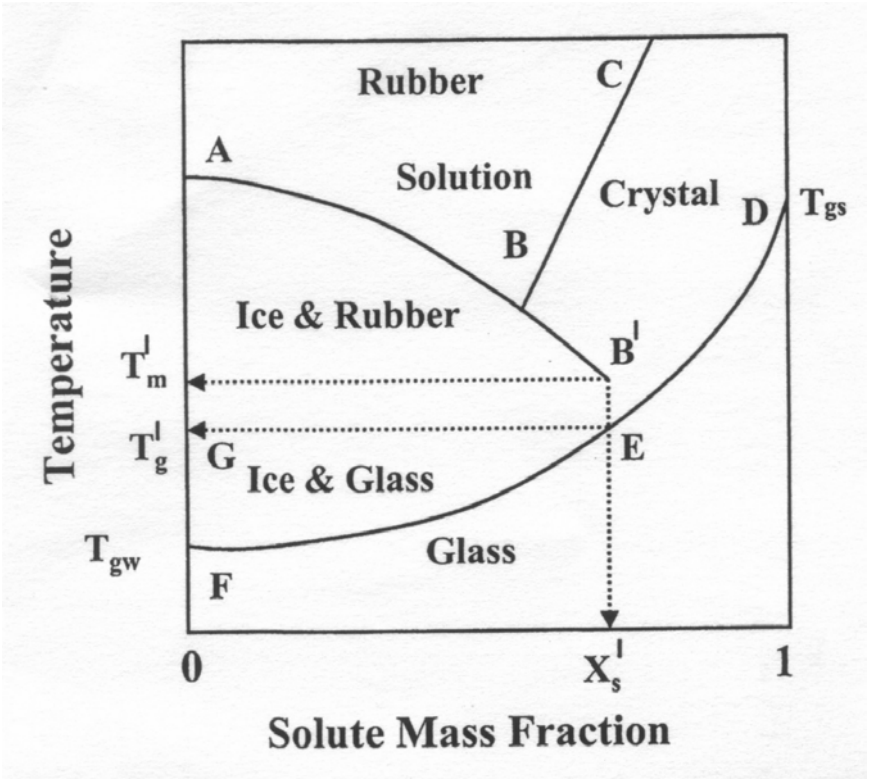

Figure 1 A typical state diagram for solution. AB: freezing curve, BC: solubility curve, B: eutectic point, DEF: glass transition line, E: glass transition temperature at maximal freeze concentration, GE: glass transition by slow or equilibrium cooling, T_{gs}: glass transition temperature of solid, T_{gw}: glass transition temperature of water, T'_{m}: end point of freezing curve, T'_g: glass transition for maximal freeze concentration temperature, X'_s: solids mass fraction at maximal freeze concentration

Source: Rahman (1999)

Differential Scanning Calorimetry (DSC) is the thermal technique used to measure changes in heat flows associated with material transitions. DSC measurements provide both qualitative and quantitative data on endothermic (heat absorbing) and exothermic (heat evolving) processes. DSC is commonly used to determine the glass transition temperature and crystalline point of polymeric materials.

We use this technique it to study what we call the thermal transitions. They are the changes that take place in a polymer when it is heat. The melting of a crystalline polymer is one example . The glass transition is also a thermal transition of materials. Glass transition may be identified by DSC because it corresponds to a rearrangement of solid amorphous matrix involving the breaking of bounds and creation of new ones. The glass transition on heating is observed as an endothermic step in a DSC thermogram. This change in the heat capacity (Cp) because the glassy and rubbery states have different physical properties, including Cp (Ma,Harwalkar and Maurice, 1990; Lund, 1983; Roos, 1995a; Roos, 1998).

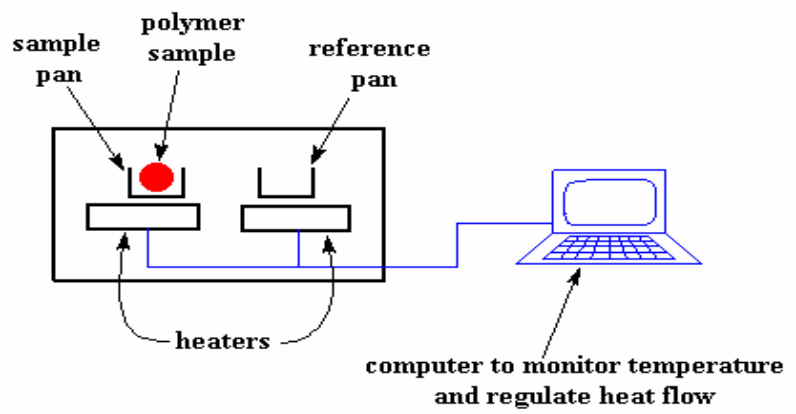

Figure 2 Schematic Diagram of Differential Scanning Calorimetry (DSC)
Source: Anonymous (1997)

DSC equipment consists of two pans. One pan is sample pan and the other is the reference pan. Each pan sit on top of a heater which controlled by the computer on heating two pan at a specific rate, usually 10°C per minute (Figure 2). The computer makes absolutely sure that the heating the rate stays exactly the same throughout the experiment and it makes sure that the two separate panes, with their two separate heaters, heat at the same rate as each other. Having extra material means that it will take more heat to keep the temperature of sample pan increasing at the same rate as the reference pan. So the heater underneath the sample pan works harder than the heater underneath the reference pan. It has out put more heat. By measuring

just how much more heat it has to put out in a DSC experiment. Figure 3 is plotted on x-axis the temperature and the y-axis the difference in heat output of the two heaters at the given temperature.

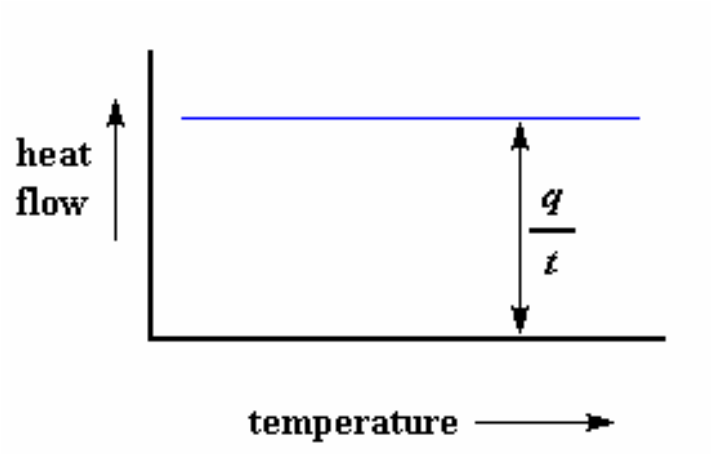

Figure 3 Graph shows the change of heat flow varied by the temperature.
Source: Anonymous (1997)

The heat flow is the heat supplied per unit time (q/t) and the heating rate is the temperature increase per unit time (ΔT/t). The heat capacity (Cp) is the certain amount of heat obtained at the certain temperature increase. Hence equation 1,

(1)

$$Cp = \frac{q/t}{\Delta T/t} = \frac{q}{\Delta T}$$

In a DSC, a heating system monitors the temperature of a sample and a reference pan, varying the heating rate to the pans such that the temperature of the sample and the reference pan remain the same during a scan of temperature. The output of DSC is a plot of energy versus temperature (Figure 4). The resulting thermogram relates the difference in energy supplied to the two pans which allows peak areas on a DSC thermogram to correspond directly to changes in enthalpy. From DSC thermogram the glass transition temperature is determined by the onset of the endothermic peak, a base line before and during the

transition is used and the temperature corresponding to the intersection of these two lines is called the onset of glass transition.

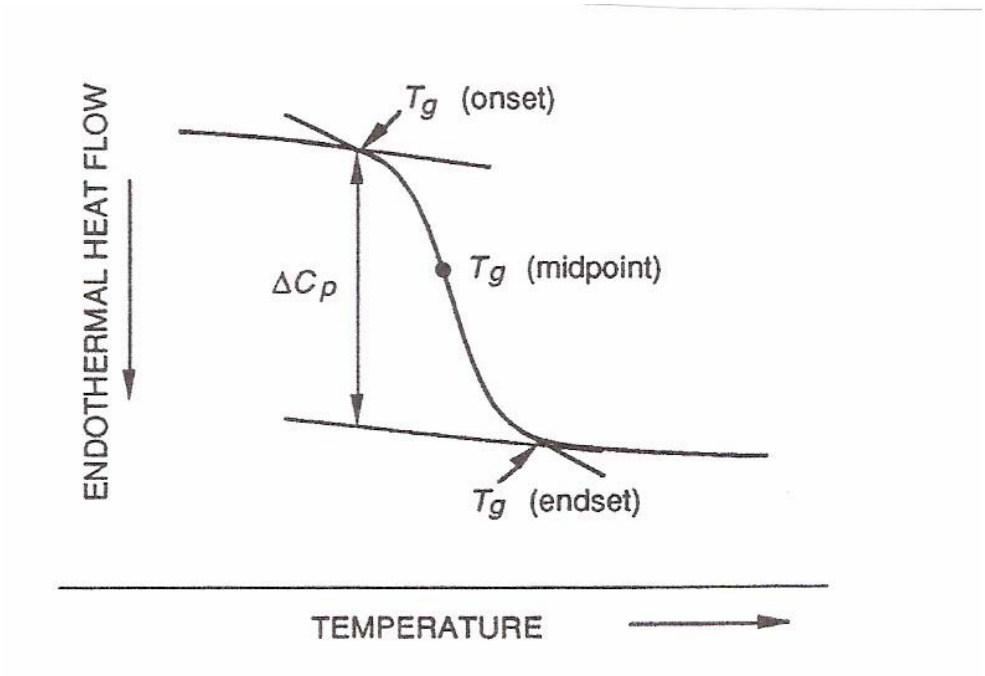

Figure 4 Determination of second-order and glass transition temperatures, T_g, and change in heat capacity, ΔC_p, that occurs over the glass transition temperature range from DSC thermograms. The endothermal step change in heat flow during heating of glassy materials occurs due to ΔC_p at the second-order transition temperature.

Source: Roos (1995b)

4. Water Activity of Foods

Water activity is defined as the ratio of vapour pressure of water in a system to the vapour pressure of pure water or the equilibrium relative humidity of the air surrounding the system at the same temperature. It is a function of moisture and temperature of food. Most fresh foods can be considered as high-moisture foods and their shelf life is largely controlled by the growth of microorganisms. High-moisture foods have an a_w of 0.90 to 0.999 and they usually contain more than 50% w/w water.

These foods include fresh meat and seafood, various diary products, and fruits and vegetables as well as beverages. Most bacteria, molds, and yeasts are likely to grow in high-moisture foods. However, the types of spoilage microorganisms and their species are highly dependent on both a_w and pH as well as other hurdles (Eskin and Robinson, 2000).

Intermediate moisture foods (IMF) have an a_w of 0.60 to 0.90 and the water content is 10 to 50%. These foods include many traditional low-moisture foods, such as grains, nuts and dehydrated fruits and a number of processed foods. All of these categories had examples of traditional and novel foods. Traditional food as is consumed included salted and cured meats, salted fish, Parma ham, dried fruits, some cheeses, and jams. Pet foods and some novel fruit products were classified as consumed as is novel foods. Examples of traditional and novel IMF products consumed after rehydration were jellies, meat-filled pasta, and condensed milk and soup, sauce, and meal concentrates, respectively. The traditional and novel IMF products consumed after dehydration included some fruit cakes/pies/puddings and pop-tarts, respectively (Eskin and Robinson, 2000).

Although microbial spoilage is prevented at a_w below 0.60, low-moisture foods may exhibit deleterious changes, such as structural transformations, enzymatic changes, browning, and oxidation, depending on a_w, temperature, and extent of water plasticization. As shown in Figure 5, critical a_w values can be defined for various changes and microbial growth resulting in loss of stability in lactose hydrolysed skin milk and amylopectin. However, the critical values are specific for each food material and they may be dependent on food composition and plasticization behavior (Eskin and Robinson, 2000).

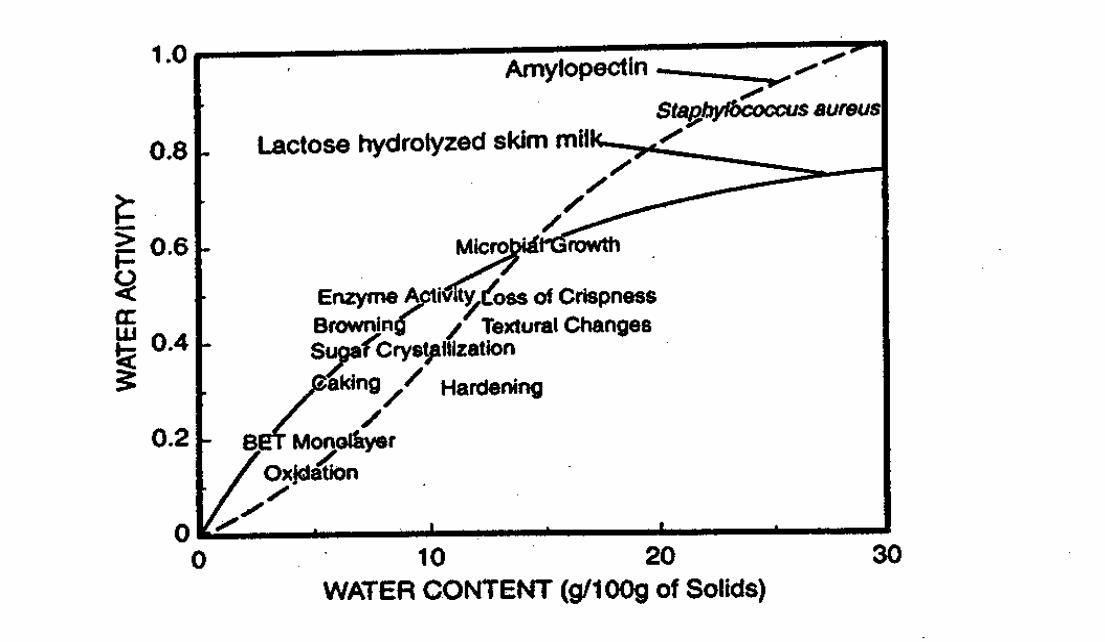

Figure 5. Critical water activity and water content ranges for various changes and microbial growth occuring in food materials. The sorption isotherms of lactose hydrolyzed skin milk and amylopectin are shown as examples of extreme values for water activities and water contents.

Source: Eskin and Robinson (2000)

The relationship between moisture content and the corresponding water activity of a food over a wide range at constant temperature is represented in a graphical form known as moisture sorption isotherm (MSI). An isotherm allows using changes in moisture level of the food for prediction of the equilibrium moisture level of a food stored in an environment of known RH and temperature. These are indispensable tools of the food technologists (Karel *et al*., 1975; Labuza, 1984).

Moisture Sorption Isotherm (MSI)

Food moisture isotherms and the equations of this relationship are important for the solution of engineering problems. Knowledge of the water adsorption characteristics is needed for shelf life predictions and determination of critical moisture and water activity (a_w) for acceptability of products that deteriorate mainly

by moisture gain, such as cookies and snacks (Katz and Labuza, 1981), and are important in drying, packaging and storage, as well as ingredient mixing. In most cases the sorption data are obtained at one temperature, usually at the storage temperature. However, for the thermodynamic analysis of sorption and modeling the drying and storage stability processes, it is necessary to obtain the isotherms in a range of temperatures. The knowledge of the dependency of the sorption phenomena on temperature provides valuable information about the changes related to the system's energy. An important thermodynamic parameter is the net sorption isosteric heat which measures the binding energy or the forces between water vapor molecules and the adsorbent surfaces. The level of moisture content at which the heat of sorption approaches the heat of vaporization of water is often taken as indicative of the amount of ' bound water' existing in the food (Duckworth, 1972).

The water sorption isotherms of various nonsoluble food components (bio-polymers) as well as of model systems prepared by wet mixing of such constituents followed by freeze-drying, were measured and analyzed. An attempt to predict product isotherms from knowledge of component isotherm and weight fractions of components gave satisfactory result in various cases while in others the predicted product equilibrium moisture contents were significantly higher than the experimental values. This was attributed to the interaction between constituents leading to a reduction of water-binding capacity (Iglesias, Chirife, and Boquet 1980).

A plot of water content of a food (expressed as mass of water per unit mass of dry material) versus a_w is known as a moisture sorption isotherm (MSI). Information derived from MSIs are useful for (a) concentration and dehydration processes, because the water removal is related to relative vapor pressure (RPV), (b) formulating food mixtures so as to avoid moisture transfer among the ingredients, (c) determining the moisture barrier properties needed in a packaging material, (d) determining what moisture content will curtail growth of microorganisms of interest, and (e) predicting the chemical and physical stability of food as a function of water content. Several substances that have MSIs of markedly different shapes are resorption (or adsorption)

isotherms prepared by adding water to previously dried samples. Desorption isotherms are also common (Fennema, 1996).

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The shapes of isotherms showing sorption of gases by solid materials may have various forms. According to the classification of Brunauer adsorption isotherms may have five basic forms (Brunauer *et al*., 1938), which are shown in Figure 6.Water adsorption isotherms of biological and food materials often follow the shape of sigmoid, type II isotherm. Foods such as fruits, confections, and coffee extract that contain large amounts of sugar and other small, soluble molecules and are not rich in polymeric materials exhibit a type III (J-type) isotherm. The shape and position of the isotherm are determined by several factors including sample composition, physical structure of the sample (e.g., crystalline or amorphous), sample pretreatments, temperature, and methodology (Roos, 1995b and Fennema, 1996).

Five types of isotherms (Figure 6) are describe by Brunauer *et al*., 1940.
Type 1 is the well known Langmuir isotherm, obtained by the monomolecular adsorption of gas by porous solids in a finite volume of voids. Type 2 is the sigmoid isotherm, which is obtained for soluble products and shows an asymptotic trend as water activity tends towards 1. Type 3, known as the Flory- Huggins isotherm, accounts for the adsorption of solvent or plasticizer like glycerol, for example, above the glass transition temperature. The Type 4 isotherm describes the adsorption by a swellable hydrophilic solid until a maximum of hydration of sites is reached. Type 5 is the B.E.T. (Brunauer, Emmett and Teller, 1938) multilayer adsorption isotherm, observed for the adsorption of water vapour on charcoal and related to types 2 and 3 isotherms (Mathlouthi and Roge, 2003).

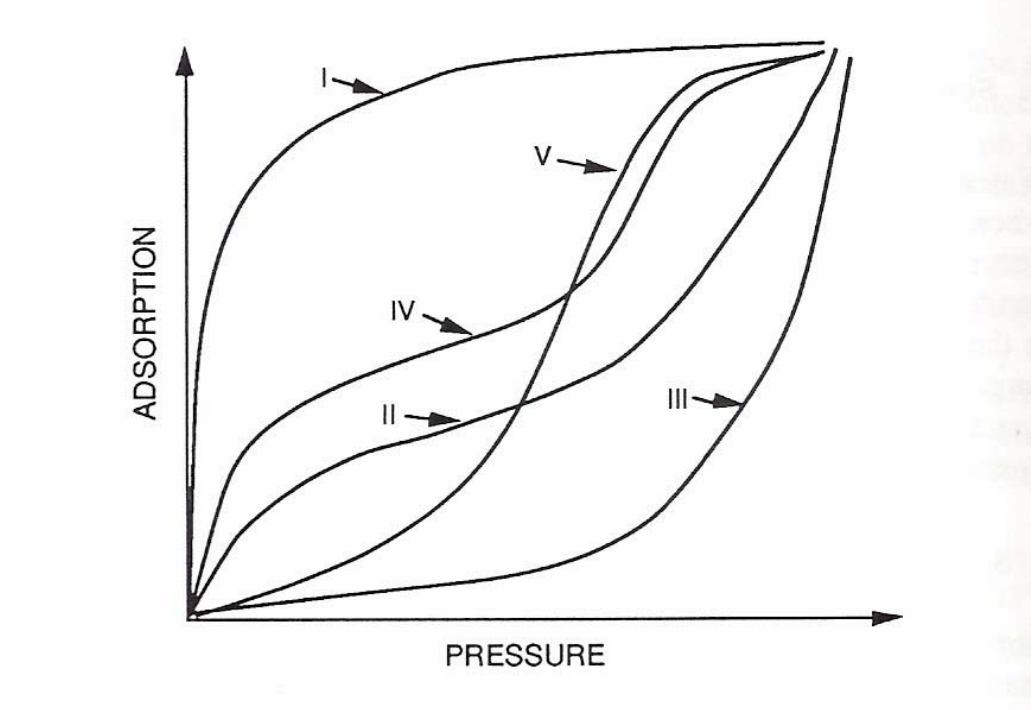

Figure 6 Brunauer's five types of adsorption isotherms.
Source: Roos (1995b)

As an aid to understanding the meaning and usefulness of sorption isotherms it is sometimes appropriate to divide them into zones (Figure 7). As water is added (resorption), sample composition moves from Zone I(dry) to Zone III (high moisture) and the properties of water associated with each zone differ. Water present in Zone I of the isotherm is most strongly sorbed and least mobile. The water associated with accessible polar sites by water-ion or water-dipole interactions, is unfreezable at –40 ° C, has no ability to dissolve solutes, and is not present in sufficient amount to have a plasticizing effect on the solid. In Zone II and III, water is sufficient to complete a true monolayer hydration shell for macromolecules such as globular proteins, and is sufficient to lower the glass transition temperature of macromolecules so that sample temperature and T_g are equal. Further addition of water (Zone III) causes a glass-rubber transition in samples containing glassy regions, a very large decrease in viscosity, a very large increase in molecular mobility, and commensurate increases in the rates of many reactions. This water is freezable, aviable as a solvent, and readily supports the growth of microorganisms (Fennema, 1996).

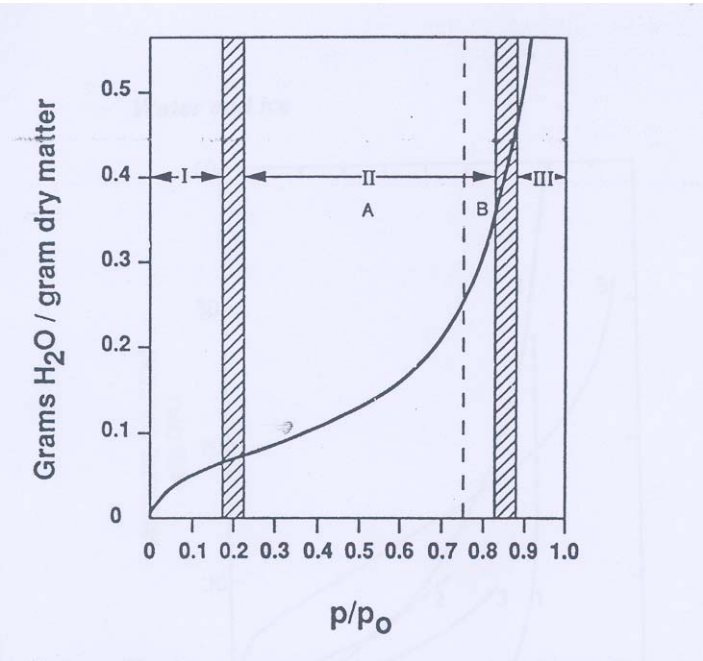

Figure 7 Generalized moisture sorption isotherm for the low-moisture segment of a food (20°C).

Source: Fennema (1996)

Water sorption isotherms show relationships between a_w and water content at constant temperature. Thus sorption isotherms are employed in process design and control, such as in predicting the end-point of drying and optimizing ingredient selection in food formulation (Rahman and Labuza, 1999).

Modeling studies of sorption properties are particular important in predicting shelf life of low and intermediate-moisture foods (Labuza *et al*., 1970, Labuza, 1980, Simatos and Karel, 1988). The Brunau-Emmett-Teller (BET) (Brunauer *et al*., 1938) and Guggenheim-Anderson-deBor (GAB) (van den Berg and Bruin, 1981) equations are well-known sorption models that provide the monolayer value (M_0) often considered as the optimal water content for stability of low-moisture foods (Labuza *et al*., 1970, Labuza, 1980). Several mathematical models have been used to predict water sorption of foods (Boquet and *et al*., 1978; Iglesias and Chirfe, 1982; Roos, 1993a; Joppila and Roos, 1994; Timmermann et al., 2001). The applicability of the

BET model (Eq.2) is limited to the a_w range of 0.1 to 0.5 (Labuza, 1968), while the GAB model (Eq.3) is applicable over a wide a_w range (van den Berg *et al*., 1981).

$$M = \frac{(M_0 C a_w)}{(1 - a_w)(1 + (C - 1)a_w)} \tag{2}$$

Where a_w is water activity; M is water content of sample on dry basis; M_0 is the monolayer water content; C is the surface heat constant.

$$M = \frac{(M_o CK a_w)}{((1 - Ka_w)(1 - ka_w + Cka_w))} \tag{3}$$

Where a_w is water activity; M is water content of sample on dry basis; M_0 is the monolayer water content; C is the Guggenheim constant; K is the constant correcting properties of multilayer molecules with respect to bulk liquid.

5. Water Sorption Isotherm and Glass Transition in Foods

Katz and Labuza (1981) studied the sorption isotherm of potato chips, popcorn, puffed corn curls, and saltines. In their study, sensory panels were used to determine the crispness and textural quality of humidified products by magnitude estimation technique coupled to a verbal concept scale. Critical water activities (a_c) where the products became organoleptically unacceptable, generally fell in the 0.35-0.50 a_W range. Instron analyses showed that the force-deformation curve changed distinctly near the a_c for saltines and puffed corn curls, while the curve changed more gradually with increasing a_w for popcorn. Potato chips did not produce a consistently shaped force-deformation curve. The cohesiveness value of popcorn was found to be a good indicator of its sensory crispness.

Roos (1987) reported the effects of moisture content on thermal behavior of strawberries. The phase transition was determined using differential scanning calorimetry (DSC). It was found that the glass transition temperature (T_g) of the dried amorphous material was a function of moisture content. Further, the surface

temperature during freeze-drying was reported to affect the glass transition temperature. The DSC data and sorption isotherms were suggested to be useful in the evaluation of processing conditions suitable for different food materials. Differential scanning calorimetry was used to determine the thermal transitions in fresh and freeze-dried strawberries and the moisture dependence of these transitions. The freeze-dried strawberry samples had a glass transition at 30-60 °C and melting endotherm of dried products was similar to that for freeze-dried sugars. The glass transition temperature of humidified sample was a linear function of the water activity; it decreased with increasing moisture content.

Paakkonen and Roos (1990) have studied the water sorption isotherms for freeze-dried horseradish roots (*Armoracia rusticana*). The isotherms were determined using the interval sorption technique, and the thermal behavior of dried and rehumidified products was analyzed using differential scanning calorimetry. The hygroscopicity of the dried material increased when the surface temperature during freeze-drying was increased from 20°C to 60°C. Both sorption and thermal data showed that drying at high surface temperatures affected the physical structure of the material, resulting in increased water adsorption, decreased glass transition temperature, and increased unfreezeable water content. Water sorption isotherms and thermal data can be used to determine the proper drying and storage conditions for horseradish roots.

Lateef *et al*. (1997) determined the moisture sorption characteristics for two products of cassava, namely fufu and tapioca, at 25°C, 32 °C and 45°C for water activity ranging from 0.1 to 0.96. At a given water activity, the results showed that the moisture content decreased with an increasing temperature for fufu and tapioca. Eight sorption models were used to analyze the data. The GAB model showed the best fit, whereas the BET model was the poorest over the whole range of water activity.

Palou *et al*. (1997) analyzed on major components of three cookies and two corn snacks and evaluated the moisture adsorption characteristics at 25°C, 35°C and

45 °C. They found that the main composition differences among these products were fat and total carbohydrate content. The isotherms of each product were different ($p \leq 0.05$) and significantly affected by temperature. The mathematical description of the adsorption data was obtained applying some of the most common sorption equations. Peleg's model gave the best description of the experimental data, followed by the GAB equation.

Khalloufi *et al*. (2000) determined the T_g of four types of berry powders as a function of water content using DSC. The equilibrium moisture content was also measured using gravimetric method and the GAB model was used to predict water activity. The combined effects of T_g and a_w were incorporated into a new mathematical expression. They found that the mean percent error of the model predictions was less than 3.6 % when compared to the experimental data.

Telis and Sorbal (2001) have found that glass transition temperature of freeze-dried pineapple conditioned by adsorption at various water activities at 25°C was determined by differential scaning calorimetry (DSC). The glass transition curve showed that T_g decreased with an increase in moisture content and the experimental data could be well-correlated by the Gordon-Taylor equation.

Nowakowski and Hartel (2002) reported that moisture sorption into sugar led to significant changes in the physico-chemical properties. An increase in moisture content reduced the glass transition temperature although the effect was dependent on the type of corn syrup. In general, higher corn syrup content and addition of high-maltose corn syrup resulted in slightly higher T_g for a given moisture content. Higher corn syrup concentration increased not only hardness but also stickiness. Stickiness increased as a function of moisture until a maximum was reached, whereupon further moisture sorption reduced stickiness. A maximum in stickiness occurred when T_g values were still above room temperature, indicating that surface moisture was considerably higher than bulk moisture content.

Konopacka *et al*. (2002) studied on the sorption isotherm of fat-free apple chips. The sorption isotherm obtained indicated the absence of a monolayer and that was typical for type III according to the Brunauer classification. At water activity below 0.12, apple chips demonstrated excellent crispness and were highly acceptable as a snack food. They were extremely hygroscopic and lost crispness easily. The critical water activity (a_c) was found to be 0.18 which corresponds to a water content of 3.5 g H_2O/ 100 g solids. These values were much lower than those found for other crispy snack foods.

Moraga *et al*. (2004) studied on the water sorption isotherms and glass transition as a function of moisture content in strawberries. Sorption experiments were carried out in chambers at controlled a_w at 30°C. Samples studied were whole and homogenized tissue, fresh (for the desorption process) and previously freeze-dried (for the adsorption process). Glass transition of samples equilibrated to different moisture contents were analysed by DSC. GAB model was fitted to sorption data and Gordon and Taylor equation was used to model the water plasticization effect. Strawberry pretreatments caused changes in the tissue structure that affected the water binding capacity of different product phases at equilibrium with a determined a_w value. This implied differences in the relationships between the mean equilibrium moisture content of the product and both the a_w value (equal for all phase at equilibrium) and glass transition temperature of the amorphous soluble solids.

Ahmed *et al.* (2005) studied on water sorption isotherms of freeze dried and control (without freeze drying) date paste of cultivar *Khalas* at 20°C using the static saturated saline solution method. The GAB equation fitted adequately for the whole range of water activity for both date paste samples. The monolayer moisture contents ranged between 0.102 and 0.12 for freeze dried and control samples, respectively. The glass transition temperature of saturated salt equilibrated paste sample was measured using differential scanning calorimetry. Glass transition temperature of both samples decreased linearly with an increase in water activity. Water adsorption characteristics of freeze dried and control samples differed from each other and were supported by glass transition temperatures.

6. Applications of Glass Transition Concept in Foods

The glass transition temperature (T_g) can be applied in determining proper temperature and humidity conditions of agglomeration and in reducing quality changes occurring during dehydration. Major applications in producing high quality dehydrated foods include collapse reduction and improvement in flavor retention in the dehydration processes. A model could also be used to predict collapse temperature of dried materials.

Dry cereal products may be in the glassy state and are described as hard, stiff, brittle and crisp. As these foods gain moisture or their temperature increases, they may enter the rubbery state and become soft and thus losing the desired properties. The glass transition temperature of dried foods is extremely important in prediction of conditions for proper drying, agglomeration, and storage (Roos and Karel, 1991c).

The physical state is believed to affect kinetics of deteriorative reactions in vicinity of T_g. Both physical state and the moisture content are strongly related to the non enzymatic browning and various enzymatic reactions; in this way, it has been demonstrated an increase in rate of browning above T_g in model systems (Roos, 1995a).

Frozen foods are not stable and during the course of storage and distribution they are continually deteriorating at the commercially significant rates. A great effort has been done on improving the freezing process to ensure that a high degree of quality is incorporated originally. However, much of this advantage can be lost due to instability of the products stroage. Scientific research is now beginning to concentrate on producting products which are more stable and less susceptible to damage. In this way the study of glassy state becomes an important step on product formulation. Although freeze-concentration of solutes and phase separation of component compounds such as lipids may increase reaction rates, rates of deteriorative changes in frozen foods are reduced as a result of decreased temperature. Frozen foods are stable below glass transition temperature of the maximally freeze- concentrated (T_g')

but at temperatures above T_g' rates of deteriorative changes increase. If the storage temperature of frozen foods is below T_g, the freeze-concentrated phase is a glassy solid and the evolution of product is supposedly very slow. On the other hand, if the storage temperature is above T_g, the freeze-concentrated phase is a super-cooled melt and a tremendous reduction in viscosity is observed. Thus in frozen foods, the reduction in viscosity associated with storage temperatures above T_g, may result in an acceleration of all diffusion-controlled reactions affecting the product stability (Williams; Landel and Ferry ,1995; Roos *et al*., 1996).

Water as a plasticizer may have a significant effect on molecular mobility above a critical, temperature-dependent value. Simatos and Karel, 1988 and Slade and Levine, 1991 suggested that reaction rates affect diffusion-controlled amorphous foods. At temperatures below T_g, the rates of diffusion-controlled reactions are expected to be extremely low. A significant increase in reaction rates above T_g may be observed as a result of enhanced diffusion (Figure 8a). The rate of deteriorative changes in low-moisture foods is likely to depend on molecular mobility (Duckworth, 1981). The mobility of food components affects their physicochemical and physical properties. At temperatures above T_g diffusivity increases as the viscosity decreases (Karel, 1985).

The rate of the various reactions may also be related to physical state, molecular mobility, water plasticization, and glass transition of amorphous food solids, as shown in Figure 8b. Structural transformations as well as diffusion-controlled deteriorative reactions and those affected by crystallization phenomena occur at increasing rates with increasing a_w above the critical a_w. It is likely that water contents lower than critical water content are needed for maximum stability.
Figure 8b relates deteriorative changes, which are governed by T_g to water activity.

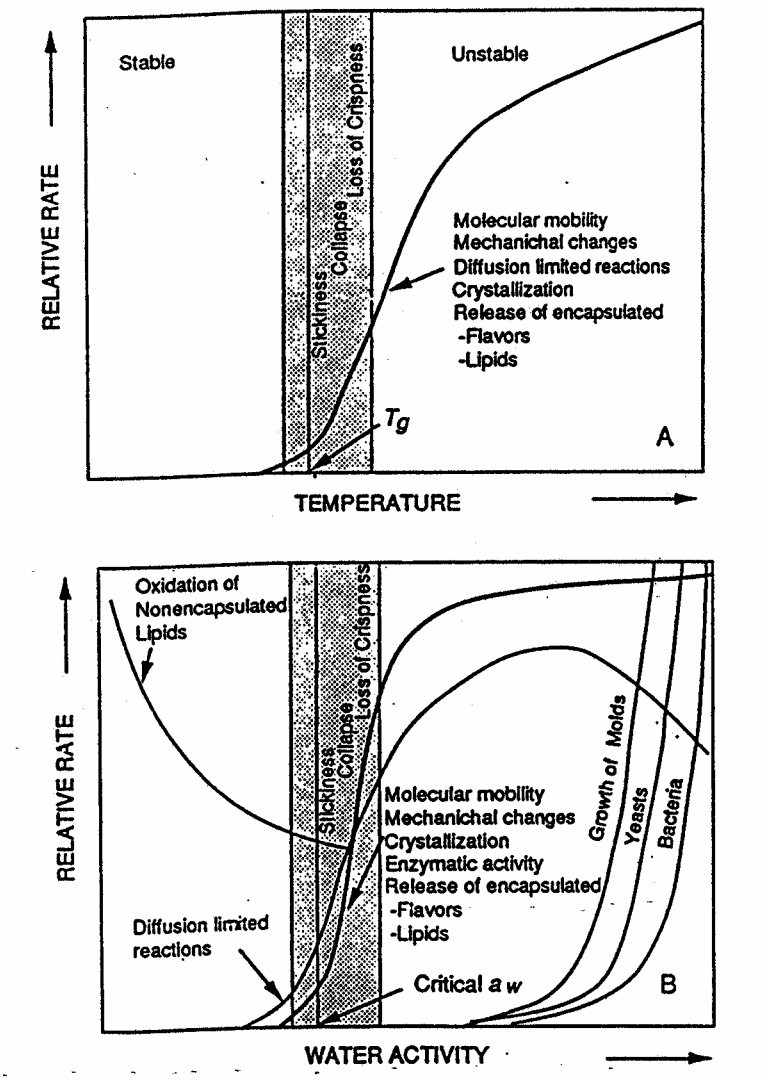

Figure 8. (a) Top: Effect of glass transition on stability and rates of mechanical and deteriorative changes. (b) Bottom: Effect of water plasticization and depression of the glass transition temperature (T_g) to below ambient temperature on rates of mechanical and deteriorative changes. The critical water activity may in some case be located with the (a_w) range for the growth of various microorganisms.

Source: Roos *et al*. (1996)

Applying the glass transition theory allows for an understanding of textural properties of food systems and helps explaining textural changes which occur during processing and storage. Texture is an important sensory attribute, and the loss of the desired texture leads to a loss in product quality and reduction in shelf-life. Glass

transition theory provides a clear approach to understanding the texture changes of crisp snacks as water content increases. At increasing water contents, the materials also have higher water activity and several reactions in low-moisture food systems have been shown to exhibit higher rates above specific water contents and water activity (Silver and Karel, 1981; Chen and et al., 1999; Bell and Hageman, 1994; Kouassi and Roos, 2000). Glass transition temperature and water activity are important tools to predict available water in food and the physical state of solid foods (Roos, 1995a).

7. Physicochemical Properties of Food and Food Stability

The physical state and physicochemical properties of food materials affect their behavior during processing, storage, distribution and consumption. Although fresh foods have diverse structural characteristics and compositions, their main components are carbohydrates, lipids, proteins, and water. Water interacts primary with hydrophobic lipids. The composition of the carbohydrate fraction of foods varies from low molecular weight sugars dissolved in water to all polymers that may be plasticized or softened by water, but may not be water soluble (Roos *et al*., 1996).

Water activity has been used as a common measure of low- and intermediate-moisture foods' stability at various storage conditions. Water plasticization of amorphous lactose or any other polar amorphous biological material increases the molecular mobility and, then resulting in glass transition, there is a rapid change in the physical state from a highly viscous solid-like glassy state to a supercooled liquid state (Levine and Slade, 1986; Roos and Karel, 1991b; Slade and Levine, 1991; Roos, 1993a; Karel *et al*., 1993).

The effect of water activity on chemical reactions which are important to food stability has been studied extensively. Glass transition theory considers the effect of the state of a system on reactions which is a relatively new approach developed by Williams, Landel and Ferry may also be applicable for describing the temperature dependence of chemical reactions within some food systems. These two parameters

are examined, with emphasis on applicability and application of each approach. Understanding the relationship among moisture, temperature and chemical reaction rates can be very useful for food stability prediction purposes. Both water activity and glass transition theory can be used to understand the influence of water on rates of chemical reactions. Water activity essentially considers the state of water in a food. Its relationship to chemical reaction rates is fairly complex and dependent upon the particular chemical reaction of interest (Nelson and Labuza, 1994).

Products stored below their glass transition are often stable for long periods of time. Hence, water sorption and glass transition of solids need to be prevented. Also products stored in the vicinity of their glass transition have reduced stability (Roos and Karel, 1992; Nowakowski and Hartel, 2002).

8. Effect of Glass Transitions on Processing and Storage

A major research topic in food science and technology is the description, preferably in a quantitative manner of quality changes which occur in foods during processing and storage. The complexity of food composition, the great range of environmental conditions to which foods are exposed in processing and in storage, the variety of chemical and physical processes which food components can be involved, and, finally, the difficulty in defining "quality", these are an enormous task. Traditionally, food scientists have approached this task by making in process design and in choosing storage conditions. One of the most common assumption used is the changes, which occur during processing and storage depend on only two parameters: time (t) and temperature (T). Furthermore it is usually assumed that an index of quality (Q) or an index of deterioration (ID) may be defined. ID may be defined as (Q_0-Q) where Q_0 is the initial quality. If ID depends on time and temperature and the zero order reaction causing quality changes which are used widely in evaluating processes and which base on the Arrhenius equation (Eq. 4) is:

$$-\frac{dQ}{dt} = k \exp[-\frac{E}{RT}] \tag{4}$$

Where k is a constant, E is another constant (the so-called activation energy for the process) and R is the gas constant.

The formulation forms the basis of most accelerated storage tests and has been used to compare the severity of different water removal processes for foods. It has been proposed that effects of moisture and temperature on rates of changes occurring in processing and storage are related to the physical state of food and specifically to the temperature above the glass transition temperature (T_g) (Blanshard and Lillford, 1993).

Glass transition occurs over a range of temperatures and not at a single temperature as a first order transition like melting. The main consequence of glass transition is the increase of molecular mobility and free volume. Heating above glass transition temperature (T_g) leads to physical and physico-chemical deteriorative changes, which makes glass transition so relevant in food processing operations (like freezing, drying and storage) and affects on quality attributes such as texture, stability, flavor release and biological spoilage. The consequence in food products is that a small change in temperature in the vicinity of T_g which will result in pronounced changes in the sensory properties of texture, drastically affects diffusion-controlled properties and rates of microbial and biochemical metabolisms (Roos, 1995b).

Crispness is essential to quality of various cereal and snack foods. Crispness of low-moisture foods is affected by water content, and it may be lost as a result of plasticization of the physical structure by temperature and water (Katz and Labuza, 1981; Sauvageot and Blond, 1991). A critical water activity at which crispness is lost has been found to be specific for each product, but a change occurs often over 0.35 and 0.50 a_w (Katz and Labuza, 1981; Hsieh *et al*., 1990). Loss of crispness is a result of glass transition that may occur during storage when the critical water content or a_w is exceeded, depressing the T_g of the material to be below ambient temperature.

Roos *et al*. (1996) reported that thermal and water plasticization during processing and storage may cause depression the T_g to be below ambient temperature. State diagrams that T_g dependence on water content with water sorption data may be used to relate various temperature, moisture content, and time-dependent changes that affect the shelf life of low-moisture and frozen foods.

Roos (1987) established a linear relationship between a_w and T_g. The linearity often applies over the a_w range of 0.1 to 0.8, but the relationship over the whole a_w range is sigmoid (Roos and Karel, 1991a; Roos, 1993a). The relationship between T_g and a_w at constant temperature provides a simple method for prediction of effects of relative humility (RH) during storage on T_g. Such prediction is useful in evaluating stability of various low moisture foods, such as food powders, low moisture cereal, and snack foods. Roos (1993a) suggested combining use of sorption models and the Gordon-Taylor equation for description of water plasticization. The models can be fitted to experimental data and used to show the T_g and water sorption in a single plot. The information in Figure 9 is useful in locating critical values for a_w and water content, defined as those decreasing the T_g to storage temperature (Roos, 1993a; Jouppila and Roos, 1994; Roos, 1995b).

Water and soluble solids such as sugars are the main fruit components. During fruit processing or storage, phase transitions such as liquid-gas or liquid-solid changes can occur in the water of the aqueous phase. In the process such as freezing, concentration, air-drying, freeze-drying, spray-drying, baking, extrusion, etc., with a time short enough for the removal of water or cooling, the formation of an amorphous state which is a non-equilbrium state is usual (Roos, 1995b). When the glass transition temperature (T_g) is reached by increasing temperature, amorphous materials may change from a solid glassy state to a liquid like rubbery one with increasing the molecular mobility. The importance of the T_g of amorphous food materials for processing and storage stability has been recognized and emphasized by Levine and Slade (Slade and Levien, 1991). Above the glass transition temperature, various time-dependent structural transformations may occur in amorphous foods. Structural collapse of dehydrated structures, similar to stickiness and caking of food powders are

related to drastic decrease in the viscosity above the T_g (Levine and Slade, 1988; Roos and Karel, 1991 a; Slade and Levine 1991).

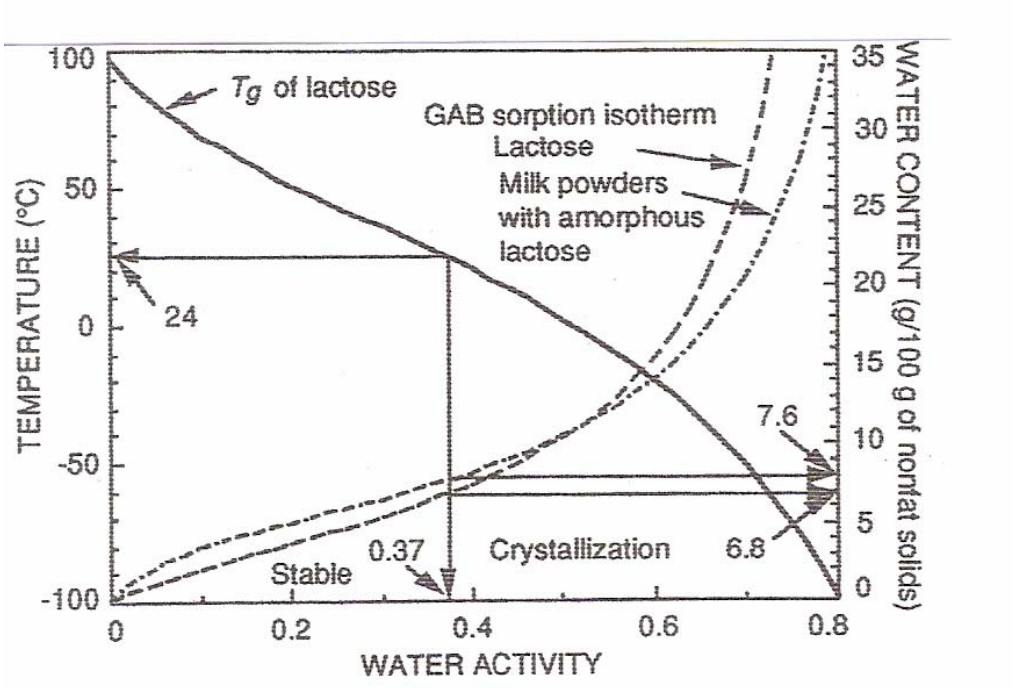

Figure 9 Glass transition temperature, T_g as a function of water activity and sorption isotherm at 24° C for nonfat milk solids. The critical a_w and the corresponding water content depress the T_g to storage temperature.

Source: Jouppilia and Roos (1994)

Martinez *et al*. (2004) and Roos *et al*. (1998) have found that the molecular mobility increase above the T_g may allow for the crystallization of amorphous compounds, especially in food products that contain low molecular weight sugars such as fruits. On the other hand, crispy foods such as breakfast cereals, extruded snacks, and other crispy cereal foods are often amorphous and lose the crispy texture due to thermal or water plasticization.

Roos and Karel (1991b) used dehydrated sugar solutions to model the thermal behavior of amorphous foods. The effects of temperature, moisture content and time on physical state of such foods were studied. They found that the glass transition temperature (T_g), crystallization temperature (T_{cr}) and melting temperature (T_m) decreased with increasing moisture content. The T_g of a sucrose/ fructose model had a

slightly lower value than the empirical "sticky point" at all moisture contents studied. Crystallization above T_g was time-dependent, and relaxation time of this process followed the Williams-Landau-Ferry (WLF) equation .

There is literature concerning the glass transition of foodstuffs such as fruits, vegetables, and meats, as a function of water content. Since most products undergo a significant change in humidity during processing. Several mathematical expressions linking mechanical properties of polymers, composition, viscosity, and molecular weight are available. Many of these expressions have been tested with satisfaction for some solutions of carbohydrates (Roos and Karel 1991a, 1991b, 1995b; Roos and Himberg 1994). As reported by Roos (1987, 1995a) the effect of water on T_g can expressed in terms of water activity. This relationship has been already studies for some pure carbohydrates (Roos 1995a) and other food products (Roos 1987; Paakkonen and Roos 1990). Some authors used a linear regression (Eq. 5) to predict the T_g as function of a_w at 25 °C (Roos 1987; Paakkonen and Roos 1990; Tsimidou and Biliaderis 1997).

$$T_g = T_{gs} + (T_{gw} - T_{gs})a_w \quad (5)$$

Where T_{gs} and T_{gw} are glass transition temperature of dry solids and water, respectively.

The relationship between T_g and a_w can be considered linear in range from 0.1-0.8 of water activity. It was pointed out that a true relationship is sigmoid for an entire range of water activity (Roos and Karel, 1991a).

The Gordon-Taylor equation, 1952 (Eq.6) has proven to be particularly useful in fitting experimental data on T_g and composition of amorphous sugars (Roos and Karel, 1991a, c; Roos, 1993 a, b), maltodextrins (Roos and Karel,1991 b, c) and foods (Roos, 1993a; Joppila and Roos, 1994). The equation may be solved the value for constant value, k, with experimental T_g data, various weight fractions, X_s and water X_w. The glass transition temperature of anhydrous solids, T_{gs}, may be obtained

experimentally, and T_{gw} of -135 °C is often used for amorphous water (Slade and Levine, 1991; Roos and Karel, 1991 a, b, c).

$$T_g = \frac{T_{g_s} X_s + k T_{g_w} X_w}{X_s + k X_w} \quad (6)$$

Where T_g , T_{gs}, and T_{gw} are glass transition temperatures of the sample, solid matrix and water, respectively. X_s and X_w are the corresponding percentages of solid and water contents, and k is an empirical parameter.

9. Glass Transition Temperature and Molecular weight

The glass transition temperature is mainly a function of water content, molecular weight (MW) and nature of dry matter compounds in a given substance (Genin and Renn 1995; Roos 1995a). It was reported that T_g of polymers increased noticeably with an increase in molecular weight up to a particular value, after which there is no further change with respect to MW (Roos , 1995a).

Chemical composition of material impacts both T_g and mechanical properties in the glassy state (Levine and Slade, 1986). According to Ferry, (1980), T_g increased as the average molecular weight increased in a series of homologous linear polymers. Roos and Karel, (1991c) showed that T_g increased as the molecular weight increased in a series of maltodextrin (DE 4 to 20). Other composition factors also affected T_g.

Jagtiani *et al*., 1988 reported that drying of sugar-rich mango pulp into powder is difficult, mainly due to the low molecular weight sugars, such as fructose (0.0265 kg per kg of pulp) glucose (0.0068 kg per kg of pulp) sucrose (0.095 kg per kg of pulp) and acids (0.00346 kg per kg of pulp as citric acid) present in the pulp. These materials have low glass transition (sucrose: 62°C fructose: -5°C, glucose: 32°C temperatures) (Jaya and Das, 2004). Due to their low molecular weights (sucrose: 342, glucose: 180, fructose: 180) the molecular mobility of materials is high when the temperature is just above the glass transition temperature (T_g). They are very hygroscopic in their amorphous state and loose free flowing nature at high moisture

content. While drying at temperatures normally prevailing in spray dryers, they tend to stick to the walls of the dryer and finally give paste like structure instead of powder.

The dependence of the glass transition temperature on the average molecular mass of the system has previously been mentioned. The addition of polymers could therefore increase the T_g of product and hence its stability at a given temperature (T) above T_g. Thus, an optimization of storage stability becomes an exercise of determining the appropriate T_g and then, if possible, maintaining the product during storage at a lower temperature and obviously hermetically sealed to avoid water interchange with the atmosphere (Roos, 1995a). The most common approach to dry such products is to add high molecular weight additives (such as maltodextrin), to raise T_g (Bhandari and Howes, 1999).

10. Maltodextrin

Maltodextrin is obtained by acid and/or enzymatic hydrolysis of starch, but to a lower extent than that required to produce starch syrups. Among the wide choice of commercially available maltodextrins, choosing the appropriate one for these applications is a matter of a compromise between its properties in solution (before process) and its properties at the glassy state (after process). Maltodextrins are usually supplied with dextrose equivalent value (DE) as the only information from which all properties seem to be empirically guessed. The DE of maltodextrins has, however, been shown to be inadequate to predict product performances in various applications (Avaltroni *et al*., 2004).

Roos (1993b) evaluated the stability of maltodextrin, horseradish root and strawberry samples which created a homologous family of various molecular weight. The critical water activity corresponding to the critical water content was then determined using the sorption isotherms at 25°C. The result indicated that molecular weight of material required a rise in critical water activity from 0.09 to 0.70 in order to depress the T_g to ambient temperature. Schaller-Povolny *et al.,* 2000 compared water activity and glass transition data of four different molecular weights of inulin.

Similarly, their study indicated that increasing molecular weight increased the critical water activity from 0.44 to 0.60 required at a given T_g.

Bhandari *et al*. (1993) produced blackcurrent, raspberry and apricot juice powders by spray drying. A mixture of the juice and maltodextrin having dextrose equivalent (DE) 36 were used and mixed at 60° C. They fixed the proportion of juice solid and maltodextrin in the ratios 65:35; 55:45 and 60:40 respectively.

Jaya and Das (2004) studied on vacuum drying of mango pulp. The mango pulp was added with various levels of maltodextrin (MD) ranging between 0.25 and 0.65 kg per kg of mango solid. Glycerol monostearate (GMS) and tricalcium phosphate (TCP) were added at the levels varying between 0.01 and 0.02 kg per kg of mango solid. MD was used to eliminate the stickiness of the mango powder and to get less hygroscopic powder. GMS was used as foam stabilizer and TCP as anticaking agents, respectively. Hygroscopic, degree of caking, dispersibility, flowability, sticky point temperature of the dry powder at 5% (db) moisture content and overall color difference between the reconstituted powder and the pulp, were examined. Based on these properties of mango powder, an optimum feed mix composition of 0.43-0.57 kg MD per kg of mango solids was obtained. The optimum requirement for the TCP and GMS were found to be 0.015 kg per kg of mango solid (Jaya and H. Das, 2004). In recent years, stickiness and agglomeration problems in powder food products have been related to their low T_g value.

Silva *et al* (2005) determined the state diagram for freeze-dried natural camu-camu pulp and for pulp with 30% maltodextrin DE 20 using differential scanning calorimetry (DSC). Freeze-dried samples were equilibrated at 25°C over saturated salt solutions in order to achieve water activities between 0.11 and 0.90. Higher water activities were obtained by direct water addition on freeze-dried product. Gordon-Taylor model was able to predict the plasticizing effect of water in the low and intermediate moisture content range. In the high moisture domain (a_w>0.90), T_g was practically constant, representing the glass transition temperature of maximally concentrated phase (T'_g), which were –58.8°C and –40.1°C for natural pulp and pulp with maltodextrin, respectively.