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Characterization of Food Polymers Using State Diagrams

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ABSTRACT

Food polymers often exist in an amorphous nonequilibrium state, which is formed in processes in which temperature is decreased below melting point or water is removed by evaporation or by ice formation. Amorphous materials have a glass transition temperature (T_g*) below which they are in a glassy state. Above* T_g*, they exist as liquid-like 'rubbers'. Most food polymers are thermoplastic and subject to water plasticization. Above* T_g*, various properties of the materials are changed. The most important changes are an exponential increase of molecular mobility and decrease of viscosity, which govern time-dependent structural transformations such as stickiness and collapse in food processing and storage. Above* T_g*, molecular mobility improves diffusion, which affects crystallization, reaction rates, and food deterioration. At low temperatures the physical state is important to frozen food stability.* T_g *values can be used to establish state diagrams, which describe the effect of composition on stability and show temperature and moisture effects on viscosity, structure, and crystallization. State diagrams may also show the formation of the amorphous state and describe various temperature-, moisture-, and time-dependent phenomena.*

INTRODUCTION

Food characteristics are related to their composition and to the physical state of the component compounds (Kauzmann, 1948; Lazar *et al.*, 1956; Makower & Dye, 1956; White & Cakebread, 1966; Rasmussen & Luyet, 1969; Bellows & King, 1973; Tsourouflis *et al.*, 1976; To & Flink, 1978*a*, *b*, *c*; Dowton *et al.*, 1982; Roos & Karel, 1990; Slade & Levine, 1991). Carbohydrates and proteins can be described as food polymers in which water acts as a plasticizer (Slade & Levine, 1991). These materials may form supersaturated amorphous or partially amorphous nonequilibrium structures (Slade & Levine, 1991) in processes in which temperature is rapidly decreased below the melting point of the component compounds or water is rapidly removed by evaporation or by ice formation (Kauzmann, 1948; White & Cakebread, 1966; Rasmussen & Luyet, 1969; Bellows & King, 1973; Roos & Karel, 1991*a*, *b*).

The physical properties of the amorphous materials can be related to their glass transition temperature (T_g) (Slade & Levine, 1991). T_g defines a second-order phase change temperature at which a solid 'glass' is transformed to a liquid-like 'rubber' (Kauzmann, 1948). Since most food polymers are thermoplastic and subject to water plasticization, their physical properties are controlled by temperature and water content (Slade & Levine, 1991). As the temperature is increased above T_g various changes such as increase of free volume, decrease of viscosity, increase of specific heat, and increase of thermal expansion are noticed (Kauzmann, 1948; White & Cakebread, 1966). The most important changes affecting food behavior are related to the exponential increase of molecular mobility, and decrease of viscosity (Roos & Karel, 1991*a*, *b*; Slade & Levine, 1991). These factors govern various time-dependent and often viscosity related structural transformations such as stickiness (Lazar *et al.*, 1956; Downton *et al.*, 1982), collapse (loss of structure, decreased volume) (Tsourouflis *et al.*, 1976; To & Flink, 1978*a*, *b*, *c*), and crystallization (Roos & Karel, 1991*a*, 1992) during food processing and storage (Levine & Slade, 1986; Roos & Karel, 1991*a*; Slade & Levine, 1991). The increasing molecular mobility improves diffusion resulting in time-dependent crystallization of amorphous compounds (Makower & Dye, 1956; To & Flink, 1978*c*; Roos & Karel, 1990, 1992). Increasing diffusion may also promote food deterioration (Levine & Slade, 1986, 1988; Simatos & Karel, 1988; Slade & Levine, 1991). At low temperatures crystallization of water during freezing and frozen storage is affected by the physical state of the material, which is important in cryopreservation, freeze-drying, and to frozen food stability (Levine & Slade, 1986, 1988; Roos & Karel, 1991*a*).

It has been presumed that amorphous foods are stable in their solid, glassy state below T_g as the molecules are 'frozen' in the high viscosity (10^{12} Pa s) solid glass (White & Cakebread, 1966; Levine & Slade, 1986; Slade & Levine, 1991). Both thermal and water plasticization during processing and storage decrease stability in the rubbery state by increasing temperature difference to T_g ($T-T_g$) (Slade & Levine, 1991; Roos & Karel, 1991*b*). A state diagram proposed by Franks *et al.* (1977) represents states in which a system can exist as a function of temperature, concentration, time, and pressure (Levine & Slade, 1986). Simplified state diagrams show the physical state of food materials as a function of concentration and temperature (Roos & Karel, 1991*b*). These state diagrams describe the effect of food composition on stability, and show the effect of temperature and moisture content on material characteristics. Stage diagrams may also be used to show the formation of the amorphous state in food processing, and to describe various temperature-, moisture-, and time-dependent phenomena typical of amorphous and frozen foods. The purpose of this review is to describe the use of experimental data on transition temperatures for establishing state diagrams, and the use of state diagrams to characterize food behavior during processing and storage.

GLASS TRANSITIONS OF FOOD COMPONENTS

Glass transition of anhydrous compounds

Glass transition temperatures of anhydrous food components can be related to dehydrated food stability and they are needed in establishing state diagrams. The T_g values of amorphous compounds and food materials are most often determined by differential scanning calorimetry (DSC). Recent studies, however, have reported the use of mechanical spectrometry (Cocero & Kokini, 1991; Roos & Karel 1991*d*), nuclear magnetic resonance (NMR) (Abblett *et al.*, 1986; Kalichevsky *et al.*, 1992, 1993), dynamic mechanical thermal analysis (DMTA) (Kalichevsky *et al.*, 1992, 1993) and thermal mechanical analysis (TMA) (LeMeste *et al.*, 1992), and dielectric thermal analysis (DETA) (Kalichevsky *et al.*, 1992) for the determination of T_g in food components. DSC detects the typical change of specific heat (Δc_p) at T_g (Fig. 1). It should be noted that the various analytical methods give slightly different T_g values (Kalichevsky *et al.*, 1992). The T_g value of a single sample also depends on the sample thermal history and even the same analytical method may give varying T_g values. Usually T_g values reported are either onset or midpoint temperatures of the T_g temperature range.

T_g values for various anhydrous mono-, di-, and oligosaccharides have been demonstrated experimentally (e.g. Orford *et al.*, 1989; Slade & Levine, 1991; Roos, 1993*a*). T_g values for common carbohydrates are given in Table 1 with respective Δc_p values, melting points (T_f) and the ratio T_f/T_g. The T_f/T_g values are useful in the characterization of the physical properties of single amorphous

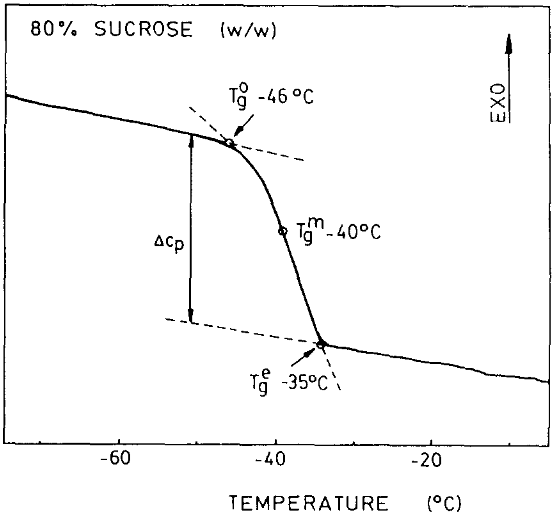

Fig. 1. Glass transition temperature range of 80% sucrose solution as determined using differential scanning calorimetry (Roos & Karel, 1991*a*). The onset, midpoint, and endset temperatures of the glass transition region are labeled as T_g^o, T_g^m, and T_g^e, respectively. Δc_p indicates the change of specific heat at the glass transition temperature region.

TABLE 1

Glass Transition Temperatures (T_g), Change of Specific Heat at T_g (Δc_p), Melting Temperature (T_f), and the Ratio of T_f/T_g for Anhydrous Pentoses, Hexoses, Disaccharides and Alditols (Roos, 1993*a*)

Compound	T_g *(°C)*[a]	Δc_p *(J/g °C)*	T_f *(°C)*[a]	T_f/T_g[a]
Pentoses				
Arabinose	−2	0·66	150 (160)	1·56 (1·60)
Ribose	−20	0·67	70 (86)	1·36 (1·42)
Xylose	6	0·66	143 (157)	1·49 (1·54)
Hexoses				
Fructose	5	0·75	108 (127)	1·37 (1·44)
Fucose	26	—	133 (145)	1·36 (1·40)
Galactose	30	0·50	163 (170)	1·44 (1·46)
Glucose	31	0·63	143 (158)	1·37 (1·42)
Mannose	25	0·72	120 (134)	1·32 (1·37)
Rhamnose	−7	0·69	— —	— —
Sorbose	19	0·69	153 (163)	1·46 (1·49)
Disaccharides				
Lactose	101	—	— (214)	— (1·30)
Maltose	87	0·61	— —	— —
Melibiose	85	0·58	— —	— —
Sucrose	62	0·60	173 (190)	1·33 (1·38)
Trehalose	100	0·55	— —	— —
Alditols				
Maltitol	39	0·56	139 (149)	1·32 (1·35)
Sorbitol	−9	0·96	85 (99)	1·36 (1·41)
Xylitol	−29	1·02	89 (95)	1·48 (1·51)

[a] Onset temperatures for the transitions; the values in parenthesis refer to the peak temperature values of the melting endotherms.

components (Slade & Levine, 1991). Roos (1993*a*) reported that sugars with high T_f/T_g values tend to crystallize rapidly. The most important single factor affecting T_g values of anhydrous food homopolymers such as glucose polymers, e.g. maltodextrins, is molecular weight (Levine & Slade, 1986; Roos & Karel, 1991*e*). T_g values of amorphous glucose polymers have been shown to increase with increasing molecular weight (Orford *et al.*, 1989; Roos & Karel, 1991*c*, *e*), which is known to be typical of synthetic polymers. Fox and Flory (1950) observed that the T_g of homopolymers was related to their molecular weight (M). The T_g was reported to decrease linearly with increasing value of $1/M$ according to eqn (1). Similarly, the T_g of maltodextrins has been shown to decrease with increasing $1/M$ (Roos & Karel, 1991*c*, *e*). This allows prediction of the T_g value of high molecular weight compounds:

$$T_g = T_g(\infty) - K_g M^{-1} \qquad (1)$$

where M is molecular weight; K_g is constant; and $T_g(\infty)$ is the limiting T_g at high molecular weight.

The T_g values of anhydrous high molecular weight food polymers such as polysaccharides (Orford *et al.*, 1989; Roos & Karel, 1991*c*) and proteins (Kakivaya & Hoeve, 1975; Cocero & Kokini, 1991; Kalichevsky *et al.*, 1993) are usually high, and the materials tend to decompose at temperatures below T_g (Roos & Karel, 1991*c*). Thus, T_g values of many anhydrous food polymers cannot be experimentally determined. Based on the T_g values of maltodextrins, Roos and Karel (1991*e*) predicted a T_g value for anhydrous starch of 243°C, which was higher than 151°C predicted by van den Berg (1981), but close to 227°C reported by Orford *et al.* (1989). The T_g values of starch, gluten (Hoseney *et al.*, 1986), glutenin (Cocero & Kokini, 1991), and amylopectin–protein mixtures (Kalichevsky & Blanshard, 1992) are important in the characterization of extruded and cereal foods (Slade & Levine, 1991).

Water plasticization

Water plasticizes amorphous food materials and the water content defines location of the T_g. Water decreases drastically the T_g of food polymers, and even traces of water may significantly decrease T_g values (Slade & Levine, 1991). In state diagrams the decrease of T_g with increasing water content is shown by a continuous T_g curve. Water plasticization is typical of low molecular weight carbohydrates (Parks & Thomas, 1934; Levine & Slade, 1988; Roos, 1993*a*), oligosaccharides (Levine & Slade, 1986; Orford *et al.*, 1989; Orford *et al.*, 1990), polysaccharides (Roos & Karel, 1991*c*; Slade & Levine, 1991), proteins (Cocero & Kokini, 1991; Slade & Levine, 1992), and also water plasticizable polymers (Oksanen & Zografi, 1990; Slade & Levine, 1991).

The effect of water on T_g of various food materials has been predicted with eqn (2) (Fig. 2) (Roos & Karel, 1991*a*, *b*; Roos, 1993*a*, *b*), which originally was

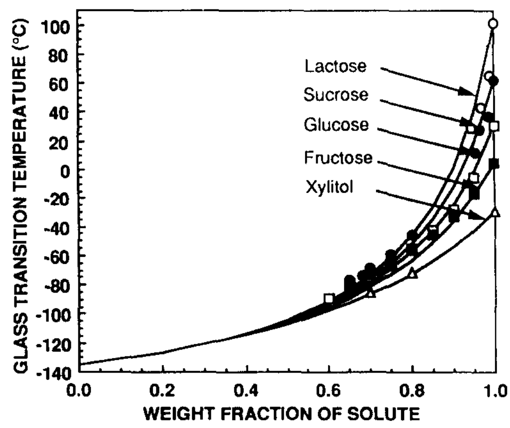

Fig. 2. Glass transition temperatures (T_g) of common mono- and disaccharides as a function of water content according to Roos (1993*a*). Experimental T_g values are indicated with symbols. The T_g curves are calculated with eqn (2) using T_g = 135°C for water (Johari *et al.*, 1987).

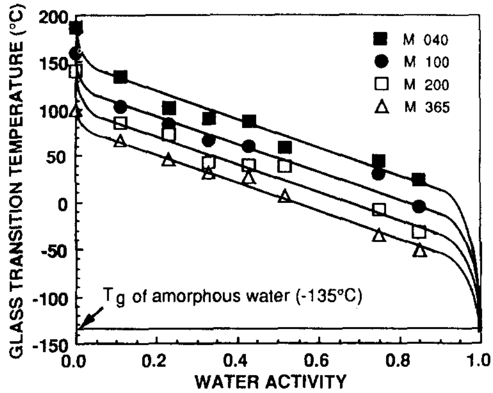

Fig. 3. Glass transition temperatures (T_g) of maltodextrins (Maltrin® M040, M100, M200, and M365 with respective dextrose equivalents of 5, 10, 20, and 36) as a function of water activity (data from Roos and Karel, 1991*c*).

reported to describe composition-dependence of T_g of binary blends of miscible polymers (Gordon & Taylor, 1952). Equation (2) is useful in the prediction of the T_g curve shown in state diagrams. In practical applications the effect of water on T_g can also be expressed in terms of water activity (a_w). The effect of a_w on T_g can be predicted by plotting T_g against a_w and using linear regression as shown in Fig. 3 (Roos, 1987). The true relationship, however, is sigmoid (Roos & Karel, 1991*c*). As shown by Roos (1993*b*), a combined use of eqn (2) and sorption isotherm models allows evaluation of food stability (stability based on the assumption that stability is lost above T_g) at various storage conditions (Fig. 4).

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{2}$$

where w_1 and w_2 are weight fractions of component compounds; T_{g1} and T_{g2} are glass transition temperatures of the component compounds; and k is constant.

Couchman (1978) and Couchman and Karasz (1978) reported that the k value in eqn (2) is equal to $k = \Delta c_{p2}/\Delta c_{p1}$ (Δc_p values of the component compounds). The modified equation has also been used in modeling of the T_g data of food components (Orford *et al.*, 1989; Kalichevsky & Blanshard, 1992, 1993; Kalichevsky *et al.*, 1993). However, exact Δc_p values are difficult to obtain experimentally and various values have been reported for amorphous water (Sugisaki *et al.*, 1968; Angell & Tucker, 1980; Johari *et al.*, 1987). Roos and Karel (1991*a*, *b*, *d*, *e*) have used experimentally determined T_g values at various water contents to calculate k values for sugars. Roos (1993*a*) reported that the k value of various sugars could be related to their anhydrous T_g value. A linear relationship between k and T_g was then used to derive k values for various carbohydrates (Fig. 5). Typical T_g values for food components with calculated T_g curves are shown in Fig. 2.

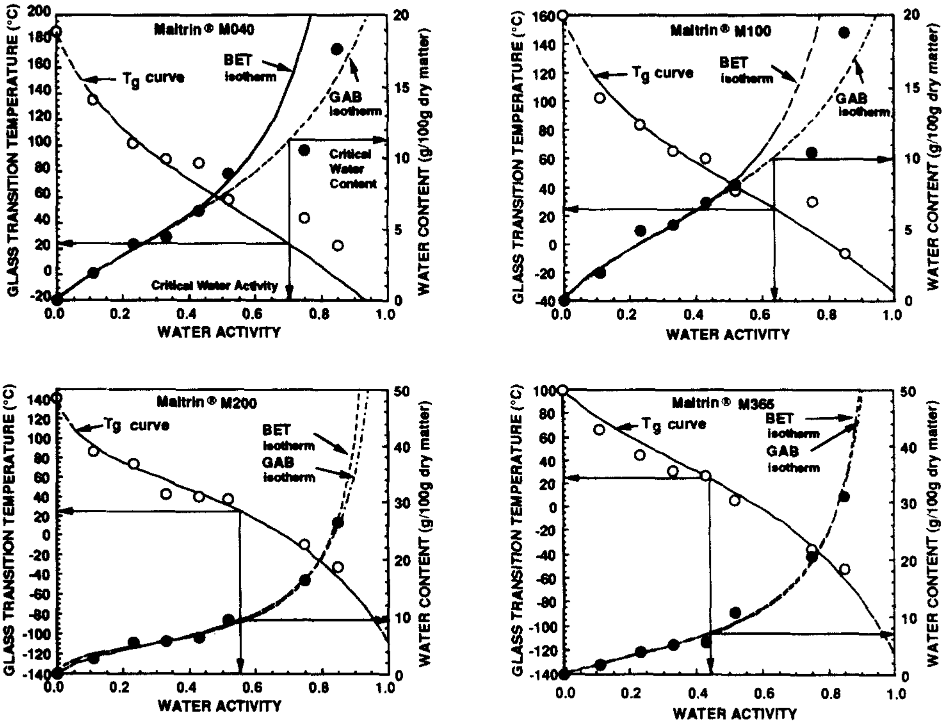

Fig. 4. Water adsorption isotherms and glass transition temperatures (T_g) as a function of water activity for maltodextrins (Maltrin® M040, M100, M200, and M365 with respective dextrose equivalents of 5, 10, 20, and 36). The adsorption isotherms were calculated with the BET and GAB water adsorption models. The water contents obtained with the GAB model were used to calculate the T_g curve with eqn (2). The arrows indicate critical water activity values and water contents for stability at 25°C. After Roos (1993*b*).

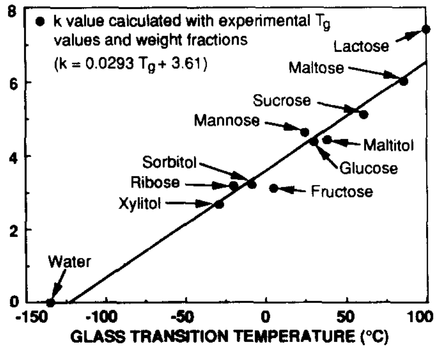

Fig. 5. *k* values (eqn (2)) of sugars as a function of the anhydrous glass transition temperature (T_g). The regression equation obtained allows prediction of the constant *k* in eqn (2) based on the anhydrous T_g value. After Roos (1993*a*).

Ice formation in food materials

State diagrams can be used to characterize ice formation in food materials and changes, which may occur in frozen foods at various storage conditions. Ice formation in food materials results in an increased solute concentration as water is removed from the solution as ice crystals. Solutions with low solute concentrations form ice below their equilibrium freezing point. As the equilibrium freezing point decreases with increasing solute concentration, the amount of ice formed increases with decreasing temperature (Rasmussen & Luyet, 1969; Franks *et al.*, 1977; Roos & Karel, 1991*a*, *d*). Both the decreasing temperature and increasing solute concentration increase the apparent T_g as well as the viscosity of the unfrozen solution (Bellows & King, 1973; Roos & Karel, 1991*a*). This presumably decreases diffusion and the rate of ice formation (Levine & Slade, 1988; Roos & Karel, 1991*d*). It has been well documented that freeze-concentrated solutes in carbohydrate solutions are amorphous matrices, which have a T_g at a temperature determined by the solute concentration in the unfrozen matrix (Rasmussen & Luyet, 1969; Simatos & Turc, 1975; Levine & Slade, 1986; Blond, 1989; Roos & Karel, 1991*a*, *d*). Roos and Karel (1991*a*, *b*, *d*, *e*) reported that maximally freeze-concentrated solutions, as defined by Levine and Slade (Levine & Slade, 1986; Slade & Levine, 1991), are formed in a relatively narrow temperature range between the T_g of the maximally freeze-concentrated solute (T'_g) and the lowest equilibrium melting point of ice within the unfrozen matrix (T'_m).

Both T'_g and T'_m have temperature values, which are independent of the initial solute concentration (Levine & Slade, 1986, 1988; Roos & Karel, 1991*a*). Solutions with the maximum amount of ice show during heating from temperatures below T'_g both T'_g and ice melting above T'_m (Levine & Slade, 1986, 1988; Roos & Karel, 1991*a*). Ice formation in carbohydrate solutions is affected by various factors including the initial solute concentration, temperature, and time (Slade & Levine, 1991). Since T_g controls viscosity of the unfrozen material, rapid cooling of solutions may result in partial freeze-concentration and ice formation during rewarming (devitrification) above T_g of the partially freeze-concentrated solution (Simatos & Turc, 1975; Simatos *et al.*, 1975; Levine & Slade, 1986, 1988; MacFarlane, 1986; Roos & Karel, 1991*a*, *d*). Devitrification is an exothermal transition, which results from the release of heat during ice formation (Rasmussen & Luyet, 1969; Simatos & Turc, 1975; Simatos *et al.*, 1975; Roos & Karel, 1991*d*). This phenomenon is typical of rapidly cooled carbohydrate solutions and its extent has been widely studied with DSC at various rewarming rates. The devitrification temperature (T_d) increases with increasing rewarming rate, indicating that ice formation above T_g is time-dependent (Roos & Karel, 1991*d*). Since devitrification leads to additional ice formation, the rate of ice formation decreases during devitrification due to a concurrent increase of the T_g of the remaining unfrozen solution (Roos & Karel, 1991*a*, *d*), which increases viscosity and delays diffusion (Levine & Slade, 1988; Roos & Karel, 1991*a*, *d*). Thus, the rate of ice formation may be assumed to depend on viscosity, and isothermal annealing above T'_g but below T'_m is necessary for maximum ice formation. Since the viscosity is governed by the temperature difference to T_g ($T - T_g$) (Williams *et al.*, 1955), the rate of ice formation is a function of $T - T_g$ (Levine & Slade, 1986; Roos & Karel, 1991*a*, *d*).

The solute concentration of the maximally freeze-concentrated unfrozen matrix (C'_g) can be calculated with the T'_g value from eqn (2) or derived from a state diagram (Levine & Slade, 1986; Roos & Karel, 1991*b*; Slade & Levine, 1991). Slade and Levine (1991) reported C'_g values for various materials, but most studies have reported that the solute concentrations in maximally freeze-concentrated carbohydrate matrices are higher and generally about 80% (Hatley *et al.*, 1991; Izzard *et al.*, 1991; Roos & Karel, 1991*a*, *d*; Roos, 1993*a*). Because of the kinetic constraints of ice formation, solutions with high initial solute concentrations (60–80%, w/w) may require several days or even weeks of annealing at $T'_g < T < T'_m$ until the maximally freeze-concentrated state is achieved (Slade & Levine, 1991; Roos & Karel, 1991*a*, *d*). At temperatures above T'_m, solute crystallization from a supersaturated freeze-concentrated solution may occur as the amount of unfrozen water increases in accord with the equilibrium melting curve. Concurrently, viscosity decreases, since the solute is diluted, which depresses T_g and increases $T - T_g$.

Both T'_g and T'_m depend on the molecular weight of the solute (Levine & Slade, 1986; Roos & Karel, 1991*e*; Slade & Levine, 1991); T'_m, T'_g, and C'_g values for typical food carbohydrates are given in Table 2. Roos and Karel (1991*e*) reported that above a certain molecular weight T'_g and T'_m have the same temperature value slightly below 0°C. This may cause fairly high amounts of unfrozen water in solutions with high molecular weight solutes such as starch and other polysaccharides. The coincidental glass transition and ice melting account for the fact that the maximally freeze-concentrated state cannot be formed. A typical state diagram shows the T_g curve as a function of concentration with T'_g and T'_m values. State diagrams for various carbohydrates (Slade & Levine, 1991; Roos, 1993*a*), as shown for glucose in Fig. 6, can be established with the data given in Tables 1 and 2.

PHYSICAL PROPERTIES RELATED TO THE AMORPHOUS STATE

Viscosity

The viscosity of a glass is higher than 10^{12} Pa s (10^{13} P) (White & Cakebread, 1966). It decreases dramatically above T_g. An empirical relationship between relaxation times of mechanical and dielectric properties and temperature difference to T_g in the rubbery state of amorphous materials (eqn (3)), including glucose, was reported by Williams *et al.* (1955). The temperature-dependence of viscosity and time to crystallization of sugars above T_g have been predicted with the Williams–Landel–Ferry (WLF) relationship by various authors (Soesanto & Williams, 1981; Ollett & Parker, 1990; Roos & Karel, 1990, 1991*a*, 1992; Slade & Levine, 1991). The most often used constants C_1 and C_2 in eqn (3) are $-17{\cdot}44$ and $51{\cdot}6$, respectively. These constants were originally reported by Williams *et al.* (1955) who, however, preferred the use of eqn (3) with another reference temperature than T_g. The reference temperature (T_s) was located at $T_s = T_g + 50$°C and the constants C_1 and C_2 were $-8{\cdot}86$ and $101{\cdot}6$, respectively. Methods to derive C_1 and C_2 values from experimental data were discussed by Nelson and Labuza (1992) and Peleg (1992).

TABLE 2

Glass Transition Temperatures of Maximally Freeze-Concentrated Solutes (T'_g), Onset Temperature for Ice Melting in the Maximally Freeze-Concentrated Solutions (T'_g), and the Amount of Unfrozen Water in the Maximally Freeze-Concentrated Matrix (C'_g) for Pentoses, Hexoses, Disaccharides, and Alditols (Roos, 1993*a*) (the estimated C'_g values were obtained with eqn (2) and the estimated *k* values)

Compound	T'_g *(°C)*				T'_m *(°C)*	*k*	C'_g *(%)*	
	Onset	*Midpoint*	*Endset*	*Lit.*[a]			*Estimate*	*Lit.*[a]
Pentoses								
Arabinose	−66	−61	−51	−47·5	−53	3·55	79·3	44·8
Ribose	−67	−62	−57	−47	−53	3·02	81·4	67·1
Xylose	−65	−60	−54	−48	−53	3·78	78·9	69·0
Hexoses								
Fructose	−57	−53	−50	−42	−46	3·76	82·5	51·0
Fucose	−62	−57	−51	−43	−48	4·37	78·4	47·4
Galactose	−56	−51	−46	−41·5	−45	4·49	80·5	56·5
Glucose	−57	−53	−50	−43	−46	4·52	80·0	70·9
Mannose	−58	−53	−47	−41	−45	4·34	80·1	74·1
Rhamnose	−60	−55	−49	−43	−47	3·40	82·8	52·6
Sorbose	−57	−52	−46	−41	−44	4·17	81·0	69·0
Disaccharides								
Lactose	−41	−36	−30	−28	−30	6·56	81·3	59·2
Maltose	−42	−37	−32	−29·5	−32	6·15	81·6	80·0
Melibiose	−42	−37	−32	−30·5	−32	6·10	81·7	—
Sucrose	−46	−41	−36	−32	−34	5·42	81·7	64·1
Trehalose	−40	−35	−30	−29·5	−30	6·54	81·6	83·3
Alditols								
Maltitol	−47	−42	−37	−34·5	−37	4·75	82·9	62·9
Sorbitol	−63	−57	−51	−43·5	−49	3·35	81·7	81·3
Xylitol	−72	−67	−61	−46·5	−57	2·76	80·2	57·1

[a] Values reported by Slade and Levine (1991).

$$\log \frac{\eta}{\eta_g} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{3}$$

where η is viscosity at temperature T; and η_g is viscosity at T_g. C_1 and C_2 are constants.

Other equations reported applicable for the description of the temperature-dependence of viscosity in supercooled liquids are the Vogel–Tamman–Fulcher (VTF) equation (eqn (4)) and the power-law equation (eqn (5)) (Ollett & Parker, 1990):

$$\eta = A \exp(B/T - T_0) \tag{4}$$

where η is viscosity; A is constant; B is constant; T is temperature; and T_0 is a reference temperature.

$$\eta = A'(T - T_g)^r \tag{5}$$

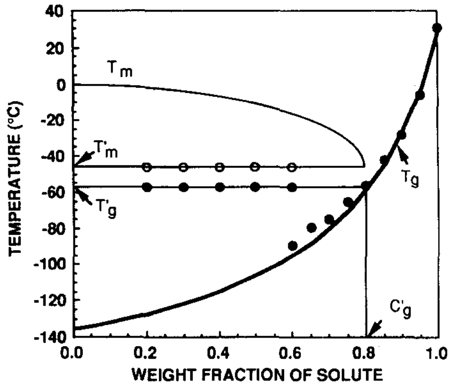

Fig. 6. State diagram of glucose. The T_g line was obtained with eqn (2). Additional lines are used to show equilibrium conditions for ice melting (T_m), onset temperature of ice melting in solutions with maximum amount of ice formed (T'_m), glass transition temperature of the maximally freeze-concentrated solute (T'_g), and the respective solute concentration (C'_g). Data from Roos and Karel (1991*d*).

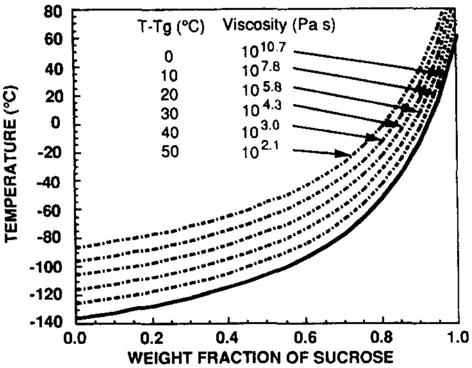

Fig. 7. State diagram of sucrose showing isoviscosity states above glass transition temperature (T_g). Data from Roos and Karel (1991*a*).

where η is viscosity; A' is constant; T is temperature; T_g is glass transition temperature; and r is constant.

The temperature-dependence of viscosity above T_g can be included in state diagrams, which show isoviscosity lines above T_g (Roos & Karel, 1991*b*; Slade & Levine, 1991). Bellows and King (1973) reported viscosity data for concentrated sucrose solutions. Those data were used by Roos and Karel (1991*a*) to predict isoviscosity states for amorphous sucrose at various $T - T_g$ values. Figure 7 shows predicted isoviscosity states of sucrose in a state diagram. Many polymers and most carbohydrates have T_f/T_g ratios between 1·3 and 1·5 (Table 1, based on the onset values of the transitions obtained using DSC) according to which the T_f is about 100°C above T_g (Slade & Levine, 1991; Roos, 1993*a*).

Below T_g and above T_f (approximately $T_g + 100°C$), Arrhenius type temperature-dependence of viscosity is assumed to apply for most food polymers (Slade & Levine, 1991). The most dramatic changes in the amorphous food polymers (e.g. stickiness, collapse, crystallization, and ice formation) occur at a fairly narrow temperature range above T_g (Roos & Karel, 1991*f*). The viscosity and T_g data can be applied, for example, to avoid collapse in freeze drying, to control stickiness in dehydration and agglomeration, to avoid or achieve crystallization in food powders and confectioneries, to control ice formation in frozen foods or in freeze-concentration, and in manufacturing foods with encapsulated compounds and in controlled release of such compounds (Bellows & King, 1973; Downton *et al.*, 1982; Flink, 1983; Wallack & King, 1988; Slade & Levine, 1991; Roos & Karel, 1991*a*, *b*, *c*, *d*, *e*, *f*, 1992; Shimada *et al.*, 1991; Roos & Karel, 1992).

Crystallization

Crystallization in the solid glassy state below T_g is kinetically inhibited (Levine & Slade, 1986). One of the earliest studies showing time-dependent crystallization of amorphous food related materials was that of Makower and Dye (1956), who found that the rate of crystallization of glucose and sucrose from the amorphous state was dependent on moisture content. Temperatures above T_g allow molecular mobility and the rearranging of molecules to the crystalline state (Levine & Slade, 1986). In amorphous foods, crystallization may occur concurrently with other changes in the physical structure at temperatures above T_g (Levine & Slade, 1986; Roos & Karel, 1990, 1991*f*). Both the rate of structural transformations and crystallization increase as the viscosity decreases with increasing $T - T_g$ (Levine & Slade, 1986; Roos & Karel, 1991*c*, *f*, 1992).

Usually the T_g values of stable food powders are well above ambient temperature (Slade & Levine, 1991). However, most food materials show substantial adsorption of water at increasing relative humidities, which facilitates crystallization as the T_g is depressed below ambient temperature (Slade & Levine, 1991). Crystallization releases adsorbed water, which in closed containers further plasticizes the remaining amorphous portion of the material (Kim *et al.*, 1981; Roos & Karel, 1992). As a result, $T - T_g$ increases, which causes an increasing rate of crystallization with increasing crystallinity (Fig. 8) (Roos & Karel, 1992). Materials which have moisture transfer with the environment, e.g. during determination of adsorption isotherms, show loss of water in proportion to crystallinity (Roos & Karel, 1992). Thus, the moisture content in the amorphous part remains fairly constant, and crystallization proceeds at a rate defined by a constant $T - T_g$ (Fig. 9) as reported by Roos and Karel (1992).

Crystallization causes the most drastic changes to the physical properties of food polymers (Makower & Dye, 1956; Roos & Karel, 1992). It may considerably affect food stability, and it may cause impaired rehydration properties of food powders (Kim *et al.*, 1981; Shimada *et al.*, 1991; Roos & Karel, 1992). It also affects textural properties, e.g. crystallization of starch in bakery products results in staling (Slade & Levine, 1991). Lactose crystallization in milk powders leads to increased free fat and flavor deterioration, and it may also promote nonenzymatic browning (Kim *et al.*, 1981; Saltmarch *et al.*, 1981). Amorphous sugars are often used to entrap flavor compounds (Tsourouflis *et al.*, 1976; To &

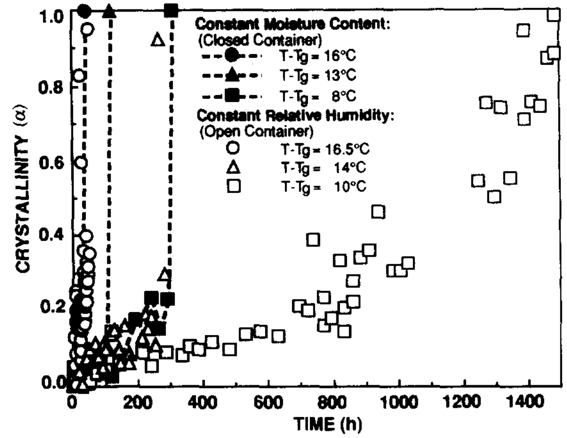

Fig. 8. Crystallization of amorphous lactose as a function of time at various temperatures above the glass transition temperature (T_g). After Roos and Karel (1992).

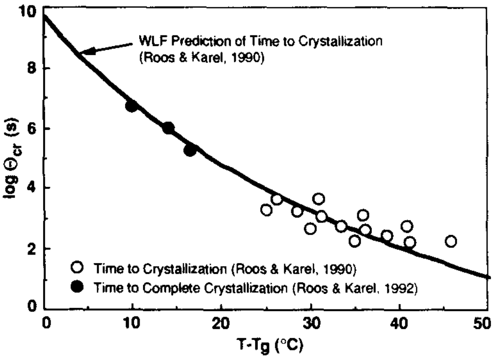

Fig. 9. WLF (eqn (3)) prediction of time to complete crystallization of amorphous lactose above glass transition temperature (T_g). After Roos and Karel (1992).

Flink, 1978*a*, *b*, *c*), which become protected from oxidation and release, probably because of slow diffusion in the glassy state (Shimada *et al.*, 1991). The crystalline materials are not able to entrap other compounds, which become completely released due to crystallization. Thus, volatiles are lost and lipids become exposed to oxygen. In food formulation high amounts of high molecular weight compounds are needed to increase T_g (Roos & Karel, 1991*c*), but crystallization can also be delayed by incorporation of high molecular weight substances (Iglesias & Chirife, 1978; Levine & Slade, 1986; Roos & Karel, 1991*f*) or other sugars (Herrington & Branfield, 1984). A state diagram showing critical values for a_w and water content can be used in selecting proper packaging materials and storage conditions for amorphous food materials (Roos, 1993*b*).

USE OF STATE DIAGRAMS

Dehydration and dehydrated foods

A rapid removal of water and transformation of the solutes to an amorphous state are typical of dehydration (Fig. 10) (Roos & Karel, 1990, 1991*b*). Low molecular weight carbohydrates have low T_g values, which is probably the main cause of the poor dehydration characteristics of such materials as fruit juices. Amorphous dehydrated food materials have large internal surface areas (e.g. spray- and freeze-dried foods), and they are usually hygroscopic (Roos & Karel, 1991*b*). Exposure of dehydrated foods and food powders to atmospheric humidity and temperature often results in structural changes, caking, and impaired flow properties (Peleg, 1983). Since T_g affects both dehydration properties (e.g. collapse in freeze-drying and stickiness in spray-drying) and storage stability of dehydrated materials, the information given in state diagrams may be used in equipment design, process control, and material storage.

Roos and Karel (1991*f*) showed that the 'sticky point', which has been frequently used in the characterization of food powders (Lazar *et al.*, 1956) is defined by T_g (Fig. 11) (Levine & Slade, 1986). The critical viscosity for stickiness of about 10^7 Pa s (Dowton *et al.*, 1982) correlates with the viscosity at the endpoint of the glass transition temperature range (Figs 7 and 11) (Roos & Karel, 1991*f*). Materials with high amounts of monosaccharides (e.g. fructose and glucose) exhibit low T_g values (Slade & Levine, 1991) and sticky points (e.g. fruit juices). T_g increases with increasing molecular weight and such materials as maltodextrins are often used to improve dehydration characteristics, since they decrease stickiness and improve product stability (Slade & Levine, 1986; Roos & Karel, 1991*b*, *e*). The effect of added compounds on the T_g of amorphous food solids can be estimated with eqn (2). Isoviscosity lines in state diagrams (Fig. 7) can be used to show critical viscosities for stickiness and time needed to

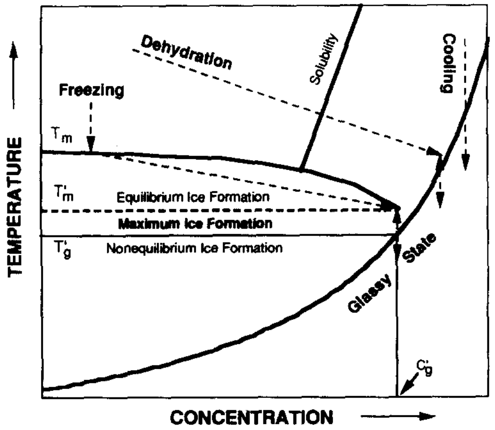

Fig. 10. Schematic state diagram showing typical processes resulting in the formation of amorphous structures in foods.

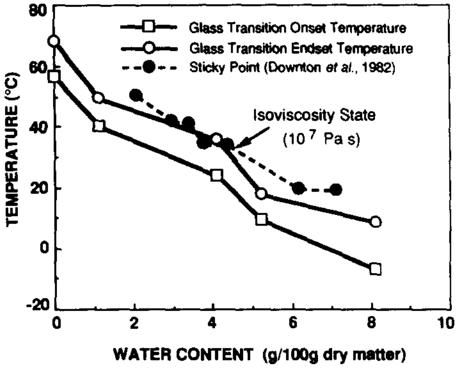

Fig. 11. Glass transition temperature (T_g) and sticky point of an amorphous mixture of sucrose and fructose (7:1) showing the relationship between T_g and stickiness. After Roos and Karel (1991*f*).

a given degree of collapse, which may be used as a quantitative prediction of stability. The extent of collapse, as determined by Tsourouflis *et al.* (1976) and To and Flink (1978*a*, *b*, *c*), depends on time and $T - T_g$ (Slade & Levine, 1986; Roos & Karel, 1991*c*). Structural changes above T_g result from material flow (reduced viscosity) and from the tendency of the liquid-like rubbery state to minimize its volume (Roos & Karel, 1991*b*). Information of stickiness and collapse temperatures is also valuable in the design of agglomeration processes, which use controlled stickiness to increase particle size of food powders (Roos & Karel, 1991*b*; Slade & Levine, 1991).

In dehydrated milk products, water content increases with increasing relative humidity until lactose crystallization occurs, resulting in loss of moisture (Bushill *et al.*, 1965; Linko *et al.*, 1981). Roos and Karel (1990) used both WLF prediction of time to crystallization and the moisture-dependence of T_g to show time-dependent crystallization of amorphous lactose during water adsorption (Figs 12 and 13). Crystallization of sugars occurs above T_g, but depending on the sugar, various isomeric forms and hydrates may be formed, this depending on moisture content and temperature. The rate of crystallization may also be affected by the physical state of the material (Roos & Karel, 1992). Stickiness and collapse of dehydrated food powders occur before crystallization of amorphous compounds (Roos & Karel, 1991*b*). Crystallization of sugars in freeze- and spray-dried porous powders may also be faster than in sugar melts (Roos & Karel, 1991*b*, 1992). However, various sugars may have different crystallization kinetics, which vary with composition (Roos & Karel, 1992, Roos, 1993*a*).

Freezing and frozen storage

T_g of most foods prior to freezing is well below the freezing point and close to that of pure water (Figs 10 and 14). Since freeze-concentration increases the effective T_g, the resulting viscosity and physical state can be estimated from state

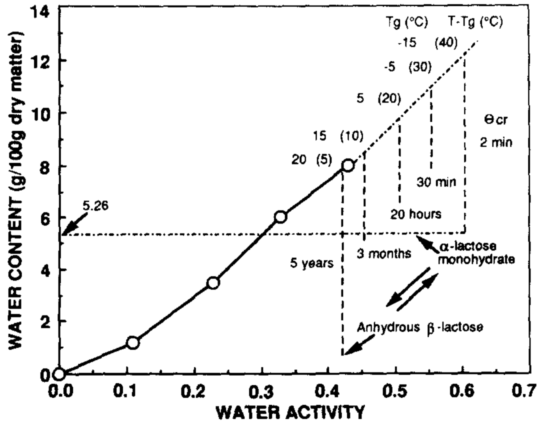

Fig. 12. Sorption isotherm of amorphous lactose showing time-dependent crystallization during water absorption. Crystallization at low water contents results in the formation of anhydrous β-lactose and at high water contents in the formation of α-lactose monohydrate with 5·26 g H_2O/200 g lactose. After Roos and Karel (1990).

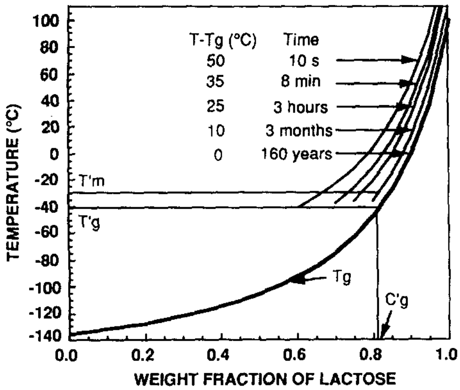

Fig. 13. State diagram of amorphous lactose showing time-dependent crystallization above glass transition temperature (T_g). The onset temperature of ice melting, glass transition temperature, and concentration of the maximally freeze-concentrated solutions are shown by T'_m, T'_g, and C'_g, respectively.

diagrams (Levine & Slade, 1988) (Fig. 14). Levine and Slade (1988) have postulated that stability is related to the temperature difference between the storage temperature and the glass transition temperature of the maximally freeze-concentrated unfrozen matrix (T'_g). This cryostabilization of foods assumes stability below T'_g and rapid decrease of stability above T'_g according to the WLF type temperature-dependence (Levine & Slade, 1988).

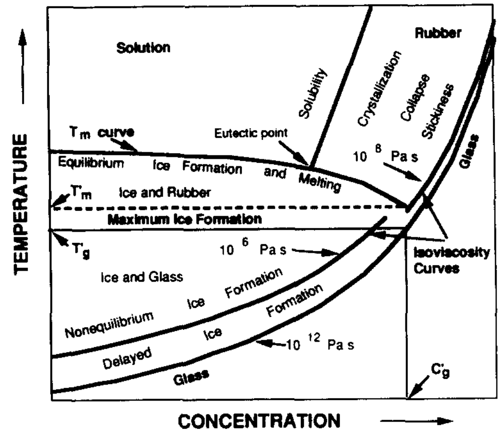

Fig. 14. Schematic state diagrams showing changes and isoviscosity states above glass transition temperature (T_g). The onset temperature of ice melting, glass transition temperature, and concentration of the maximally freeze-concentrated solutions are shown by T'_m, T'_g, and C'_g, respectively. The T_m line shows the equilibrium melting point of ice above T'_m. After Roos and Karel (1991*b*).

Melting of ice has its onset (T'_m) above T'_g and exceeding T'_m leads to concurrent dilution of the unfrozen matrix and depression of the effective T_g (Roos & Karel, 1991*a*, *d*). High molecular weight materials have T'_g above normal freezer temperatures (Slade & Levine, 1991), but products containing high amounts of sugars are usually stored above the onset temperature of ice melting (Levine & Slade, 1988; Roos & Karel, 1991*b*). Lim and Reid (1991) reported decreased reaction rates in freeze-concentrated maltodextrin solutions below T'_g. Above T'_m, viscosity decreases rapidly because of ice melting, which may increase the rate of diffusion limited reactions in frozen foods (Roos & Karel, 1991*a*, *b*). Howeve, ice melting leads also in dilution of the unfrozen matrix and eventually to a decreased concentration of potential reactants (Roos & Karel, 1991*a*). Knowledge of material characteristics as food components allows design of frozen foods to decrease deterioration during storage, to increase their stability, and to improve frozen food quality.

Food stability

Low moisture and frozen foods contain a number of compounds, mainly carbohydrates and proteins, which may be amorphous or partially amorphous (Flink, 1983; Slade & Levine, 1991). Starch is an example of a partially crystalline food polymer, which is present in cereal and several other foods. It shows physical changes, e.g. gelatinization and retrogradation, that are governed by nonequilibrium phenomena (Biliaderis *et al.*, 1986; Slade & Levine, 1991).

The physical state of amorphous food components is believed to affect the kinetics of deteriorative reactions in the vicinity of T_g (Simatos & Karel, 1988;

Slade & Levine, 1991). Rates of nonenzymatic browning and various enzymatic reactions are strongly related to moisture content. Several studies have suggested that the rate of such reactions may also be related to the physical state (Kim *et al.*, 1981; Simatos & Karel, 1988; Slade & Levine, 1991; Karmas *et al.*, 1992). The quality and palatability of various low moisture and snack foods are extremely sensitive to water plasticization. Katz and Labuza (1981) reported critical water activities (a_w) for snack food products at which they showed unacceptable textural changes. Such critical water activities and water contents can be related to T_g (Slade & Levine, 1991) as shown in Figs 4 and 14. Thus, temperature and moisture limits for product stability can be estimated from the state diagrams (Fig. 14). The critical water content and water activity values of food materials with state diagrams are useful in the design of foods, since they indicate packaging requirements and show limits for storage, relative humidity and temperature.

Generally, T_g values of food solids are determined by composition and moisture content (Slade & Levine, 1991). The effect of composition is particulary important in dehydration since the T_g value affects both the processability and storage stability of the materials (Slade & Levine, 1991). State diagrams and the relationships between product composition and physical state provide means for formulation of food products to fulfill processing requirements and provide stability during storage when reformulation is feasible (Roos & Karel, 1991*b*; Slade & Levine, 1991). State diagrams may also be used to design processes, equipment, and proper packaging and storage conditions for product requirements and maximum stability (Roos & Karel, 1991*b*; Slade & Levine, 1991). Kinetics of various changes affected by the physical state can be used to evaluate rates of food deterioration or to achieve desired properties (e.g. color and flavor) at various processes and storage conditions (Roos & Karel, 1991*b*). However, more studies should be conducted to determine physical characteristics of various food polymers, and the effects of the dynamic processes above T_g on food quality.

CONCLUSIONS

Food materials contain amorphous and partially amorphous components, which may significantly affect changes that occur during food processing and storage. Changes in the physical state of food materials are often nonequilibrium phenomena that are strongly related to water content and temperature. Rates of both physical and chemical changes show dependence of viscosity and the physical state, especially in frozen and low moisture foods. The viscosity of amorphous food materials is related to the glass transition temperature. The decrease of viscosity above T_g is responsible for various changes, including stickiness and collapse of dehydrated foods, agglomeration, crystallization of food components (e.g. lactose in milk powders), and it may affect rates of chemical reactions. T_g also controls food texture and it is obvious that crispness of various low moisture foods is lost above T_g. Determination of T_g values as a function of water content and water activity can be used to establish state diagrams, which show the T_g dependence of water content. The state diagrams may be used to predict the physical state of food materials at various conditions, and to show relationships between composition and temperature that are necessary for achieving desired changes in food processing or for maintaining food quality in processing and storage.

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