RESEARCH REVIEW

Caking in Food Powders

Roger Ruan[1,2], Young-Jin Choi[3], and Myong-Soo Chung[4]*

[1]*Department of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, MN 55108, USA*
[2]*Yangtz Scholar Distinguished Guest Professor, Nanchang University, Jiangxi 330031, China*
[3]*Department of Food Science and Biotechnology, Seoul National University, Seoul 151-921, Korea*
[4]*Department of Food Science and Technology, Ewha Womans University, Seoul 120-750, Korea*

Abstract Caking has been a serious problem in food, feed, pharmaceutical, and related industries, where dry powdered materials are produced and/or utilized. Caking of dry food powders occurs when water is redistributed or absorbed by the powders during processing and storage. The powders become sticky when their surfaces are mobilized by water, resulting in inter-particle binding, formation of clusters, and inter-particle fusion, which lead to caking. As a result of caking, the solubility of the powdered materials may decrease, lipid oxidation and enzymatic activity may increase, and sensory qualities such as flavor and crispness may deteriorate. Caking may also lead to microbial growth. For consumers, caking of powder products is a sign of poor quality and possible food safety problems. This paper provides a review of factors affecting caking, caking mechanisms, and analysis of caking based on previous studies.

Keywords: caking, dry food powder, factor affecting caking, caking mechanism, analysis of caking

Introduction

Since amorphous dried food materials have a large internal surface area, they are usually hygroscopic (1). Therefore, exposure of food powders to moist atmosphere or elevated temperature often results in structural change, caking, and impaired flow properties (2). Caking can result in anything from small soft aggregates that break easily, to rock hard lumps of variable size, to solidification of the whole powder mass. In most cases, the process is initiated by the formation of liquid bridges between particles that can later solidify by drying or cooling. This mechanism, known as "humidity caking" (2-5), is schematically described in Fig. 1. This process is typical for powders that are water-soluble or contain water-soluble materials.

Water can be absorbed from the atmosphere or may condense on the dry particles due to a temperature drop during storage. The wet surfaces may contain a saturated solution of the soluble components of the surface material. It can actually be observed that moisture absorption is accompanied by shrinkage of the powder. Bridging, the initial stage of caking, occurs as a result of surface deformation and sticking at contact points between particles, without measurable decrease in system porosity. At the onset of caking, small interparticle bridges may even disintegrate under mild shaking. Agglomeration, an intermediate stage of caking, involves an irreversible consolidation of bridges, but the high porosity of the particulate system is maintained, resulting in particle clumps with structural integrity. Compaction, an even more advanced stage in caking, is associated with a pronounced loss of system integrity as a result of thickening of interparticle bridges owing to the reduction of interparticle spaces and deformation of particle clumps

under pressure. The caking at this stage is characterized by stickiness of the powder surfaces and may develop in two main directions. If the moisture absorption is allowed to continue, all the mass is rendered wet and sticky and can hardly be considered a powder. If drying occurs at this stage, on the other hand, it will cause a resolidification, forming hard, dry lumps. At any given stage, lumps may be few or numerous, of different sizes, and of varying degrees of hardness.

In food powders, the source of the liquid bridges is produced by one or more of the following.
(i) Moisture sorption by hygroscopic materials after accidental wetting of the powder or the equipment. Water-soluble materials on the particle surface are dissolved and/or a liquid film around the particles is formed.
(ii) Condensation of moisture on the surface itself as a result of increasing the temperature, without the addition of external moisture.
(iii) Liberation of absorbed moisture when amorphous sugars crystallize (for example, the crystallization of lactose in milk powders).
(iv) Melting of fats.

In practical situations, the humidity-temperature conditions vary over time. Additional factors that affect caking are the solubility of the powder chemical components, the surface properties that regulate water absorption, and water diffusivity within the particles. These can also vary according to the origin of the material and the process history of the powder.

Factors Affecting Caking

The properties of materials such as molecular weight and moisture content and environmental conditions such as temperature, compaction pressure, and relative humidity affect flowability and caking. Due to the inhomogeneity of bulk food powders, caking and flowability problems are
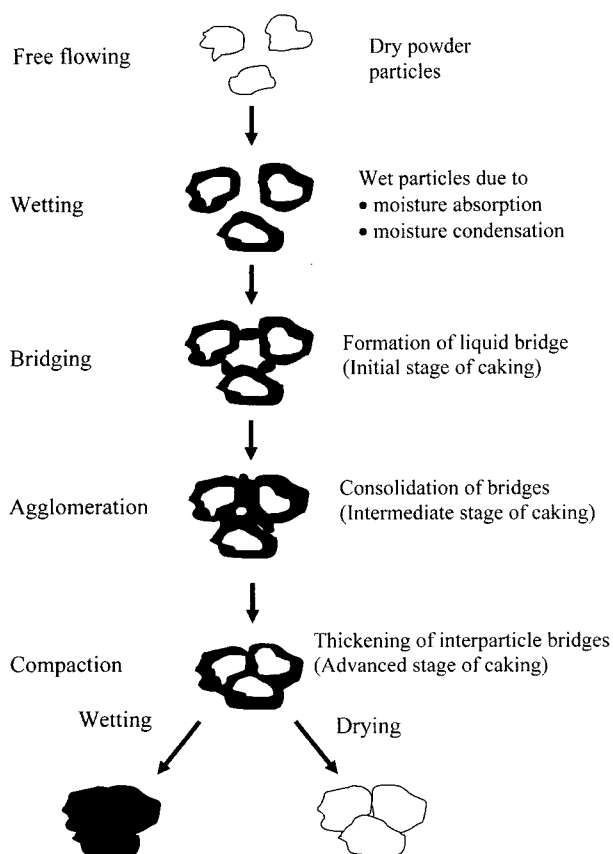
Fig. 1. Stages during a typical humidity caking process.

% Solute concentration ⟶

Fig. 2. Schematic state diagram of most amorphous food systems.

more serious. Therefore, a strict definition of caking is difficult to formulate because changes in a powder system are irregular and unpredictable except under extreme conditions (6-10). Several factors affecting caking and related research will be presented in this section.

Effect of Temperature

Conventional caking temperature Powdered food materials may cake without a change in moisture content if the temperature to which the materials are exposed exceeds a certain level. Traditionally, the 'sticky point' has been frequently used as caking temperature and defined as the temperature at which the energy needed to stir a powder sample with a propeller rises suddenly and sharply (11). The collapse temperature has been defined as a time- and moisture-dependent temperature point at which a matrix can no longer support its own weight, leading to structural changes as shown by shrinkage of volume and sticking of dry powders (4, 12). Chuy and Labuza (13) discussed that the former is a measurement of an advanced stage of caking (the compaction stage in Fig. 1), while the latter measures an initial stage of caking (the bridging stage in Fig. 1). Although these methods appear to be sufficiently sensitive to detect the abrupt change in the consistency of a powder undergoing a transition, it allows only rough estimation of caking temperature.

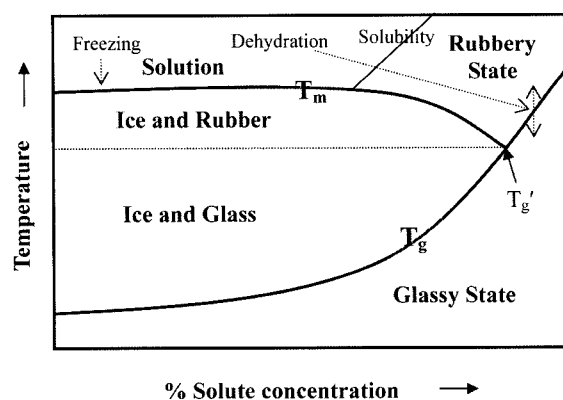**Glass transition temperature** A fundamental understand-

ing of glass transitions in amorphous food systems begins with the state diagram (14-17). Figure 2 shows a simplified state diagram illustrating major curves and regions. Transformation of the solutes to an amorphous state during typical dehydration and freezing processes and physical states at each condition are presented as a function of temperature and solute concentration. In this figure, T_m represents the equilibrium melting curve, and T_g represents the glass transition curve of the food system. T_g values of food materials vary from that of pure water at about -135°C to those of dry solutes.

Also shown in the figure are descriptors of the various regions in the state diagram. To the left of T_g' on the composition axis lie systems such as frozen foods and ice creams. To the right of T_g' are intermediate or low-moisture food systems such as candies and powders. The state diagrams can be used for showing the relationships between composition and temperature that are necessary for maintaining food quality in processing and storage and for predicting the physical state of food materials at various conditions.

Many food processes and properties have been explained by glass transition phenomena. Some examples include food texture (18), frozen storage stability (19, 20), freeze drying (21), caking/clumping (9, 22), and crystallization (23-25). Therefore, complete understanding of glass transition phenomena in any food system is essential to improving product stability and functionality.

The most important change noticed at the glass transition temperature (T_g) involves transition from a solid 'glassy' state to a liquid-like 'rubber' state, as depicted in Fig. 2. T_g is a very important characteristic of amorphous food materials since it provides valuable information about the molecular structure, conformation, and physical state. A system in the glassy state (below T_g) has a set of properties vastly different from those in the rubbery state (above T_g). The main change above T_g is an increase in molecular mobility and free volume and a decrease in viscosity, which may result in physical and physico-chemical deterioration in foods (26). Since water is the most important solvent and plasticizer for hydrophilic food components, the mobility of food components is greatly affected by the presence of water. Therefore, recognition of the role of water as a plasticizer of amorphous food

materials and the practical significance of the glass transition are of major importance to the prediction and understanding of the functional properties of food materials during processing and storage.

T_g values of binary mixture food systems have been predicted by the Gordon-Taylor equation (27), which originally was developed for describing T_g dependence of binary miscible polymer blends on the fractional concentration of their constituents. This equation was previously found to be applicable to binary amorphous food systems by Roos and Karel (28) and has been used for predicting the T_g curve shown in the state diagram (Fig. 2)

$$T_g = \frac{w_1 T_{g1} + cw_2 T_{g2}}{w_1 + cw_2} \qquad (1)$$

where T_{g1} and T_{g2} are glass transition temperatures of components in binary mixture, w_1 and w_2 are corresponding weight fractions, and c is constant. Couchman and Karasz (29) reported that c value in equation (1) is expressed as the ratio of specific heat changes at T_g, that is $\Delta C_{p2}/\Delta C_{p1}$, which is usually obtained with DSC.

The Gordon-Taylor equation has been extensively used for fitting experimental data on T_g and composition of maltodextrins (28), amorphous sugars (14), cereal proteins (30), and milk powders (25).

Caking and glass transition of amorphous powders

Amorphous food materials exist below the glass transition temperature (T_g) in a non-equilibrated, 'stable' glassy state because of the high viscosity, which assures that the material supports its own weight. The viscosity of a glass is about 10^{11} Pa·sec (14). Relevant to caking, a dramatic reduction in viscosity (or mechanical modulus) of an amorphous solid occurs at T_g. As the product temperature exceeds T_g, amorphous materials enter the rubbery state and the decreasing viscosity induces flow and deformation. It has been shown that the widely used "sticky point temperature" (11) is governed by T_g. The critical viscosity of stickiness of about 10^7 Pa·sec correlates with the viscosity at the end point of the glass transition (1).

If the system is stored at a temperature below its T_g, in other words, if the system is in the glassy state, its viscosity is extremely high and mobility is extremely low, therefore it will take a very long time for the plasticizer (usually water) to mobilize the particles, and the contact time between particles must be very long to result in bridges. In this case, caking may not happen within the shelf life. On the other hand, if the system is stored at a temperature above its T_g (or in the rubbery state), the dramatic increase in mobility and decrease in viscosity at glass transition greatly reduces the contact time and causes sticking, caking, and loss of porosity (12, 26, 31-34).

Effect of Moisture

The typical relationship between the "sticky point" and the moisture of sugar-containing powders is shown schematically in Fig. 3. The shape of the curve in this figure is very similar to that of the collapse temperature vs. moisture
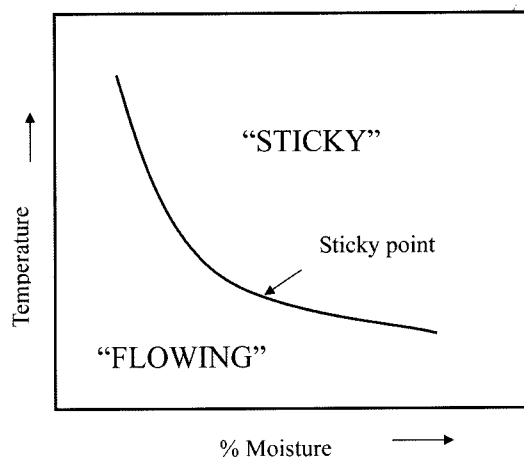

Fig. 3. Schematic view of the relationship between the "sticky point" (temperature) and moisture content (9).

content (12) or the glass transition temperature vs. moisture content (26). It has been shown (35) that the plot of the logarithm of the collapse temperature vs. moisture for sucrose is a linear relationship for moisture contents up to about 10% (dry basis). The same appears to be the case for other powdered materials such as fruit juice powders, maltodextrins, starches, and proteins, irrespective of whether the temperature is defined as the collapse temperature (12), the "sticky point temperature" (11, 36, 37) or the glass transition temperature (38, 39). In the case of starches and proteins, linearity was observed up to about 30% moisture. That is well beyond the moisture range in which sugar-rich materials can be maintained in a powdery form.

The temperature-moisture relationship of all these materials was described well by the following expression:

$$\ln \frac{T - T_s}{T_0 - T_s} = -cM \qquad (2)$$

where T is the temperature in K, T_0 is the temperature that corresponds to zero moisture content, T_s is a reference temperature which can be selected arbitrarily, M is the moisture content on a dry weight basis, and c is a constant. If the reference temperature, T_s, is selected as 273 K, Equation (2) can be reduced to the following form:

$$\ln T = \ln T_0 - cM \qquad (3)$$

where T is the temperature in °C. The regression parameters for Equation (3) estimated by several authors for a variety of materials are listed in Table 1. This table shows that the "sticky point temperature" (T_{sticky}), the collapse temperature $(T_{collapse})$, and T_g are apparently all a manifestation of the same physical phenomenon. Materials such as orange juice powder, which tend to cake at room temperature, have a low T_0 and a relatively large slope value irrespective of how they are defined. Powders such as starch that are known to be physically stable at room temperature have a high T_0 and a small slope value. This is

Table 1. Regression parameters for ln T vs. moisture content plots for various powders (Eq. 3)

Powder	Temperature definition	Intercept (ln T_0)	Slope (c)	R[1]	T_0(°C) (extrapolated)	Reference
Coffee	T_{sticky}	4.71	0.092	0.977	111	(37)
Maltodextrin/ Sucrose/ Fructose mix	T_{sticky}	4.99	0.261	0.986	147	(37)
Orange juice (glucose added)	T_{sticky}	4.19	0.204	0.998	66	(36)
Tomato juice	T_{sticky}	4.33	0.103	0.998	76	(11)
Freeze dried orange juice (slow freezed)	$T_{collapse}$	3.76	0.197	0.968	43	(12)
Freeze dried orange juice (fast freezed)	$T_{collapse}$	3.87	0.161	0.990	48	(12)
Matodextin (M-250)	$T_{collapse}$	5.37	0.172	0.996	215	(12)
Wheat gluten	T_g	5.22	0.118	0.994	184	(38)
Wheat gluten (pregelatinized)	T_g	5.74	0.107	0.993	310	(39)
Wheat gluten (native)	T_g	5.99	0.105	0.962	399	(39)

[1]Correlative coefficient.

consistent with the observation that powders with high molecular weight are more stable and less moisture-sensitive than those with low molecular weight.

Generally, the T_g of an amorphous or partially crystalline system is a function of plasticizer (e.g., water) and solid compounds in the system. A reduction in water content of the system will raise the T_g of the system; on the other hand, an increase in moisture content, for instance due to water absorption during storage, will lower the T_g.

By adjusting the moisture content of the system or using good packaging material to prevent undesirable moisture absorption, we can maintain products in the stable glassy state.

Effect of Food Composition

Food powders containing low molecular weight components, like powdered fruits and vegetables, are known for their tendency to cause flow problems and to cake, while other food powders containing high molecular weight components, like flour and starch, are known to be relatively free flowing under normal storage conditions. This can be explained by the glass transitions. That is, since T_g increases with increasing molecular weight, large molecules have higher T_g values and small molecules have lower T_g values. Thus, rice flour, which consists mainly of polysaccharides (e.g., amylose), is at the stable glassy state at room temperature due to its high T_g value. On the other hand, orange juice powder, which consists mainly of monosaccharides (e.g., fructose), is at the unstable rubbery state at room temperature due to its low T_g value. Kopelman et al. (40) reported that freeze dried lemon juice concentrate with a high composition of fructose was found to be extremely hygroscopic, to exhibit a high tendency of caking at ambient conditions of 25°C and 60% RH, and to cake even at low water activities. Considering the results of Roos and Karel (1), T_g values for dehydrated fruit juices, which are comprised of mostly fructose ($T_g = 5$°C), glucose ($T_g = 31$°C), and sucrose ($T_g = 62$°C) (14), were estimated to be below typical room temperature values. This also explains why it is recommended that the walls of

spray dryers used to dehydrate these types of products be cooled to reduce sticking problems (36).

Low molecular weight inorganic salts (41) and protein hydrolyzates (42) are known to exhibit hygroscopicity and to cause caking problems during storage. A fraction containing mainly nitrogenous compounds (presumably amino acids) was held responsible for the hygroscopicity and caking of spray-dried fermented soy sauce powders (43). An important related phenomenon is aggregation of proteins in the dried state (44). There are examples in the literature of aggregation reactions (e.g., thiol-disulfide interchanges, other covalent bonds mediated by lysine residues, and conformational changes) resulting from water sorption during processing, storage, and delivery. The aggregation of biomolecules in the 'dry' state has important implications in the modern biotechnology industry as it may be responsible for a pronounced decrease in biological activity (45).

Large molecules are often regarded as "mobility lowering" agents. Therefore, the addition of large molecules to a system will decrease the mobility and raise the T_g of the system. This presents manufacturers with the opportunity to use commercially available ingredients that have different "mobility lowering" ability so that their products can have high enough T_g values to avoid caking. For example, Roos and Karel (14) reported that maltodextrin can be used as an additive in fruit juice powders in order to improve dehydration characteristics, to decrease stickiness, and to improve product stability.

Effect of Storage Time

The time until caking of powdered onion stored at room temperature and various relative humidities was observed by Peleg and Mannheim (4). They found that the powder remained free flowing for more than 6 months at room temperature below 40% RH, but caked within a few days at storage conditions of higher than 40% RH.

Caking Kinetics

The rate of caking is believed to be mainly governed by

(9, 26, 46):

$$\Delta T = T - T_g \qquad (4)$$

where T is the storage temperature, and ΔT is the difference between the storage temperature and the glass transition temperature. Equation (4) indicates that the product will have a different shelf life at different temperatures, depending on how far the storage temperatures are from T_g. Equation (4) also suggests that we could manipulate T_g of a product to obtain desirable shelf life. A T_g much greater than ambient temperature or storage temperature is obviously desirable. Products can be designed to have different shelf life according to the climate, and transport and storage conditions (temperature and humidity). However, it is important to be cautious in the use of Equation (4) for predicting shelf life of any food at a certain condition since glass transition occurs over a temperature range and a single transition temperature is not always well-defined (47). At T_g to $T_g+100°C$, it has been studied that the temperature dependence of various time-dependent phenomena such as changes in viscosity (48), crystallization (28), nonenzymatic browning (49), stickiness (46), and collapse (50), follow the William-Landel-Ferry (WLF) relationship (51). Below T_g and above $T_g+100°C$, however, the Arrhenius type temperature dependence has been assumed to apply for most food polymers (14, 26).

Since both internal characteristics of powders such as particle size, charge, and physical states (water activity, bulk density, etc) and external factors such as environmental temperature and relative humidity, applied mechanical stress, and the presence of moisture barriers affect caking phenomena in powdered foods, modeling the kinetics of caking is a difficult task. A goal for food scientists is to predict the time required for caking during storage. A kinetic model to predict caking of powders can start with the well-known WLF equation (51).

The WLF equation was originally developed by investigating an empirical relationship between temperature and changes in mechanical relaxation properties, such as viscosity (η), for a wide variety of polymers and their solutions. It can be expressed as follows:

$$\log_{10} a_T = \frac{-C_1(T-T_s)}{C_2+T-T_s} \qquad (5)$$

where a_T is the ratio between viscosity at temperature T and viscosity at a reference temperature T_s, $(=\eta/\eta_s)$, constants C_1 and C_2 correspond to average values estimated by adjusting experimental viscosity data for various polymers. Individual values of C_1 and C_2 for these polymers were obtained by plotting $(T - T_s) / \log_{10} a_T$ versus $(T - T_s)$ using experimental data. Average values of C_1 and C_2 obtained by choosing the glass transition temperature, T_g, as the T_s, were 17.44 and 51.6°C, respectively. However, the authors of the WLF model advised against the use of average values of C_1 and C_2 since these values were derived by averaging data for different types of polymers and are not applicable to any particular system. Therefore, the WLF equation with fixed

coefficients cannot be assumed to be a generally valid model.

The WLF model is not limited to viscosity only. It can also accommodate other mechanical relaxation or rate parameters (47). The WLF equation has been widely used by many researchers to explain various phenomena in food materials such as crystallization, nonenzymatic browing reaction, ice formation, caking, etc. Roos (52) suggested that the WLF relationship can be applied to explain caking phenomena in amorphous powdered foods using T_g data and viscosity data measured at T_g to $T_g+100°C$, and can be used to avoid collapse in freeze drying and to control stickiness in dehydration and agglomeration. Also, Aguilera et al. (46) showed that the relationship between the relaxation time (τ) for caking and $T - T_g$ can be established by a WLF-type relationship. That is, a_T in Equation (5) was expressed as the ratio of the relaxation times for caking at T and T_g $(= \tau/\tau_g)$. The value of t for caking of amorphous fish hydrolyzate powder at T_g was estimated to be $t_g = 7.57 \times 10^9$ hr, corroborating that caking was not observed when a powder is in the glassy state. At $T - T_g = 20°C$, caking occurred 10^7 times faster than it did in the glassy state.

Establishment of the validity of the WLF equation as a kinetic model and determination of its constants for explaining caking phenomena in complex food powders requires results for conditions and compositions over a large temperature range.

Prevention of Caking

As should be evident at this point, the strict control of moisture content, storage at low temperatures, handling at low humidity, and packaging in moisture-barrier materials, when possible, are key factors in preventing or minimizing powder caking.

Another effective method to prevent or minimize caking of hygroscopic food powders is the addition of flow conditioners or anticaking agents to these powders to improve their flowability and/or inhibit their tendency to cake. Most commonly used food-grade commercial anticaking agents are phosphates, talcum, salts of stearic acid, silicon dioxide, silicates, starches, and modified carbohydrates, which are usually chemically and physically inert and effective at concentrations up to about 2% (53). They play a role in regulating powder behavior by one of several mechanisms.

Competition for water adsorption   Several anticaking agents, such as silicates and stearates, are of a porous nature and have large water adsorptive capacity. Therefore, they compete with the host powder for the available water, thus reducing the latter's hygroscopicity and consequently its tendency to cake. Since the increase in moisture causes a large increase in the equilibrium RH, the optimum performance of these agents is observed when the exposure to moist atmosphere is short or the available moisture is limited. In other words, if the amount of the available moisture is so large that it exceeds the water holding capacity of anticaking agents, they are ineffective. Peleg and Mannheim (4) showed that two kinds of anticaking agents, 1% aluminum silicate and 1% calcium

stearate, had no effect at all on powdered onion because the conditioned powder adsorbed moisture freely and reached equilibrium at high RH.

Acting as physical surface barriers between particles If host particles are coated with a layer of particles of anticaking agents, each host particle is physically separated, and interparticle interaction at the points of contact is between the layers of anticaking agents, resulting in low mutual attractivity. There are several possible results of this physical separation: (i) interfering with liquid bridging mechanisms (e.g., silicon dioxide); (ii) decreasing interparticle friction, by creating smoother surfaces or by acting as a lubricant placed between the considerably larger host particles (e.g., the stearates); (iii) reducing or neutralizing superficial molecular attractive forces, particularly electrostatic forces. Comparison of the angle of internal friction in conditioned and unconditioned powdered sucrose (54) showed that calcium stearate was an effective lubricant, reducing the angle of friction by 2 to 5°.

Increasing T_g of the amorphous phase This mechanism has been demonstrated for dairy-based infant formula powders with added high molecular weight carbohydrates (13). In protein hydrolyzates, it has been observed that a lower degree of hydrolysis (i.e., a higher average molecular weight) diminishes caking (42). Some lipids have been shown to exert an antiplasticization effect in lipid-compatible polymers plasticized by water, which increases T_g (46).

Analysis of Caking

Quantification of caking Although most publications state only whether caking is observed and under what conditions, quantitative methods have been utilized in some cases to characterize caking phenomena. Some of them are as follows:

(i) Measurement of hardness and compressiblity (43, 55): After storing powder samples having different bulk density, particle size, and moisture content at various temperatures and relative humidities, values of hardness and compressibility of each caked sample were determined with a hardness tester and an Instron Universal Testing machine, respectively.

(ii) Sieving method (56): After powder samples were stored under different environmental conditions for various storage times, each caked sample was sieved, and the percentage of original sample weight remaining on the sieve was determined.

(iii) Determination of bulk density and volumetric shrinkage (42, 55, 57, 58): Changes in bulk density and fractional volume of powders were determined after exposing them to several relative humidities, and critical water activity points for caking were observed.

(iv) Measurement of cohesion (9, 57): After powder samples were stored under different environmental conditions for various storage times, the yield stress of each caked sample was determined under normal load using the Jenike flow factor tester, in which cohesion

was defined as the shear stress at zero normal stress.

(v) Microstructural aspects of caking (59): Morphological changes in a powder undergoing caking can be best visualized using microscopic techniques. Thus, it is surprising that microscopic analysis has not been used to any great extent to characterize caking, but it is likely that quantitative information related to caking phenomena and the determination of caking index can be easily derived by microscopy and the aid of computational image analysis. Amorphous components in spray-dried powders are in the metastable amorphous state, and exposure to high relative humidity results in an irreversible transition to the crystalline state. Amorphous lactose crystallizes and releases water during equilibration at 42 to 52% RH (at 25°C). Scanning Electron Microscopy (SEM) was used to follow caking of skim milk powder stored at 20°C during equilibration at 43 to 94% RH. After two weeks, changes had occurred only for powder equilibrated at >54% RH, whereas at >74% RH extensive lactose crystallization and bridging between particles were observed. Image processing of scanning electron micrographs by digitization can be used to correct defects in the original microstructural image (e.g., non-informational noise), enhance or suppress data, select important features, extract numerical data (e.g., particle area or characteristic size), and perform statistical analysis.

Conventional Methods for Determining Caking Temperatures

Determination of collapse temperature (surface caking temperature) The ampule method was developed by Tsourouflis et al. (12) for measuring the collapse temperature of dried food powders. One to two g of sample from each storage condition is placed into 2-mL glass ampules which are flame-sealed. The ampules are placed in an oil bath which is heated at a controlled rate. The ampules are removed from the oil bath every 5°C and are tapped sharply on a hard surface to observe if the powder is still flowing and then quickly placed back into the oil bath. The surface caking temperature of each powder is recorded as the bath temperature at which the powder fails to separate into finite particles, and appears as clumps even after shaking and tapping sharply against a hard surface.

Determination of "sticky point" (advanced caking temperature) The test to determine "sticky points" of amorphous food powders was originally developed by Lazar et al. (11) and has been widely used for caking studies. A previously hydrated powder sample is contained in a test tube which is closed to the atmosphere via a rotating mercury seal. The tube is immersed in a constant-temperature oil bath. The bath temperature is slowly raised while the powder is intermittently stirred by hand with a small propeller embedded in the sample. At a certain temperature, which is a function of the moisture content of the powder, the force required to turn the stirrer dramatically increases. The temperature at which this occurs is usually distinct and is referred to as the "sticky point temperature"

Table 2. Methods for measurement of glass transitions

Mechanism	Method
Thermal analysis	Differential Scanning Calorimetry (DSC)
Mechanical properties	Thermal Mechanical Analysis (TMA) Dynamic Mechanical Analysis (DMA) Rheometry Instron Mechanical Spectroscopy
Spectroscopy	Electron Spin Resonance (ESR) Nuclear Magnetic Resonance (NMR)

of the powder. The bath temperature is raised about 0.5°C every minute at temperatures far away from the "sticky point", and about 0.5°C every 5 min as the "sticky point" is approached. Heating is assumed to be slow enough so that the powder temperature is the same as the bath temperature. The propeller is turned manually, 1/4 turn every other second. The test tube is firmly tapped periodically to ensure good contact of the powder with the stirrer.

Measurement of Glass Transitions

There are many experimental techniques which can be used to measure glass transitions in food systems; some of them are listed in Table 2. Differential scanning calorimetry (DSC) detects the change in heat capacity occurring over the transition temperature range. T_g is seen as a mean change in specific heat resulting in a step change in the baseline (determined using the intersect of the slope of the initial rise of the exothermic peak and the baseline). The onset temperature of the glass transition is the temperature at which the heat flux starts to rise from the baseline. For some kinds of materials, the measurement of thermal events is much less sensitive than the measurement of mechanical properties of the system. Methods that measure the mechanical properties of the system, including thermal mechanical analysis (TMA) (60, 61) and dynamic mechanical analysis (DMA) (62-65), are preferred for their sensitivity. Recently, spectroscopic methods, such as electron spin resonance (ESR) (66) and nuclear magnetic resonance (NMR) (59, 65, 67-73), have also been used for measuring glass transitions. These techniques measure the mobility of protons in foods. Because they are non-destructive and non-invasive, application of these techniques in food science and technology is receiving increasing attention.

References

1. Roos Y, Karel M. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. J. Food Sci. 56: 38-43 (1991)
2. Peleg M. Physical characteristics of food powders. pp. 293-323. In: Physical Properties of Food. Peleg M, Bagley EB (eds). AVI, Westport, CT, USA (1983)
3. Burak N. Chemicals for improving the flow properties of powders. Chem. Ind. -London 1: 844-850 (1966)
4. Peleg M, Mannheim CH. The mechanism of caking of powdered onion. J. Food Process Pres. 1: 3-11 (1977)
5. Saltmarch M, Labuza TP. Influence of relative humidity on the physicochemical state of lactose in spray-dried sweet whey powders. J. Food Sci. 45: 1231-1236 (1980)
6. Hersey JA. Ordered mixing: a new concept in powder mixing practice. Powder Technol. 11: 41-45 (1975)
7. Hersey JA, Thiel WJ, Yeung CC. Partially ordered randomized powder mixtures. Powder Technol. 24: 251-256 (1979)
8. Egermann H, Orr NA. Ordered mixtures–interactive mixtures. Powder Technol. 36: 117-118 (1983)
9. Peleg M. Glass transitions and the physical stability of food powders. pp. 435-451. In: The Glassy State in Foods. Blanshard JMV, Lillford PJ (eds). Nottingham Univ. Press, Nottingham, UK (1993)
10. Isengard H-D. Rapid water determination in foodstuffs. Trends Food Sci. Tech. 6: 155-162 (1995)
11. Lazar ME, Brown AH, Smith GS, Wong FF, Lindquist FE. Experimental production of tomato powder by spray drying. Food Technol.-Chicago 10: 129-134 (1956)
12. Tsourouflis S, Flink JM, Karel M. Loss of structure in freeze dried carbohydrate solutions. Effect of temperature, moisture contents, and composition. J. Sci. Food Agr. 27: 509-519 (1976)
13. Chuy LE, Labuza TP. Caking and stickiness of dairy-based food powders as related to glass transition. J. Food Sci. 59: 43-46 (1994)
14. Roos Y, Karel M. Applying state diagrams to food processing and development. Food Technol.-Chicago 45: 66, 68-71, 107 (1991)
15. Chinachoti P. Water mobility and it relation to functionality of sucrose-containing food systems. Food Technol.-Chicago 47: 134-140 (1993)
16. Schenz TW. Glass transitions and product stability – an overview. Food Hydrocolloid 9: 307-315 (1995)
17. Roos Y, Karel M, Kokini JL. Glass transitions in low moisture and frozen foods: effects on shelf life and quality. Food Technol.-Chicago 50: 95-108 (1996)
18. Rogers DE, Doescher LC, Hoseney RC. Textural characteristics of reheated bread. Cereal Chem. 67: 188-191 (1990)
19. Caldwell KB, Goff HD, Maurice TJ. The use of thermal mechanical analysis to determined the influence of carbohydrates on stability of frozen dairy products. J. Dairy Sci. 73: 95 (1990)
20. Levine H, Slade L. Cryostabilization technology: Thermoanalytical evaluation of food ingredients and systems. pp. 221-305. In: Thermal Analysis of Foods. Harwalker VR, Ma CY (eds). Elsevier Applied Science, London, UK (1990)
21. George RM. Freezing processes used in the food industry. Trends Food Sci. Tech. 4: 134-138 (1993)
22. Noel TR, Ring SG, Whittam MA. Glass transition in low-moisture foods. Trends Food Sci. Tech. 1: 62-67 (1990)
23. Hartel RW, Shastry AV. Sugar crystallization in food products. Crit. Rev. Food Sci. 30: 49-112 (1991)
24. Jouppila K, Roos YH. Water sorption and time-dependent phenomena of milk powders. J. Dairy Sci. 77: 1798-1808 (1994)
25. Jouppila K, Roos YH. Glass transition and crystallization in milk powders. J. Dairy Sci. 77: 2907-2915 (1994)
26. Slade L, Levine H. Beyond water activity: Recent advances based on alternative approach to the assessment of food quality and safety. Crit. Rev. Food Sci. 30: 115-360 (1991)
27. Gordon M, Taylor JS. Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. J. Appl. Chem. 2: 493-500 (1952)
28. Roos Y, Karel M. Phase transitions of mixtures of amorphous polysaccharides and sugars. Biotechnol. Progr. 7: 49-53 (1991)
29. Couchman PR, Karasz FE. A classical thermodynamic discussion of the effect of composition on glass transition temperatures. Macromolecules 11: 117-119 (1978)
30. Kokini JL, Cocero AM, Madeka H, De Graaf E. The development of state diagrams for cereal proteins. Trends Food Sci. Tech. 5: 281-288 (1994)
31. White GW, Cakebread SH. The glassy state in certain sugar-containing food products. Food Technol.-Chicago 1: 73-82 (1966)
32. To EC, Flink JM. 'Collapse', a structural transition in freeze dried carbohydrates. - I. Evaluation of analytical methods. Food Technol.-Chicago 13: 551-565 (1978)
33. To EC, Flink JM. 'Collapse', a structural transition in freeze dried carbohydrates. - II. Effect of solute composition. Food Technol.-

Chicago 13: 567-581 (1978)

34. To EC, Flink JM. 'Collapse', a structural transition in freeze dried carbohydrates. - III. Prerequisite of recrystallization. Food Technol.-Chicago 13: 583-594 (1978)

35. Flink JM. Structure and structure transitions in dried carbohydrate materials. pp. 473-521. In: Physical Properties of Foods. Peleg M, Bagley EB (eds). AVI, Westport, CT, USA (1983)

36. Brennan JG, Herrera J, Jowitt G. A study of some of the factors affecting the spray drying of concentrated orange juice, on a laboratory scale. Food Technol.-Chicago 6: 295-307 (1971)

37. Wallack DA, King CJ. Sticking and agglomeration of hygroscopic, amorphous carbohydrate and food powders. Biotechnol. Progr. 4: 31-35 (1988)

38. Hoseney RC, Zeleznak K, Lai CS. Wheat gluten: a glassy polymer. Cereal Chem. 63: 285-286 (1986)

39. Zelenznak KJ, Hoseney RC. The glass transition in starch. Cereal Chem. 64: 121-124 (1987)

40. Kopelman IJ, Meydav S, Weinberg S. Storage studies of freeze dried lemon crystals. Food Technol.-Chicago 12: 403-410 (1977)

41. Dziedzic SZ, Kearsley MW. pp. 137-168. In: Glucose Syrup: Science and Technology. Dziedzic SZ, Kearsley MW (eds). Elsevier, New York, NY, USA (1984)

42. Aguilera JM, Levi G, Karel M. Effect of water content on the glass transition and caking of fish protein hydrolyzates. Biotechnol. Progr. 9: 651-654 (1993)

43. Hamano M, Sugimoto H. Water sorption, reduction of caking and improvement of free flowingness of powdered soy sauce and *miso*. J. Food Process Pres. 2: 185-196 (1978)

44. Anjum FM, Walker CE. Review on the significance of starch and protein to wheat kernel hardness. J. Sci. Food Agr. 56: 1-13 (1991)

45. Liu WR, Langer R, Klibanov AM. Moisture-induced aggregation of lyophilized proteins in the solid state. Biotechnol. Bioeng. 37: 177-184 (1991)

46. Aguilera JM, del Valle JM, Karel M. Caking phenomena in amorphous food powders. Trends Food Sci. Tech. 6: 149-155 (1995)

47. Peleg M. On the use of the WLF model in polymers and foods. Crit. Rev. Food Sci. 32: 59-66 (1992)

48. Soesanto T, Williams MC. Volumetric interpretation of viscosity for concentrated and dilute sugar solutions. J. Phys. Chem.-US 85: 3338-3341 (1981)

49. Buera M del P, Karel M. Application of the WLF equation to describe the combined effects of moisture and temperature on nonenzymatic browning rates in food systems. J. Food Process Pres. 17: 31-45 (1993)

50. Levi G, Karel M. Volumetric shrinkage (collapse) in freeze-dried carbohydrates above their glass transition temperature. Food Res. Int. 28: 145-151 (1995)

51. Williams ML, Landel RF, Ferry JD. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. J. Phys. Chem.-US 77: 3701-3707 (1955)

52. Roos Y. Characterization of food polymers using state diagram. J. Food Eng. 24: 339-360 (1994)

53. Peleg M, Hollenbach AM. Flow conditioners and anticaking agents. Food Technol.-Chicago 38: 93-102 (1984)

54. Peleg M, Mannheim CH, Passy N. Flow properties of some food powders. J. Food Sci. 38: 959-964 (1973)

55. Barbosa-Canovas G, Malave-Lopez J, Peleg M. Density and compressibility of selected food powders mixtures. J. Food Process Eng. 10: 1-19 (1987)

56. Kim M. Effect of soluble starch pretreatment and storage condition on caking degree and moisture sorption of powdered onion. J. Korean Soc. Food Sci. 20: 272-275 (1991)

57. Moreyra R, Peleg M. Effect of equilibrium water activity on the bulk properties of selected food powders. J. Food Sci. 46: 1918-1922 (1981)

58. Lloyd RJ, Chen XD, Hargreaves JB. Glass transition and caking of spray-dried lactose. Int. J. Food Sci. Technol. 31: 305-311 (1966)

59. Lai H-M, Schmidt SJ. Lactose crystallization in skim milk powder observed by hydrodynamic equilibria, scanning electron microscopy and ^{2}H nuclear magnetic resonance. J. Food Sci. 55: 994-999 (1990)

60. Biliaderis CG, Page CM, Maurice TJ, Juliano BO. Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. J. Agr. Food Chem. 34: 6-14 (1986)

61. Lemeste M, Huang VT, Panama J, Anderson G, Lentz R. Glass transition of bread. Cereal Food World 37: 264-267 (1992)

62. Cocero AM, Kokini JL. The study of the glass transition of glutenin using small amplitude oscillatory rheological measurements and differential scanning calorimetry. J. Rheol. 35: 257-270 (1991)

63. Anglea SA, Karathanos V, Karel M. Low-temperature transition in fresh and osmotically dehydrated plant materials. Biotechnol. Prog. 9: 204-209 (1993)

64. Williams RJ. Methods for determination of glass transitions in seeds. Ann. Bot. -London 74: 525-530 (1994)

65. Chung MS, Ruan RR, Chen PL, Wang X. Physical and chemical properties of caramel systems. Lebensm.-Wiss. Technol. 32: 162-166 (1999)

66. Roosen MJGW, Hemminga MA, Walstra P. Molecular motion in glassy water-malto-oligosaccharide (maltodextrin) mixtures as studied by conventional and saturation-transfer spin-probe e.s.r. spectroscopy. Carbohyd. Res. 215: 229-237 (1991)

67. Kalichevisky MT, Jaroszkiewicz EM, Ablett S, Blanshard JMV, Lillford PJ. The glass transition of amylopectin measured by DSC, DMTA, and NMR. Carbohyd. Polym. 18: 77-88 (1992)

68. Long Z. Study of the glass transition using pulsed nuclear magnetic resonance (NMR). MS thesis, Department of Biosystems and Agricultural Engineering, University of Minnesota, St. Paul, MN, USA (1996)

69. Chung MS, Kim SH, Park KM. Observation of molecular relaxation behavior of powdered carbohydrates using low field nuclear magnetic resonance (NMR). Food Sci. Biotechnol. 11: 665-672 (2002)

70. Chung MS, Ruan RR. Storage temperature dependence on caking of food powders. Food Sci. Biotechnol. 11: 566-569 (2002)

71. Chung MS, Ruan RR, Chen PL, Chung SH, Ahn TH, Lee KH. Study of caking in powdered foods using nuclear magnetic resonance spectroscopy. J. Food Sci. 65: 134-138 (2000)

72. Chung MS, Ruan RR, Chen P, Kim JH, Ahn TH, Baik CK. Predicting caking behavior in powdered foods using low field nuclear magnetic resonance (NMR) technique. Lebensm.-Wiss. Technol. 36: 751-761 (2003)

73. Chung MS, Ruan RR, Chen PL, Lee YG, Ahn TH, Baik CK. Formulation of caking-resistant powdered soups based on NMR analysis. J. Food Sci. 66: 1147-1151 (2001)