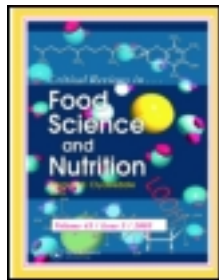


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Moisture and Shelf Life in Sugar Confections

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From hardening of marshmallow to graining of hard candies, moisture plays a critical role in determining the quality and shelf life of sugar-based confections. Water is important during the manufacturing of confections, is an important factor in governing texture, and is often the limiting parameter during storage that controls shelf life. Thus, an understanding of water relations in confections is critical to controlling quality.

Water content, which is controlled during candy manufacturing through an understanding of boiling point elevation, is one of the most important parameters that governs the texture of candies. For example, the texture of caramel progresses from soft and runny to hard and brittle as the moisture content decreases. However, knowledge of water content by itself is insufficient to controlling stability and shelf life. Understanding water activity, or the ratio of vapor pressures, is necessary to control shelf life.

A difference in water activity, either between candy and air or between two domains within the candy, is the driving force for moisture migration in confections. When the difference in water activity is large, moisture migration is rapid, although the rate of moisture migration depends on the nature of resistances to water diffusion. Barrier packaging films protect the candy from air whereas edible films inhibit moisture migration between different moisture domains within a confection.

More recently, the concept of glass transition, or the polymer science approach, has supplemented water activity as a critical parameter related to candy stability. Confections with low moisture content, such as hard candy, cotton candy, and some caramels and toffees, may contain sugars in the amorphous or glassy state. As long as these products remain below their glass transition temperature, they remain stable for very long times. However, certain glassy sugars tend to be hygroscopic, rapidly picking up moisture from the air, which causes significant changes that lead to the end of shelf life. These products need to be protected from moisture uptake during storage.

This review summarizes the concepts of water content, water activity, and glass transition and documents their importance to quality and shelf life of confections.

Keywords Moisture, confections, migration, water activity, packaging, water barriers

INTRODUCTION

“Water is life.”

Felix Franks, 2000

Water is the only inorganic liquid that occurs naturally on earth. It is also the only chemical compound commonly found in solid, liquid, and vapor forms. Water has a higher melting point, boiling point, and heat of vaporization than most other common solvents with similar molecular weight and atomic composition. It also has relatively large values for surface tension, permittivity, heat capacity, phase transition latent heat, and thermal conductivity (Table 1).

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This unusual macroscopic behavior can be explained by water's molecular structure (Franks, 2000). The composition of water (two parts hydrogen to one part oxygen) was discovered by Henry Cavendish (1731–1810) in about 1781. He reported his findings in terms of phlogiston (later the gas he made was proven to be hydrogen) and dephlogisticated air (later this was proven to be oxygen). Since then, countless studies have been done to clarify the structure of water and interactions between water molecules. For a review of the development of the structure of water, see Wallqvist and Mountain (1999).

Each hydrogen atom of a water molecule shares an electron pair with the oxygen atom. The outer electron orbitals of the oxygen atom have a hydrogen atom at each of two corners bound with covalent bonds and unshared electron pairs at the other two corners. The O–H bond length is 0.0958 nm and the H–O–H bond angle is 104.27° (Franks, 2000), very close to

Table 1 Comparison of properties of low molecular weight compounds

Compound	Molecular weight	Boiling point (°C) @ 760 mm. Hg	Surface tension (Dynes/cm) @ 20°C
Water (H ₂ O)	18	100	73
Hydrogen Sulphide (H ₂ S)	34	-60	(a)
Ammonia (NH ₃)	17	-33	(a)
Methanol (CH ₃ OH)	32	65	22
Ethanol (C ₂ H ₅ OH)	46	78	22
Ether (C ₂ H ₅ OC ₂ H ₅)	74	34	17

Source: <http://www.aquadyntech.com/h2ophysprop.html>

the 109.5 of a perfect tetrahedron (Hasted, 1972). Sharing the electron between H and O is unequal because the oxygen nucleus attracts electrons more strongly than does the hydrogen nucleus and becomes more electronegative. This unequal sharing causes two electric dipoles in the water molecule; the oxygen atom bears a partial negative charge ($2\delta^-$) and each hydrogen a partial positive charge (δ^+) (Martin and Zipse, 2005). As a result, there is an electrostatic attraction between the oxygen atom of one water molecule and the hydrogen of another, called a hydrogen bond.

The nearly tetrahedral arrangement of the orbitals about the oxygen atom allows each water molecule to form hydrogen bonds with as many as four neighboring water molecules. However, water molecules are disorganized and in continuous motion, so that each water molecule forms hydrogen bonds with an average of only 3.4 other water molecules (Fennema, 1996). The clustering ability of water molecules is apparently quite temperature sensitive (Starzak and Mathlouthi, 2003), with tetramers and pentamers suggested to dominate at room temperature, and monomers and dimers increasing as temperature increased.

Hydrogen bonds are stronger than van der Waals interactions, although they are weaker than covalent bonds. The hydrogen bonds in liquid water have a bond dissociation energy (the energy required to break a bond) of about 5 kcal/mole, compared with 0.3 kcal/mole for van der Waals interactions and 100 kcal/mole for the covalent C–C bond (Stillinger, 1980). However, in addition to water's large dipole moment, its ability to engage in multiple hydrogen bondings on a three-dimensional basis can explain its large intermolecular attractive forces (Nelson and Cox, 2000).

Understanding Water in Confections and Foods

Water is one of the most important components of confections, and of most foods. The nature of water bonding with food components and its interaction with the surrounding atmosphere affects the physical or textural characteristics of the food product as well as the food's shelf stability. Our understanding of the behavior of water in confections (and all foods) has grown over the years, progressing from the use of water content to water activity and more recently, to the principles of water mobility (and glass transitions).

In sugar-based confections, the water content is generally governed by the boiling point relationship of the sugars present

in the formulation. The final water content has a significant impact on texture and shelf life, with lower moisture content leading to harder confections that typically have longer shelf life. However, water content by itself is not sufficient to completely characterize candy quality and shelf life. Water activity, or the relative vapor pressure, of the confection is an important parameter often used to describe microbial stability, texture, and water migration during storage.

The relative vapor pressure was first defined and used as an indicator of stability of foods by Grover (1947). Relative vapor pressure, h , was defined as the ratio of the vapor pressure of the material (P) to the vapor pressure of pure water (P_i).

$$h[\%] = \left(\frac{P}{P_i} \right) 100 \quad (1)$$

Grover (1947) claimed that one can determine whether a food either gains or loses moisture based on this relative vapor pressure.

In the 1950s, Scott (1957) introduced the term "water activity" as a measure of water "availability." He claimed that "water availability," not moisture content alone, determines the stability of foods. Water activity, a_w , which in foods is often given as the ratio of the vapor pressure of water above the food, p_w , to the vapor pressure of pure water at the same temperature, p_w^0 , indicates the degree to which water is associated with food components (not available to escape from the surface) and consequently, its availability to act as a solvent and contribute in physical, chemical, and microbiological processes. Several physical principles play a role in understanding the "states" of water in foods, including the colligative effect, capillary forces, and surface interactions (Lilley, 1994).

Water availability in foods depends on the type of solutes and their concentrations, and affects physical properties such as freezing point, boiling point, vapor pressure (water activity), and density (Kuprianoff, 1958; Gur Arie et al., 1967). These properties represent the colligative effect, where solute molecules reduce the chemical potential and escaping tendency (fugacity) of water molecules (Levine and Slade, 1988; Bell and Labuza 1984).

Furthermore, foods may contain pores or capillaries in which water can exist (Blustein and Labuza, 1972). The change in hydrogen bonding between water molecules as a result of surface curvature affects the escaping tendency and chemical potential of water (Bell and Labuza, 1984). The direct interaction

with other chemical groups on molecules through dipole-dipole forces, ionic bonds, dipolar-ionic interactions, van der Waals forces, and hydrogen bonding also reduce the escaping tendency and chemical potential of water (Bell and Labuza, 1984).

In the past, these properties led to characterizing water as either “free” or “bound” (Shanbhag et al., 1970). Kuprianoff (1958) suggested that measuring the amount of unfreezable water at sub-freezing temperature was the most accurate way of measuring “bound” water in foods, as did Meryman (1966) in a subsequent study. Sorption behavior (Labuza and Rutman, 1969; Berlin et al., 1968), drying rate studies, and NMR studies on the state of water (Shanbhag et al., 1970; Mousseri et al., 1974) correlated very well with the idea that water in foods was either free or bound (Leung and Steinberg, 1979), lending greater credence to this interpretation.

To obtain comprehensive data on the water relations of food, the water content equilibrated at a range of relative humidities are determined and water sorption isotherms constructed (Duckworth, 1974). Figure 1 shows a generalized water sorption isotherm, with distinct regions being noted. The behavior of these different regions suggests that they have different types of water (Troller and Christian, 1978; Fennema, 1996). Monolayer water in region I is very stable, behaving in many ways as part of the food solid and is believed to be nonfreezable at any temperature (Duckworth, 1974). Thus, water in region I is often called “bound water.” On the other side, water in region III is called free water (Troller and Christian, 1978; Fennema, 1996) because the energy required for vaporization is similar to that of pure water.

More recently, the molecular mobility approach has been used to understand the role of water in foods (Fennema, 1996). In the 1960s, several researchers had begun investigating the amorphous/glassy state of sugars (White and Cakebread, 1966; Makower and Dye, 1956). However, it was not until the 1980s, that Levine and Slade (1988) popularized the polymer science approach to food science, documenting that the glass transition temperature (T_g) had significant ramifications on food stability.

Solid confections can either be in the thermodynamically stable crystalline state or in an amorphous state. Regions in

the amorphous state can exist in a rubbery or glassy state. The temperature where the regions change from glassy state to rubbery state (and vice versa) is called the glass temperature of the food (Slade and Levine, 1987, 1991). When foods go through the glass transition, their thermodynamic properties, molecular mobility, dielectric constants, and mechanical properties change (Sperling, 1986). Many foods exhibit a specific glass transition temperature, or more correctly, the transition occurs over a range of temperatures. Recent studies have applied these principles to confections.

In the following sections, the concepts discussed above are developed further with specific application to confectionery products.

WATER CONTENT

Water in confections is necessary for processing of the raw materials into finished products. It affects product texture and is one of the primary factors affecting shelf life.

One of the main functions of water in confectionery formulas is to dissolve the ingredients and help with mixing. In most candies, the water is used to dissolve and prepare the slurry of sugar and corn (glucose) syrup. Depending on the method of cooking, between 20 and 35% of water by weight of sugar solids is required to dissolve the slurry. However, less water can be used for quicker evaporation if the sugar can still be dissolved properly, for example, by use of pressure dissolvers to maintain liquid water at elevated temperatures. Sometimes no water is added, which is the case when liquid sugar and corn syrup is used for syrup preparation, since no extra water is needed for dissolution.

The properties of water used as a confectionery ingredient are also critical for the quality of the product. For example, the pH of water used in confections should be carefully controlled. Acidic water, with pH less than about 6, can lead to an increase in reducing sugars during cooking since inversion is promoted at high temperatures and low pH (Atkinson et al., 1952). Excessive inversion can cause discoloration of the cooked syrup and stickiness of the final product.

Water is also important in determining texture, whether of a hard or soft candy (Jackson, 1995). Confections typically have relatively low water contents, at least compared to many other food categories. Water content may vary from as high as about 30% in sugar syrup confections to as low as 1–2% in hard candies. Table 2 provides an approximate range of moisture content for a wide variety of confections. As can be seen, some candy categories span quite a wide range of water contents. Caramel, for example, can have water content as low as 4–5% in a caramel-type hard candy or as high as about 18% in very soft, fluid caramels. In this case, water content has a distinct impact on the texture of the caramel. In hard candies, high water content can potentially lead to graining or stickiness, softer texture, and faster flavor loss, whereas very low water content may give a hard and brittle texture. In fondants, a change in moisture content affects the amount of soluble sugars and thus, the proportions

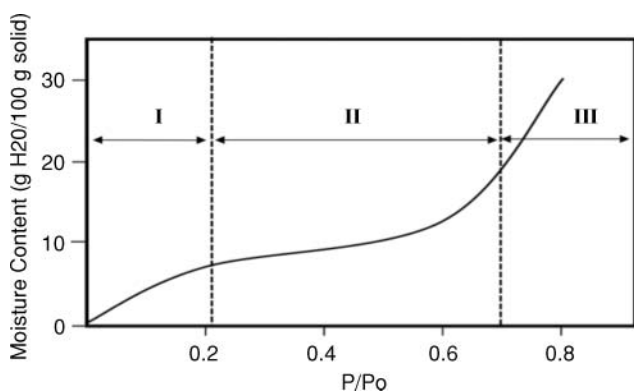


Figure 1 Typical moisture sorption curve for foods showing the different regions of water (I, bound water; II, intermediate; III, free water). (adapted from Fennema, 1996).

Table 2 Range of water content and water activity (a_w) in confections (adapted from Bussiere and Serpelloni, 1985)

Category	Crystallinity ^a (%)	Moisture (%)	a_w
Hard candy	0–2	2–5	.25–.40
Caramel, fudge, toffee	0–30	6–18	.45–.60
Chewy candies	0–10	6–10	.45–.60
Nougat	0–20	5–10	.40–.65
Marshmallow	0–20	12–20	.60–.75
Gummies and jellies	0	8–22	.50–.75
Jams	0	30–40	.80–.85
Fondants and creams	35–55	10–18	.65–.80
Chewing gum	30–40	3–6	.40–.65
Soft panned coating	60–75	3–6	.40–.65
Hard panned coating	80–95	0–1	.40–.75
Tablets and lozenges	75–95	0–1	.40–.75

^aEstimated.

of crystalline sugar versus sugar dissolved in solution (Hartel, 2001).

Water Content Determination Methods

Numerous methods have been used to quantify the amount of water in a food, from simple drying methods to more sophisticated spectroscopic analyses. However, three categories of methods, loss on drying, Karl Fischer titration, distillation and refractometry, are mainly used in the confectionery industry (Beard, 2001). A brief description of these methods, and their variants, for measuring water in confections is provided here.

Loss on Drying

Despite its downfalls, oven drying is one of the most common methods used to measure water content in foods and especially confections. A weighed food sample is placed in an oven at elevated temperature, from 100 to 135°C (Beard, 2001). The temperature should be high enough to promote drying as quickly as possible without being too high that the water boils or the sample degrades in some other way. The sample stays in the oven until there is no change in weight between two subsequent readings. The weight difference through the heating time gives the water content of the sample.

The period of drying and heating temperature must be specified for each type of product; for example, it takes 3 h at 105°C for sugar (Mathlouthi, 2001). Choice of drying conditions (temperature, pressure) is critical since improper control of conditions can lead to variability in results (Isengard, 1995, 2001; Isengard et al., 2001). Incomplete removal of water and the loss of volatiles other than water may also lead to inaccurate results (Beard, 2001). Other sources of error include the formation of a crust at the surface of the product, which slows down the escape of water, and decomposition due to the Maillard reaction or caramelization of sugars, which produce water (Mathlouthi, 2001; Troller and Christian, 1978). Decomposition compounds

produced during the measurement may increase the weight loss during drying and make the measurement less accurate. Using low temperature during drying to avoid decomposition is possible, but then the energy may be insufficient for water to be liberated from the sample. Oven drying remains an official method, mostly because it is simple and can be carried out in every analytical laboratory (Isengard, 2001; Isengard, 1995). Variations of the oven drying method have been developed to obtain more accurate measurements and in shorter times.

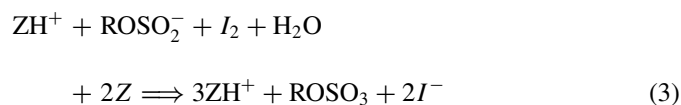
Vacuum-oven drying is based on the weight loss during heating under reduced pressure and at lower temperature (70°C) for longer time (6 h) (Troller and Christian, 1978). The method is less destructive for heat sensitive products than atmospheric drying (Mathlouthi, 2001). However, the duration of drying must be sufficiently long to allow the sample to come to steady state (Makower and Myers, 1943). In addition, particle size distribution and air flow may affect reproducibility of results (Troller and Christian, 1978).

Other drying techniques have been used to enhance drying and minimize negative changes. Majonnier-style drying involves adding a small amount of water to the sample to prevent hardening during drying at high temperatures. Caramel and sweetened condensed milk are examples of products that might harden at high temperature. Adding a small amount of water helps to prevent hardening and allows water to more readily leave the sample (Beard, 2001). Two-stage drying is a method where two different temperatures are applied to the sample to prevent the formation of crust on the sample surface. Application of a lower temperature initially to remove surface moisture followed by a higher temperature to remove interior moisture is the basis of the method (Beard, 2001).

The use of more efficient heating sources can also enhance drying, although water left in the sample and volatile losses may again be reasons for inaccurate measurements (Isengard, 2001). Thermal radiation supplies efficient heating and therefore, water is liberated more rapidly from the sample (Isengard and Prager, 2003). Infrared drying was compared with the Karl Fischer method (next section) and oven drying on products with high sugar content (Isengard and Prager, 2003). They found that infrared drying results were not as accurate as the results from the Karl Fischer method. Halogen drying is a relatively new version of infrared drying. It reduces drying time due to more efficient heating while it provides the high temperature necessary to liberate water from sugars—as polar substances they have strong interaction with water (Heinze and Isengard, 2001). However, formation of volatiles and crust on the sample surface still may cause error in readings (Heinze and Isengard, 2001). Microwave energy may also be used as a heating source to shorten drying time (Heinze and Isengard, 2001).

Karl Fischer Titration

The Karl Fischer method of water measurement is based on a two-step chemical reaction to identify water.



In the first step (Eq. 2), sulfur dioxide is esterified with alcohol reagent (methanol/formamide), and the ester is neutralized by base (Z) to yield alkyl sulphide. In the second step, iodine oxidizes alkyl sulphide in the presence of water. I_2 is used as a titrating reagent for the determination of "end-point." When all the water is consumed, iodine cannot react and is present in the solution with iodide. The existence of the redox couple iodine/iodide corresponds to the redox reaction at the electrodes, which are submerged in the working medium and cause the voltage to drop sharply. The dramatic drop indicates "the end-point" (Mathlouthi, 2001; Isengard, 2001; Isengard and Heinze, 2003).

The Karl Fischer method is useful for the analyses of dried fruits and vegetables, candies, roasted coffee, and fats (Pomeranz and Meloan, 1994). Although Karl Fischer titration is not as rapid as some other methods (e.g., NMR or NIR spectroscopy), it is still considered to be a fast method (20–25 minutes) and can be used in on-line processing (Isengard, 1995, 2001; Beard, 2001). The reagent reacts only with water, which eliminates the error coming from detection of the volatile constituents (Knetchel Laboratories, 1969; Beard, 2001). However, a shortcoming of the method is that results are affected by type of sample and particle size (Troller and Christian, 1978). Another problem can arise if water does not contact directly with the KF reagent, which can occur if the sample is insoluble. Instead of the total water content, only the surface water may be measured. The liberation of all water in the sample can be accomplished by addition of an appropriate solvent (i.e., methanol, formamide, etc.), reducing the particle size or elevating the temperature (Schoffski, 1998; Wunsch and Grunke, 1998).

Karl Fisher titration has been found to be reliable and sufficiently rapid (Supartona and Isengard, 1998). It is widely used for confectionery applications.

Refractometer

For fluid systems, like sugar syrups, measurement of the refractive index of the sample allows determination of water content (inverse of solids content). As light changes velocity (direction and speed) when it goes through any substance, refractive index, or the ratio of the velocity of light in a vacuum to its velocity in the sample (Pancoast and Junk, 1980), can be used to determine the percentage of dry substance and therefore, the moisture content of the sample (Beard, 2001; Minifie, 1970). However, the calibration between the refractive index and the concentration of dry substances depends on the type of dissolved material (Pancoast and Junk, 1980). For pure sucrose solutions, the refractive index is directly correlated to concentration so that the refractometer scale reading can be given directly

in concentration (weight percent). The refractive indices for a variety of confectionery sugars are compiled in Pancoast and Junk (1980).

However, most confectionery syrups of interest contain mixtures of sucrose and other sweeteners (e.g., corn syrup, invert sugar, etc.). In this case, the refractive index of the solution depends on the relative ratios of the component ingredients. Pancoast and Junk (1980) have prepared tables in which the correlation between the refractive index of different products and the solid content is given.

Since most refractometers read in a scale of sucrose weight percent, the readings off a refractometer used for confectionery sugar mixtures give slightly erroneous results. When refractometer readings are used directly for measuring concentration of confectionery mixtures, the scale reading is more correctly termed °Brix to represent the equivalent sucrose concentration of a syrup with that refractive index. °Brix values do not represent the exact total solids (or water) content, with the errors increasing when less sucrose is present in the mixture. For many confectionery applications, no correction factors are used and °Brix is assumed to be sufficiently close to the true total solids concentration (and water content by difference).

Although using a refractometer is a very rapid method (less than three minutes) (Beard, 2001), it requires samples to be homogenous and representative to give accurate results. The refractive index is also very sensitive to temperature (Beard, 2001), so to be most accurate, the refractometer should always be used at a consistent temperature.

Spectroscopy

Spectroscopic methods for measurement of water are based on food properties when the sample is exposed to electromagnetic radiation. The common spectroscopic methods, Nuclear Magnetic Resonance (NMR), Near Infrared (NIR), and Microwave (MW), are explained briefly in the following sections.

Nuclear Magnetic Resonance (NMR) Spectroscopy. The NMR spectroscopy was first used for water determination in foods by Bloch et al. (1946) and Purcell et al. (1946). With the appearance of commercial instruments, the use of NMR in the determination of water content in foods rapidly increased (Shaw et al., 1953; Shaw and Elskén, 1953, 1956).

NMR spectroscopic measurement of water content is based on the measurement of magnetic properties of hydrogen atoms in water. In an external magnetic field, the spin axes of these hydrogen nuclei are oriented in a specific direction by the applied field. When exposed to superimposed radio-frequency pulses of a specific frequency, the protons absorb energy and spin slightly off-axis. Between pulses, the protons release this absorbed energy, and the cycle of energy absorption and emission, known as resonance, characterizes the protons of the molecular species. The NMR resonance spectrum of a hydrogen atom in a water molecule is different from that in a carbohydrate or protein molecule. Characterization of the proton spectrum for water in a food leads to quantification of the water content of

the sample (Troller and Christian, 1978; Ruan and Chen, 1998). Since “bound” water exhibits a broader signal than free water, this technique is more adapted to distinguish between free water and bound water than for the accurate determination of water content (Troller and Christian, 1978; Mathlouthi, 2001). Precise calibration of the water content of the analyzed product based on a good reference method is needed (Mathlouthi, 2001).

Advantages of NMR techniques for measurement of water content include (Ruan and Chen, 1998) that it is a rapid, nondestructive, and noninvasive method, it requires less sample preparation than other methods, it offers the possibility of automation because data acquisition can be real-time and data are electronic signals, and provides simultaneous determination of moisture and fat content. However, NMR is rarely used for water determination due to its high price (Isengard, 1995).

Near Infrared (NIR) Spectroscopy. The NIR measurement of water content is based on the absorption of electromagnetic energy by water molecules at different wavelengths (1950 and 1450 nm) (Vornhof and Thomas, 1970; Mathlouthi, 2001). Water gives signals at 1450 and 1940 nm, based on different vibrational modes, which are used to quantify the water content (Isengard, 2001). However, a product-specific calibration is the key to accurate moisture measurement (Isengard, 2001). Color, particle size, thickness, and texture of the product can influence the results (Mathlouthi, 2001), so great care is needed in sample preparation. One potential disadvantage is that only surface water may be measured, giving inaccurate results for the water content of the whole product (Mathlouthi, 2001).

Microwave Spectroscopy. The use of microwave spectroscopy for measurement of water is based on the dipolar character of the water molecule. The sample is placed between the receiver and emitter parts of the microwave and the water content of the sample can be correlated to the shift in wavelength and decrease in intensity (Isengard, 1995).

Parameters that affect measurement of water content by microwave spectroscopy include thickness and density of the sample. Thus, the method is more suitable for measuring mobile water than crystallization water or bound water (Mathlouthi, 2001). The application of microwave spectroscopy for measuring water content in confections is not widespread.

Dielectric Techniques

Different foods have molecules with different polarities, which can be oriented by means of an external field. The dielectric constant of water (80) is quite different from most food

components (protein: 4–6; fats: 2–5) (Breen and Monaghan, 1975) so that an empirical calibration for dielectric constant, based on a primary measurement method, can be used to measure water content of a food.

Breen and Monaghan (1975) measured the water content of licorice candy by using a dielectric technique calibrated by oven drying. The accuracy of the technique was verified by a good correlation between the two methods.

The advantage of dielectric measurement of water content is that, after calibration, it is a very rapid method (Beard, 2001). However, there are several factors that potentially limit its usage. For example, the moisture range of the sample must be between 0 and 50%, and the sample should not have any components with high dielectric constant (Breen and Monaghan, 1975).

COLLIGATIVE EFFECTS

The presence of a solute in a solvent can lead to changes in physical properties of that solution. These physical properties, vapor pressure, boiling point, osmotic pressure, and freezing point, are known as the colligative properties. The word colligative, which comes from the Latin word *colligatus* meaning “bound together,” is used to show that these properties are all interrelated. In ideal solutions, the degree of change in colligative properties is only proportional to the mole fraction of the solute (Walstra, 2003).

The two colligative properties of particular importance to the confectioner are water activity, or relative vapor pressure, and boiling point elevation.

Water Activity

Water activity, a colligative property based on the number and size of molecules dissolved in water, is primarily influenced by the presence of dissolved sugars, other sweeteners (e.g., polyols), salts (e.g., caramel), and humectants in confections. It has been used for many years to characterize physicochemical properties and microbial stability of foods. It is widely accepted that microbial growth is directly related to water activity (Table 3), with certain types of microbes unable to grow when water activity is below some critical value. Fortunately, water activity in confections (Table 2) generally falls below the critical values for microbial growth, with few exceptions. Therefore, the end of shelf life due to microbial growth in confections

Table 3 Growth of microorganisms dependent on water activity (a_w)

Water activity range	Microorganisms that can grow	Confections
>0.88	Normal bacteria and pathogens, many yeasts	Ganache, very soft fondant
0.80–0.88	Normal molds, some yeasts	Soft fondant, soft jellies, etc.
0.70–0.80	Molds, yeasts	Fondant, fudge, jellies, grained nougats, marshmallow, etc.
0.60–0.70	Osmophilic yeasts, some molds	Fudge, fondant, hard jellies, nougat, soft caramel, etc.
<0.60	None	Caramel, toffee, jellies, gum, hard candy, chocolate, etc.

Sources: Beuchat (1981), Fontana (2006), Minifie (1999).

is generally not an issue. However, the end of shelf life due to moisture loss or gain, with subsequent changes in textural and other properties, is often the main problem in confections. Thus, an understanding of water activity is important for control of shelf life and stability.

Thermodynamic Definition of Water Activity

In the food industry, water activity is generally defined as the ratio of the vapor pressures of the food to that of pure water (Nielsen, 1998; de Man, 1999). However, thermodynamically, the ratio of vapor pressures is not the true thermodynamic water activity under all conditions and is often incorrect in many conditions of importance to shelf life of foods and confections.

Thermodynamically, water activity, a_w , is the ratio of chemical potentials, often simplified to the ratio of fugacities (Reid et al., 1987; Sereno et al., 2001):

$$a_w(T, P, x) = f_w(T, P, x) / f_w^o(T, P^o) \quad (4)$$

where, f_w is the fugacity of the water in the food with mole fraction of water, x , and f_w^o is the fugacity of pure water at the same temperature, T , and pressure, P . Fugacity is sometimes called the “escaping tendency,” indicative of the ability of the molecule to escape from the food surface.

Under conditions where there is equilibrium between water in the food and the air, and assuming ideal solutions, the fugacity ratio can be expressed as a ratio of vapor pressures to give the commonly accepted form for water activity, a_w (Sereno et al., 2001; Nielsen, 1998; deMan, 1999):

$$a_w = p_w(T, P, x) / p_w^o(T, P) \quad (5)$$

where, p_w is the vapor pressure measured in the air above a food and p_w^o is the vapor pressure of pure water at the same temperature and pressure.

Again, Equation (5) is not true under all conditions since it assumes ideal solutions and complete equilibration between water in the food and water in the air. At the high sugar contents found in confections, neither assumption may be true. The ability for the water in the confection to truly equilibrate with the air surrounding it depends on the ability of the water molecule to migrate/diffuse within the confection. In hard candy, for example, it is doubtful that sufficient time can ever be allowed for the water to completely equilibrate between candy and air. The same is probably true, although to a lesser extent, for hard, amorphous candies like caramel and toffee. Grinding these candies into a fine powder provides the best opportunity to expose the maximum surface area to the air and allow near equilibration.

Despite limitations to the water activity approach at low water content, it is widely used in the food industry, and as long as the limitations are recognized, water activity can still provide

useful information. For example, a difference in water activity between two components of a confection will lead to moisture migration until the two components have attained approximately the same water activity. Moisture migration occurs to alleviate the thermodynamic difference until equilibrium (equal chemical potentials) is reached.

Equilibration in moisture between the confection and the surrounding air space (both within a package and external to the package) also occurs. Since water activity is the ratio of vapor pressures, it is in the same general form as relative humidity (RH) of the air. Typically, water activity is used to predict an Equilibrium Relative Humidity (ERH), or the RH at which the candy neither gains nor loses water from the air. ERH is then given as (Nielsen, 1998):

$$\text{ERH}(\%) = a_w(100) \quad (6)$$

Again, ERH is the relative humidity at which the product does not gain or lose moisture to the air surrounding the confection (Jackson, 1995). If the surrounding atmosphere has a different RH from this value, the confection will either gain or lose moisture as it strives to equilibrate with the air.

Packaging is, in part, designed to protect the confection from moisture gain or loss to the surrounding environment. Many confections, such as hard candies, gum, and caramels, are wrapped individually and then bagged in an overwrap package. This provides two layers of protection against moisture migration, at least until the package is opened. Other confections, such as candy bars, however, have only a single package layer protecting it from the environment. Equilibration between moisture in the candy and the air within the package occurs rapidly with slower equilibration of moisture between the internal air space and the outside, ambient air depending on the barrier properties of the package layer.

Prediction of Water Activity

Over the years, numerous methods have been developed to calculate or predict water activity of confections. Many of these methods have been reviewed by Teng and Seow (1981), Vega-Mercado et al. (1994), and more recently by Sereno et al. (2001). Methods to calculate water activity include

- (1) completely empirical approaches,
- (2) semi-empirical approaches based on thermodynamic principles, and
- (3) the local composition models where solution properties are calculated from group contribution methods (Sereno et al., 2001).

Recent developments in predictive methods for water activity have been primarily in the area of solutions used for osmotic dehydration (Sereno et al., 2001), which generally contain

mixtures of sugars and salts. This discussion will focus on those predictive methods most relevant to confectionery systems.

Empirical methods. One of the first methods (if not the first) of predicting water activity in confectionery products was developed by Grover (1947). In this empirical approach, the relative vapor pressure (or equilibrium relative humidity) was calculated by first summing the contributions of each of the ingredients in the confection to give an equivalent sucrose concentration, E_s , according to an equation of the form:

$$E_s = \sum cf \quad (7)$$

where, c is the concentration of each ingredient and f is an empirical conversion factor appropriate for each ingredient. The relative vapor pressure was then determined from a table that contained sucrose concentration effects on relative vapor pressure.

Another well-known empirical equation for predicting water activity of sugar syrups is that developed by Money and Born (1951). In a similar manner as Grover (1947), different sugars were assigned empirical parameters that were used to calculate equilibrium relative humidity of various sugar mixtures. The equation gave a reasonable fit to experimental values of relative vapor pressure over a narrow range of sugar concentrations, but for some reason predicted 104% RH for 100% water and went to infinity at 0% water.

Over the years, these empirical methods did not gain much favor in predicting water activity in confections, in part, because more accurate methods have been developed since then.

Semi-Empirical Models. One of the most common, and most successful, methods for predicting water activity in confections is the method originally developed by Norrish (1964, 1966). This model is based on the thermodynamic definition of water activity as related to molar concentrations of confectionery syrups, but uses an empirical fitting of interaction parameters based on experimental data. In this sense, the method of Norrish is often called a semi-empirical model for predicting water activity. The Norrish equation for prediction of ERH is (Norrish, 1964):

$$\log(\text{ERH}) = \log(x_w) - \sum [(-K_i)^{0.5} x_i]^2 \quad (8)$$

Here, x_w is mole fraction of water in the solution, the x_i are mole fractions of each contributing ingredient in the mixture and $(-K_i)$ are the empirical constants determined by Norrish (1966). To use the Norrish equation, K values for confectionery ingredients must be known along with molecular weight of each component (to determine mole fractions). Since glucose syrup is a complex mixture of saccharides without a unique molecular weight, Norrish (1964) provided K values and average molecular weights for a range of glucose syrups (Table 4).

The K values as given by Norrish (1964) show some interesting correlations between the behavior of the ingredient with

Table 4 Empirical parameters (K) and molecular weight (MW) of confectionery ingredients for use in the Norrish equation (Norrish, 1964)

Ingredient	$-K$	MW
Sucrose	2.60	342
Glucose syrup (42 DE)	2.31	460
Glucose syrup (64 DE)	1.96	353
Invert sugar, glucose, fructose	0.70	180
Sorbitol	0.85	182
Glycerol	0.38	92
Propylene glycol	0.2 ¹	76

¹Value from Bussiere and Serpelloni (1985).

respect to lowering water activity. As predicted thermodynamically, ingredients with lower molecular weight have lower K values, indicative of their greater effect in lowering water activity. It is clear from the K values in Table 4 why sorbitol and especially glycerol are such effective humectants in that they lower water activity significantly even at relatively low usage levels in a confection.

Chirife et al. (1980), studying sugar and polyol solutions, refined the method of Norrish (1966) and published a slightly revised set of K values for the Norrish equation, as shown in Table 5.

Comparing the K values for sucrose, glucose, and glycerol between the two studies, Chirife et al. (1980) found slightly higher values than Norrish (1966). The Chirife et al. (1980) values have generally been considered as more accurate.

One issue with the use of the Norrish equation is how to handle corn (glucose) syrups. Rather than add the contributions of each class of saccharide contained in these common sweeteners (glucose, maltose, maltotriose, higher saccharides, etc.), corn syrups have traditionally been taken as a single ingredient and assigned some average characteristic effect. Norrish (1966) assigned different K values to each corn syrup, dependent on the extent of hydrolysis of the starch (DE, or dextrose equivalent). The average molecular weight was given by the following equation:

$$\text{MW} = 660 - 4.8(\text{DE}) \quad (9)$$

Table 5 Values of Norrish constant, K , as given by Chirife et al. (1980)

Ingredient	K^1
Sucrose	2.81
Maltose	1.97
Glucose	0.98
Xylose	0.67
Sorbitol	0.72
Erythritol	0.58
Glycerol	0.50
Mannitol	0.39

¹Note that Chirife et al. (1980) provide K values in terms of a natural log expression, rather than the \log_{10} expression of Norrish (1966). K values here are converted to the Norrish form.

The dependence of the K values provided by Norrish (1966) on DE was given as (Bussiere and Serpollini, 1985):

$$K = 0.019(\text{DE}) - 3.173 \quad (10)$$

Bussiere and Serpollini (1985) also developed their own expression for K values and average MW of corn syrups, and found slightly different results from Norrish (1966). Their expressions were given as:

$$\text{MW} = 552 - 3.64(\text{DE}) \quad (11)$$

$$K = 0.02(\text{DE}) - 3.28 \quad (12)$$

Differences between the studies may arise from

- (1) more sophisticated methods of a_w measurement by Bussiere and Serpollini (1985) or
- (2) use of slightly different glucose syrups.

It is well known that manufacturing methods for glucose syrups can differ and the starting starch material can be different, both of which may result in different saccharide profiles for the same DE. Perhaps a future goal might be to better characterize the effects of saccharide profile in corn syrups on water activity. Until then, prediction of water activity of confections with substantial quantities of glucose syrups based on the Norrish equation is likely to be relatively inaccurate and therefore, calculated values must be taken only as estimates of the true values.

Confectionery products often contain more than just sweeteners, with ingredients such as stabilizers (proteins, gelatin, starch, pectin, etc.), dairy ingredients (sweetened condensed milk, evaporated milk, etc.), and lipids (butter, vegetable fats, etc.). The influence of these ingredients on water activity of complex confections has not been studied in any detail, yet has substantial commercial importance. Ross (1975) considered the effects of various "nonsolute" ingredients on water activity of intermediate moisture foods, but did not discuss confections in particular. This is another area of interest where additional work is needed to develop accurate predictive models.

Local Composition Contribution Methods. Water activity, as well as other thermodynamic properties, can be predicted given sufficient understanding of the molecular interactions occurring in solution. Such approaches to prediction of solution equilibria are often called group contribution methods because they use characteristic interaction parameters of the chemical groups on the different molecules (LeMaguer, 1992; Sereno et al., 2001). For example, Leschke (1987) used a thermodynamic interaction parameter approach to predict boiling point elevations of sugar solutions.

The method most often used to predict thermodynamic properties of sugar solutions is the UNIFAC (UNIQUAC functional group activity coefficients) method. This method accounts

for molecular size, shape, and energies of interaction between molecules in proximity in the solution (Le Maguer, 1992; Sereno et al., 2001). These interactions are what determine the thermodynamic properties like water activity, osmotic pressure, and boiling point temperature.

The UNIFAC model has been used to characterize thermodynamic properties of various sugar solutions, although none have been directly applied to confectionery systems. Catte et al. (1995) studied aqueous solutions of glucose, mannose, galactose, fructose, sucrose, lactose, and maltose. However, no mixtures were studied, just pure aqueous solutions of these sugars. Peres and Macedo (1997) used the UNIFAC model to calculate water activity of glucose, fructose, and sucrose and found good agreement with experimental data, although values for the sucrose-water system had relative deviations of 9%. They were also able to successfully predict water activity values for ternary and quaternary mixtures of these sugars, extending this approach to more commercially relevant confectionery syrups. Ninni et al. (2000) extended the UNIFAC model to calculate water activity in polyol solutions.

Future improvement in group contribution methods may eventually lead to their use for accurately prediction of water activity (and boiling point elevation) for complex confectionery mixtures.

Measurement of Water Activity

A variety of methods have been developed to measure water activity of foods and confections (Troller and Christian, 1978; von Elbe, 1986). Kilara (1981) states that "the desirable" water activity method would be accurate, reproducible, sensitive, rapid, durable, portable, usable, and low-priced.

Proper sample preparation is a critical concern for accurate water activity measurement in many confections, particularly those that rapidly gain or lose moisture to the environment. Typically, the sample to be measured must be ground to expose interior surfaces and allow more rapid equilibration. However, sample preparation of certain types of confections (e.g., hard candy) under humid conditions can lead to inaccurate measurements. Careful control of humidity to avoid moisture gain or loss between sample preparation and measurement is required.

Hygrometry. Hygrometry is a method used for calculating water activity by measuring humidity of the air directly in contact with the sample. Different hygrometers are based on the responses of certain materials to moisture.

Hair hygrometer. The hair hygrometer method is based on the principle that the length of a hair changes as the keratinaceous protein of the hair absorbs moisture from the air. Three or more strands of hair (horse, human, etc.) are fixed at one end of the unit and the other end is connected to a sensitive arm attached to a recorder pen or a dial (Troller and Christian, 1978). The food is placed in the chamber with the hair, and the reading gives equilibrium relative humidity (or water activity times 100) by the correlation of the change in the length of hair (Troller and Christian, 1978).

Equilibrium conditions require sufficient time; however, this time can be shortened by circulating air through the system. Although, hair hygrometers lack sensitivity (only good to 0.03 a_w) they are useful for range-finding and for a rough estimation of water activity (Troller and Christian, 1978). Low cost is an advantage of using the method.

Electronic hygrometer. Electronic hygrometry is based on the measurement of conductivity or resistance of a hygroscopic salt in equilibrium with the surrounding atmosphere. The salt's ability to conduct electricity is measurably changed as moisture is absorbed or desorbed by the salt (Troller and Christian, 1978). The instrument has a sensor, a sample chamber, and a potentiometer. According to the water activity of the sample in the chamber, a hygroscopic material, usually LiCl or sulfonated polystyrene, in the sensor gives different conductivity or resistance. The sensor works as an electric transducer and changes in capacitance are read in response to changes in relative humidity (Mathlouthi, 2001). The instrument must be calibrated with solutions of known a_w .

Electric hygrometry is considered precise, quick, and convenient. However, the units are relatively expensive and are subject to contamination from glycols, ammonia, acetate ions, and other organic volatiles (Kilara, 1981).

Dew Point. Dew point measurement of a_w of confections is a commonly used technique due to the convenience and short measurement times. The dew point is the temperature at which condensation of water vapor occurs (saturation is reached) as air is cooled (no change in water content). To measure a_w , an air stream in equilibrium with the food sample is directed at a cooled mirror or sight glass. A beam of light from a neon lamp is directed onto the mirror and reflected into a photodetector cell. When condensation occurs on the mirror (meaning the dew point is reached), a change in reflectance is sensed by a photodetector. The equilibrium (dew point) temperature is related to ERH through a standard relation between relative humidity and dew point temperature.

Dew point measurement gives accurate results over the entire range of a_w (von Elbe, 1986) and in a relatively short time (1–2 h). The main limitation of the dew point method is that it can be affected by certain volatiles, such as ethanol and propylene, which can co-condense on the mirror.

The accuracy and time required to reach equilibrium can be reduced by crushing, slicing, or grinding the samples, thereby exposing a greater surface area to the air. This also allows homogenization of the sample. For multi-domain foods with a center and outer coating that have different a_w , like hard candy with a chewy or gum center, the two domains must be separated prior to measurement. Also, careful control of the humidity during sample preparation is needed to ensure accurate measurements since grinding of a candy in conditions of high humidity can cause sufficient moisture sorption to give erroneous readings.

Sorption Isotherms. The sorption isotherm method is based on the determination of equilibrium relative humidity, or the point at which the sample neither gains nor loses moisture. After measuring the amount of water gained or lost by the sample

in a determined time (often only 1 to 2 hours), moisture contents are plotted against a_w . This plot intersects with the line presenting zero moisture change at the a_w value of the sample (Labuza et al., 1976; Troller and Christian, 1978). This method has provided good results for confectionery products (Smith, 1965; d'Alton, 1969), with accuracy within ± 0.02 (Sloan and Labuza, 1975, 1976). However, despite a reduction in measurement time through automation of this method, sorption isotherms are generally no longer used for measurement of a_w .

Boiling Point Elevation

The boiling point of a solution is the temperature where the total vapor pressure above the solution reaches ambient pressure. With solute addition, vapor pressure of the solution decreases and as a result, higher temperature is necessary to reach the point where total vapor pressure equals ambient pressure (Walstra, 2003). The change in boiling point, ΔT_b , or boiling point elevation, is given by (Walstra, 2003)

$$\Delta T_b = -\frac{T_{b,1}^2}{\Delta H_{v,1}} R \ln(x_1) \approx -28 \ln(x_1) \approx 0.51 m_2 \quad (13)$$

where $T_{b,1}$ is the boiling temperature of the pure solvent, ΔH_v is the enthalpy of vaporization (40.6 kJ/mol for water at 100°C and atmospheric pressure), x_1 is the solvent (water) mole fraction, and m_2 is the solute concentration (moles/L).

Literature data for boiling point temperature of sugar solutions, particularly at higher concentration, is highly inconsistent (Norrish, 1967; Jackson, 1995). This can mostly be attributed to the difficulty in measuring the exact water content at a specific boiling temperature since evaporation continues during cooling (Batterham and Norgate, 1975). Rapid cooling is essential to obtain the most accurate results. Tables of boiling point elevation for various sugar solutions of importance to confections can be found in Norrish (1967) and Pancoast and Junk (1980); however, the values at high dissolved solids contents should be used with caution for the reasons noted above.

Solute concentration and molecular weight determine the degree of boiling point elevation. Based on its lower molecular weight, glucose (dextrose) solutions boil at higher temperature than sucrose solutions of equivalent weight percentage (Jackson, 1995). For example, Fig. 2 compares the boiling point elevation of sucrose and dextrose solutions.

The effects of glucose syrup on boiling point elevation depend on the specific saccharide composition (Norrish, 1967; Pancoast and Junk, 1980). Higher DE corn syrups give higher boiling point elevation than lower DE corn syrups, but corn syrups of the same DE from different manufacturers might have slightly different boiling point elevation.

Another factor that affects boiling temperature is the pressure (Jackson, 1995). The boiling point is defined as when vapor pressure reaches ambient pressure, so changing ambient pressure affects boiling temperature, with a decrease in boiling

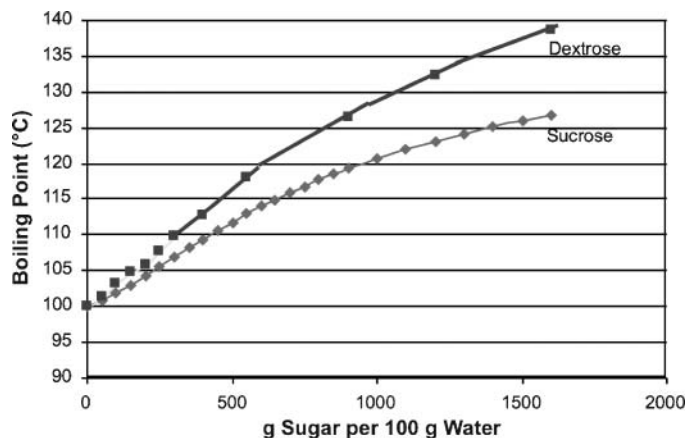


Figure 2 Boiling point elevation curves for different sucrose and dextrose concentration (plotted from data provided by Pancoast and Junk, 1980).

temperature with a decrease in vapor pressure (Fig. 3). As well understood by confectioners, boiling temperatures are reduced when cooking takes place under vacuum. However, even reduced atmospheric pressure, whether caused by a low pressure weather system or from a manufacturing facility at high elevations, can cause a significant reduction in boiling temperature. A confectioner who cooks to a specific temperature every day may wind up with small variations in water content (up to 0.5%) due to normal variations in atmospheric pressure.

Colligative Effects of Confectionery Ingredients

Each of the ingredients used in confectionery formulations has its own effect on water, dependent on the nature of the ingredient and its concentration in the final product (Cakebread, 1969). Typically, ingredients with lower molecular weight have the most effect on reducing a_w , through the colligative effect in solution, although other factors may moderate this effect.

For example, the solubility of an ingredient in water also impacts its effectiveness at reducing a_w . Components that are not soluble or that do not mix with water, do not directly affect a_w . Thus, emulsified fats, dispersed crystals, and many solid

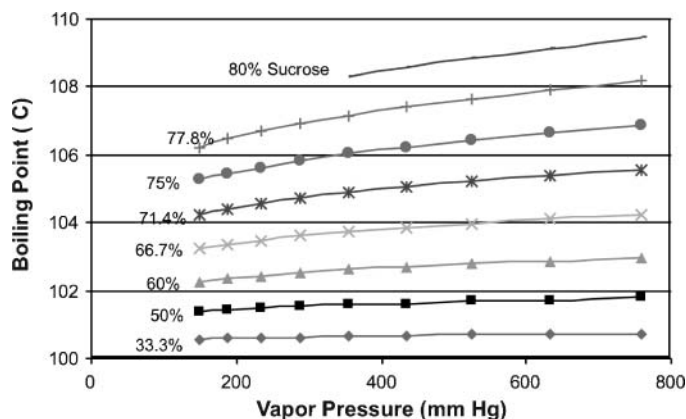


Figure 3 Boiling point elevation under different pressure (drawn from data provided by Pancoast and Junk, 1980).

Table 6 Water activity (a_w) of saturated solutions of confectionery ingredients at 25°C (from Bussiere and Serpelloni, 1985)

Ingredient	Solubility (%)	a_w
Sucrose	67.4	0.844
Glucose	51.0	0.891
Fructose	80.0	0.634
Lactose	18.7	0.931
Sorbitol	73.0	0.725
Mannitol	18.0	0.977

particulates (e.g., starch granules) typically do not affect a_w in confections. In fondant, for example, it is the liquid phase that governs water activity. Thus, the water content of the liquid phase, the dissolved solids concentration, and the nature of the solutes (humectants, etc.) found in the liquid phase determine a_w of fondant.

Ingredients with high solubility and low molecular weight have the greatest effect on reducing a_w . A_w values of common confectionery ingredients at their maximum solubility at room temperature are shown in Table 6. High molecular weight soluble ingredients used in confections, such as proteins, hydrocolloids, and gums, generally have little effect on reducing a_w .

A humectant is a substance that promotes retention of water and helps to keep a confection moist. A humectant is typically a molecule that contains hydroxyl groups with an affinity to form hydrogen bonds with molecules of water. Humectants also typically reduce a_w of a confection. Common humectants used in confections include corn syrups (especially high DE corn syrups and high fructose corn syrup), invert sugar, fructose, glucose, and polyols (propylene glycol, glycerol, sorbitol, isomalt, lactitol, mannitol, maltitol, and maltitol syrups).

WATER MOBILITY

Water activity is an equilibrium thermodynamic descriptor; however, foods are rarely if ever in an equilibrium state so that the measured properties of foods are time-dependent. This principle, in part, has led to the polymer science approach to food design, the characterization of water in terms of its mobility, and use of the glass transition to better understand performance, stability, and shelf life of many foods (Slade and Levine, 1987; 1991; Levine and Slade, 1988, 1992).

The definition of a glass was first proposed by Jones (1956) as any liquid or super-cooled liquid whose viscosity is higher than 10^{13} Poise (note that other sources say 10^{12} Pa-s; Roos, 1995). Glasses are described as regions of matter characterized by a limited order arrangement of molecules (random, with no long-scale ordering) in contrast with a crystal, which has extended regions of order (substantial long-range ordering), and a gas, which has no such regions. A glass transformation temperature, T_g , was defined as the temperature where the transformation from liquid to glass or vice versa takes place (White and Cakebread, 1966), although we now recognize that this transition usually takes place over a range of temperatures (Roos, 1995).

The importance of T_g to confections has been recognized for many years. For example, White and Cakebread (1966) discussed the correlation between glass transition and the control of moisture in hard candy and other sugar-containing food products over half a century ago. Yet, the application of T_g to understand and control moisture in food systems came with the polymer science approach, as made popular in the mid-1980s by Slade and Levine (1987, 1991).

Many foods, particularly dried foods and confections with low water content, are in the amorphous metastable state, where the material lacks long-range molecular order. The amorphous phase can be divided into the glassy state and rubbery state. An amorphous glassy material has a high internal viscosity and low internal mobility (Roos, 1995), whereas the rubbery state has a viscous, more fluid-like state. The temperature (or range of temperatures) where the transition between glassy state and a more fluid-like rubbery state occurs is the glass transition temperature (T_g) (Kauzmann, 1948).

T_g has been proposed as a physicochemical parameter that is an indicator of food properties, stability, and safety (Levine and Slade, 1992). Keeping any product at a temperature below T_g severely retards diffusion-based modes of deterioration. Above T_g , molecular mobility increases and viscosity decreases, which leads to time-dependent structural transformations such as stickiness and collapse during food processing and storage (Roos, 1995). From a kinetic perspective, reactant molecules must exhibit a minimum degree of mobility to collide with, orient toward and react with one another (Sherwin et al., 2002; Sherwin and Labuza, 2006), which occur only at dramatically reduced rates when the product is held below T_g .

The glass transition temperature depends on molecular weight, degree of cross-linking of polymer, and plasticizer (e.g., water) concentration (Graaf et al., 1993). Carbohydrates with low molecular weight generally have lower T_g , whereas those with high molecular weight generally have higher T_g (White and

Table 7 Glass transition temperature (T_g) of sweeteners (dry state) found in confectionery products

Compound	T_g (°C)
Fructose	5
Glucose	31
Lactose	101
Maltose	87
Sucrose	62–70
Raffinose	70
Sorbitol	–9
Xylitol	–29
Maltitol	39
Isomalt	63.6
42 DE corn syrup solids	79
20 DE corn syrup solids	139
Polydextrose	90.8
Hydrogenated starch hydrolysate (MW 504)	54.6
Hydrogenated starch hydrolysate (MW 644)	75.0

Sources: Roos and Karel (1991), Noel et al. (1991), Roos (1995), Fennema (1996), Raudonus et al. (2000).

Table 8 Effect of water content on glass transition temperature (T_g) of sucrose

Water content (%)	T_g (°C)
0	69
1	61
2	50
3	42
4	35
5	29

Source: Nowakowski, 2000

Cakebread, 1966; Slade and Levine, 1991; Roos, 1995). Table 7 shows T_g values for a variety of compounds important for confectionery manufacture, whereas Table 8 shows the strong effect of water content in decreasing T_g of sucrose. Only a few percent of water can cause a large decrease in the T_g of a confection.

When different sugars are mixed, as in most confectionery formulations, T_g of the mixture depends on the relative ratios of the sugars added, the T_g values of each sugar found in the mixture, and, of course, the water content. According to Table 7, the T_g of 42 DE corn syrup solids is slightly higher than that of sucrose so mixtures of the two sugars should have T_g somewhere between those values (Table 9) and thus, addition of 42 DE corn syrup causes the T_g of the mixture to increase slightly. Use of 20 DE corn syrup, however, generally causes a much more significant increase in T_g of the mixture (Nowakowski, 2000).

During cooking of sugar syrups, inversion of sucrose into glucose and fructose often occurs. This mixture, according to Table 7 (which shows T_g values for the two components) has a much lower T_g than sucrose, perhaps around 15°C, which is a value often cited for honey solids (Bhandari and Hartel, 2005). Thus, inversion of a confectionery syrup during cooking leads to a decrease in T_g and thus, to reduced stability of the sugar glass.

Although it is widely accepted that molecular mobility decreases dramatically when a confection is held below its T_g , mobility does not decrease to zero, especially for smaller molecules like water (Fennema, 1996). In sugar glasses held below their T_g , water still has substantial mobility. Levine and Slade (2002) discussed molecular mobility in terms of the concept of average T_g for mixtures of components. The measured T_g of a mixture should be considered the point where a molecule with an average molecular weight of the system

Table 9 Glass transition temperatures (onset of calorimeter scan) for dry (less than 1%) corn syrup–sucrose mixtures (Gabarra and Hartel, 1998)

Addition Level (%) ¹	20 DE ²	42 DE ²
0	63.9 ± 1.4	63.9 ± 1.4
10	66.8 ± 0.4	64.1 ± 2.2
20	65.8 ± 2.6	66.9 ± 0.7
50	73.6 ± 3.0	69.1 ± 2.0
75	91.6 ± 1.3	70.9 ± 1.6
100	139.3 ± 0.8	79.0 ± 2.9

¹Addition on a dry solids basis (g corn syrup solids/100 g total solids).

²DE–dextrose equivalent.

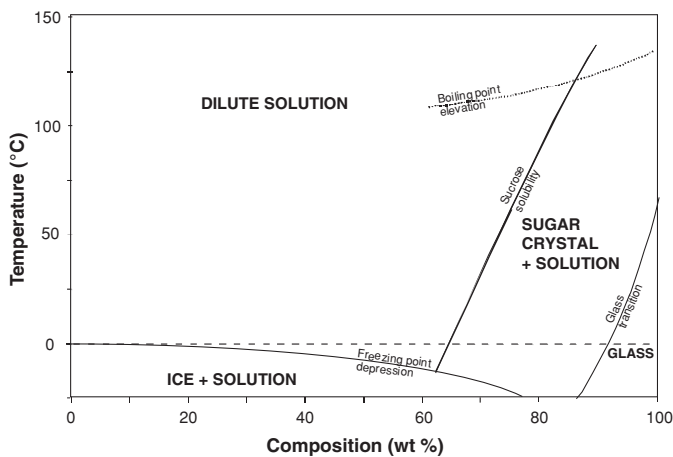


Figure 4 State diagram for pure sucrose-water binary system (from Hartel, 2001).

would be immobilized. In mixtures of sugars with water, the water molecule is significantly smaller than the sugars, so it will have considerable mobility even when the temperature is slightly below T_g . Thus, even when a hard candy is maintained at a temperature below T_g , penetration of water molecules into the matrix can occur, albeit at a slow rate dependent on the difference in storage temperature and T_g . Furthermore, flavor molecules in that same hard candy sugar glass also has some mobility even if the candy is held below the average T_g . The area of molecular mobility below T_g has a significant impact on the shelf life and stability of amorphous or glassy candies like hard candy and deserves future attention to seek ways to limit flavor loss and moisture uptake of these confections.

To document what state of matter might be expected at different temperatures and water contents, a state diagram is often used. The state diagram combines the phase boundary lines for solute (solubility curve) and solvent (freezing point curve) in a binary system, with the glass transition condition superimposed (Slade and Levine, 1991; Roos, 1995). A state diagram for sucrose-water is shown in Fig. 4 (Hartel, 2001). State diagrams determine the range of temperatures where a confection with known moisture content can be safely stored (Roos, 1995), but also can be used to document the path of processing steps on the state of a confectionery system (Hartel, 2001).

MOISTURE TRANSPORT

A freshly packaged confectionery product undergoes water migration as it seeks equilibrium among the various elements of the product (Cakebread, 1976). Figure 5 schematically shows the types of exchange that can take place in a complex product.

If there are multiple regions within the product with different water activity, water will migrate between these regions until the a_w values of all regions/domains are the same (equilibration). There is also moisture exchange with the air in any headspace

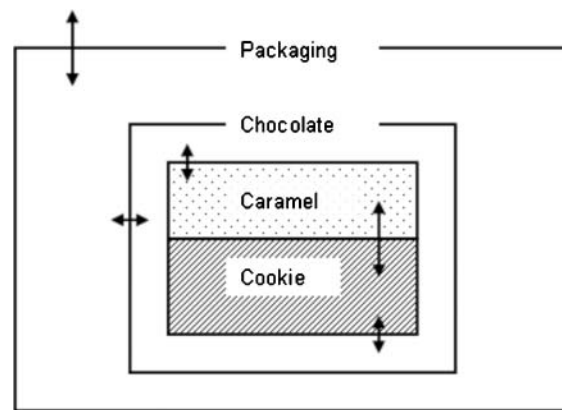


Figure 5 Moisture migration pathways for chocolate-covered candy bar system.

within the package. If the package is a perfect moisture barrier, the headspace attains a RH in equilibrium with the water in the confection (ERH). However, moisture exchange through the package, between the headspace and outside air, also occurs, at a rate depending on the difference in RH between inside and out, and the barrier properties of the package material. Since external storage conditions (temperature and RH) are continually changing, water migration out of (or in to) the product occurs continuously throughout its shelf life.

Compare a commercial packaged chocolate-covered candy bar made with caramel and a cookie over its shelf life (Table 10). Early in its shelf life (within one month of production), there was still a significant difference in water activity between the caramel and cookie. However, over time, the water activity values nearly equilibrated between caramel and cookie. Interestingly, under the conditions of storage in this experiment, the entire bar lost moisture through the package and the water activity of both components decreased significantly. Note that the a_w values of both caramel and cookie decreased despite being surrounded by chocolate, a relatively good water barrier. Not surprisingly, the texture of this product changed dramatically, with the caramel getting hard and chewy (originally soft) and the cookie becoming stale due to moisture loss.

To help understand changes in moisture content in confectionery products with multiple elements, it is important to understand the sorption and desorption behavior of each element. Furthermore, the rate of exchange of moisture is governed by the thermodynamic driving force and ability of water molecules to

Table 10 Change in water activity of commercial, packaged chocolate-covered bar containing caramel and cookie (Hartel, unpublished results)

Water activity	Early ¹	Aged ²
Bar average	0.32	0.21
Caramel	0.31	0.22
Cookie	0.23	0.20

¹ Within one month of manufacture.

² Stored for one year at about 22°C and 40–55% relative humidity.

move through and between each element of the candy. The end of shelf life then depends on the rate of moisture migration and the effect of water content on the physico-chemical properties of the candy.

Sorption/Desorption Curves

Sorption and desorption profiles for a food are generally created by graphing equilibrium moisture content (on a dry basis) versus water activity (a_w) or relative vapor pressure (RVP) at constant temperature. These profiles are commonly known as moisture sorption isotherms. Sorption curves show equilibrium relations between water in the candy and the surrounding air, but do not give information about the rate of moisture exchange.

Traditionally, saturated salt solutions have been used to determine moisture sorption isotherms because they produce a constant vapor pressure in the atmosphere above the solution at constant temperature (Bell and Labuza, 2000). The vapor pressure is dependant on the salt being used as well as temperature. Saturated salt solutions tend to decrease relative vapor pressure as temperature increases because of increased solubility (Bell and Labuza, 2000). Isotherms can be generated gravimetrically by determining equilibrium moisture content over a range of water activities. Samples are held at constant relative humidity over different saturated salt solutions and allowed to equilibrate. Bell and Labuza (2000) recommend weighing samples at seven-day intervals until the moisture content does not fluctuate by more than two milligrams per gram dry matter. Methods of determining the moisture content include oven drying (air, vacuum, or microwave) as well as the Karl Fischer titration (see Section titled Water Content Determination Methods). Once the equilibrium moisture content has been determined, dry basis moisture content is plotted versus water activity (or relative vapor pressure) to give the sorption isotherm.

New automatic methods, known as controlled atmosphere microbalances, allow sorption isotherms to be generated using very small (milligram) samples (Bell and Labuza, 2000). These machines use computers to measure change in mass of samples at a given relative humidity enclosed in a microbalance. When a defined equilibrium has been reached, the program automatically cycles to the next humidity and repeats the process (Bell and Labuza, 2000). Because sample sizes are small, the sample must be homogeneous. Other automatic systems measure larger samples at regular intervals by moving samples into a weighing cell at regular intervals. This system allows multiple products to be used and relative humidity is changed in steps at weekly intervals (Bell and Labuza, 2000).

Many foods show a sigmoidal-shaped isotherm, represented by the Type II isotherm in Fig. 6. The Type I isotherm is seen in anti-caking agents that hold large amounts of moisture at low a_w where moisture binds strongly to the ingredients and fills nonswelling cavities (Bell and Labuza, 2000). Some amorphous carbohydrates also show Type I isotherms. Sugar glasses, like hard candy and cotton candy, are extremely hygroscopic and

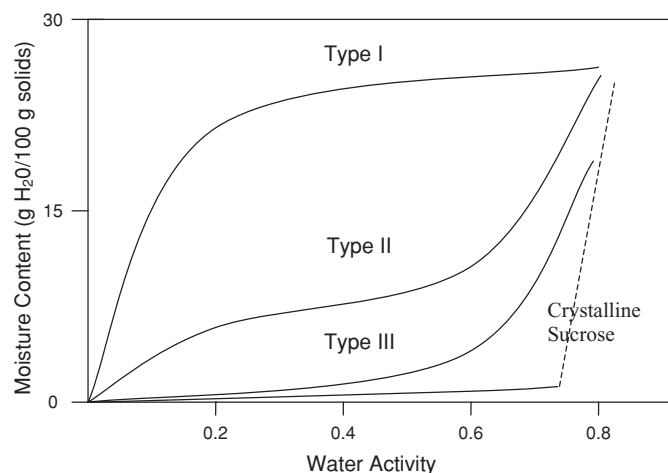


Figure 6 Common moisture sorption isotherms (adapted from Bell and Labuza, 2000).

follow Type I isotherms. Iglesias et al. (1997) found that the sorption isotherm of freeze-dried amorphous trehalose followed Type-1 sorption behavior.

Foods with high levels of small, soluble molecules and small amounts of polymeric compounds may exhibit a Type III curve (Fennema, 1996). Many candies, including caramel, fudge, and nougat may have sorption isotherms that follow either Type II or Type III behavior. Hadjikinova et al. (2003) found Type III sorption curves for sugar-free hard candies made with sorbitol and isomalt.

For pure crystalline ingredients (e.g., sucrose), moisture is only able to interact by hydrogen bonding at the surface of the crystal (Bell and Labuza, 2000) since the packing arrangement of the crystal lattice excludes foreign molecules such as water. Thus, moisture content remains low and nearly constant until a_w is high enough to cause dissolution of the crystal surface (Fig. 6) at the deliquescent point (Bell and Labuza, 2000). Above this relative humidity, water is able to dissolve the crystal and the moisture content increases quickly.

Principles of Moisture Migration

For moisture to move within a system, there needs to be a driving force, or a difference in the thermodynamic state of the water that causes water to migrate from one state to another to allow equilibration. The thermodynamic driving force is expressed in terms of a difference in chemical potential, μ , of water between two regions. However, since chemical potential is not easily measured, a difference in water activity is generally used to characterize the driving force for moisture migration (Labuza and Hyman, 1998).

The rate at which moisture migrates from one region of a food to another is dependent on the magnitude of the driving force and the ability of water molecules to move from the region of higher water activity to the region of lower water activity. The general equation that governs the rate of moisture migration can

be written as:

$$\text{Rate} = \frac{\text{Driving Force}}{\text{Sum of Resistances}} \quad (14)$$

The driving force for moisture migration is related to the differences in water activity between two domains with the candy and the RH of the surrounding air. The resistances to moisture migration are related to how fast water molecules move either through the candy matrix or the package in which the candy is contained. Diffusion of liquid water is the primary mechanism of moisture migration within confections, although other mechanisms (vapor diffusion, capillary flow, etc.) may play a role at times. For packaging materials, the rate of water vapor diffusion governs the resistance to water migration.

Driving Force

When a material is in equilibrium, no net chemical reactions or exchange of material occurs. Any change in the energy of the system can be expressed by the change in Gibbs free energy, dG :

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (15)$$

Here, S is entropy, T is temperature, V is volume, P is pressure, μ_i values are chemical activities of each species (water, sucrose, etc.), and n_i are molar concentrations of those component ingredients. At equilibrium, $dG = 0$ for a system and no net exchange of any species within the system occurs. For equilibrium, the chemical potential of each species must be constant and in a system with two regions (e.g., a multi-domain confection as diagrammed in Fig. 5), the chemical potentials of each species in each domain must be constant (Levine, 1995; Bird et al., 2002).

Chemical potential is often defined in terms of activity of a species, say water, as:

$$\mu_w = \mu_w^o + RT \ln(a_w) = \mu_w^o + RT \ln(p_w/p_w^o) \quad (16)$$

where, μ_w is the chemical potential of water, μ_w^o is a reference chemical potential, R is the ideal gas law constant, T is the temperature, a_w is water activity, p_w is the partial water vapor pressure above the food and p_w^o is the vapor pressure of pure water (Labuza and Hyman, 1998). This approximation assumes that the system exhibits ideal solution behavior, something that is certainly not true in most, if not all, confections. Despite this shortcoming, the water activity, or relative vapor pressure is often used to describe chemical potential and equilibrium in foods. Thus, if the domains diagrammed in Fig. 4 are all at equilibrium with each other, then the water activities of each domain must all be the same.

If the system is not in chemical equilibrium, meaning the chemical potential of any species is not equal across domains, material transfer occurs until equilibrium is reached. In the case

of moisture, if the water activities of the different domains are not equal, there will be a driving force for moisture migration between domains; however, transport of salts, lipids, flavors, and other components across the domains follows the same general principles.

Mechanisms

Mechanisms for moisture migration differ slightly for sorption and desorption. In the case of sorption of moisture into a product from humid air, the steps involve first moisture adsorption onto the surface polar sites followed by penetration (by diffusion or some other mechanism of mass transfer) into the candy matrix. When a product loses moisture to dryer air, the water simply moves through the candy matrix (again by diffusion or some other mass transfer mechanism) until it reaches the surface, where it is removed by air convection.

Adsorption of Moisture to the Food Surface. As moisture is added to a dry food product, adsorption first occurs at accessible, polar surface sites. This moisture is strongly bound and has little mobility. Monolayer coverage is reached when all of the polar surface sites are associated with a single layer of moisture (Fennema, 1996). The value for monolayer moisture content has been observed to decrease with increasing temperature, as documented by Iglesias and Chirife (1984)

$$\ln(X_m) = \beta + \alpha T \quad (17)$$

Here, X_m represents the monolayer moisture content on a dry basis (g water/100 g dry solid) and temperature, T ($^{\circ}\text{C}$). α and β are parameters that are calculated from least squares analysis of a plot of $\ln(X_m)$ versus T . This equation has been used to estimate monolayer moisture content between 5–60 $^{\circ}\text{C}$ for meats and starchy foods (Iglesias and Chirife, 1984).

Above the monolayer value, moisture first adsorbs to remaining available surface sites by hydrogen bonding. This moisture plasticizes solutes and many reactions accelerate as the reactant mobility increases. Once a complete monolayer has been formed, further adsorption creates a bulk phase. This moisture can be frozen, decreases viscosity, and supports microbial growth (Fennema, 1996).

Moisture Transport Rates. Diffusion is the main mechanism for moisture transfer in most food systems. The rate of diffusion is dependent on the structure and chemical characteristics of each component. Diffusion depends on the concentration of diffusing species, temperature, and the properties of the matrix through which diffusion is occurring (Guinee and Fox, 2004). Porosity of the structural elements through which diffusion occurs and the local viscosity of the adsorbed aqueous phase are important factors that affect the rate of diffusion (Labuza and Hyman, 1998). In amorphous systems such as hard candies and low water content caramels, diffusion rates differ depending on whether the matrix is in the glassy or rubbery state. In the glassy state, molecular mobility is severely limited and therefore, diffusion-limited processes or reactions occur at lower rates

when the temperature is less than T_g (Chirife and Buera, 1994).

Moisture transfer in food systems is unsteady state, meaning the concentrations of water in each domain are changing with time. Although it is a difference in chemical potential, or water activity, that defines the driving force for moisture migration (Bird et al., 2002), mass transfer is always characterized based on water content according to Fick's Law, a phenomenological law that is used to describe experimental diffusion data (Geurts et al., 1974). For unsteady state diffusion, Fick's second law is used; for example, for mass transfer in one dimension, Fick's Law is written as:

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (18)$$

where C is the concentration of the diffusing component, t is time, x is the dimension in which the species is diffusing, and D is the diffusivity of the species in the matrix (Singh and Heldman, 2001). The rate of diffusion is influenced not only by the ability of water molecules to diffuse through the matrix, but by the boundary surface conditions and the geometry of the food (Singh and Heldman, 2001). In general, D is a function of water content, making it a function of penetration distance (x) and time (t).

Fick's second law can be solved by computer-based equation solvers as long as the appropriate boundary conditions and physical properties are known. Analytical solutions are also available with certain assumptions (constant diffusivity, long time, etc.) and certain geometries (Bird et al., 2002). However, little has been done to characterize moisture migration in confections based on these fundamental principles.

One reason for this lack of fundamental understanding is the complexity of most confectionery systems. Even determining physical properties in confections is extremely challenging. For example, despite its importance for understanding and controlling moisture migration in confections, diffusivity values for water molecules in matrices of importance to confections is virtually unavailable. Some data for mutual diffusion coefficients of sucrose and water can be found in Zhymeria (1972); however, these values do not extend beyond 85% solids concentration and only apply for solutions of sucrose in water, not for the complex amorphous matrices generally found in confections.

In some circumstances, Fick's second law can be simplified to a first-order differential equation. For example, Fick's first law of diffusion can be used to describe how diffusion rates across a packaging film are affected by relative vapor pressure between the candy and the external air:

$$\frac{dm}{dt} = \frac{k}{x} (p_1 - p_2) \quad (19)$$

Here, dm/dt is the moisture exchange per unit time, k is the effective permeability of water, x is the length of the diffusion path, p_1 is the water vapor pressure in the first region, and p_2 is the vapor pressure in the second region (Labuza and Hyman,

1998). As vapor pressures move towards equality, the rate of moisture exchange decreases. Equation (19) is often used to characterize moisture migration through a package into or out of a food product, making the assumption that water is rapidly transported from the surface to the interior of the food (for sorption processes). In many circumstances of importance to shelf life of confections, these assumptions are not true; therefore, Fick's first law is limited in its usefulness for many confectionery systems.

Physico-Chemical Changes

Changes in water content due to moisture migration can affect both chemical reactions and physical properties of confections. These changes may be desirable, causing development of flavors and textures, but most often, the changes are detrimental and decrease consumer acceptability of the product. Whether a candy picks up or loses moisture depends on the difference in candy a_w and ambient storage RH.

Moisture Loss

Many candies are prone to losing moisture to the environment, as documented by the chocolate-covered caramel cookie example given in Table 10. In candies where a_w is greater than ambient RH, typically about 50%, moisture migrates out of the candy and through the package, causing a decrease in water content in the candy. This decrease in moisture generally leads to hardening of the candy. As seen in Table 2, many candies are prone to hardening due to moisture loss; these include caramel and fudge, chewy candies, nougat and marshmallow, gummies and jelly candies, fondants and creams, chewing and bubble gum, and soft-panned candies. Specific studies related to moisture loss in confections are detailed in Section titled Water in Confections.

Moisture Uptake

Some candies, particularly those with low a_w , are prone to picking up moisture from the environment. As seen in Table 2, hard candy, toffee and some low a_w caramels are probably the primary candies where this is a concern. Cotton candy, a sugar glass with a high surface area, is extremely prone to changes related to moisture sorption. If ambient RH is high, as in some humid environments, confections such as caramel and fudge, gum, hard chewy candies, and panned candies also may be prone to moisture uptake.

When a confection picks up moisture from the surroundings, numerous changes can take place. Because of the relatively slow diffusion of water molecules into the interior of the candy piece, a surface layer with elevated moisture content often forms first (Nowakowski and Hartel, 2002). This is evidenced by an increase in surface stickiness of the candy, often making the candy difficult to remove from the package. Gradually, mois-

ture migrates into the interior of the candy, causing softening of the matrix due to the elevated water content. Water acts as a plasticizer and T_g decreases as the moisture content increases (Roos and Karel, 1991). The increased water content and reduction in T_g of the candy matrix enhances mobility of all molecules that make up the confection. Flavor molecules, which may have been trapped within the amorphous candy matrix prior to moisture sorption, now have sufficient mobility to diffuse out of the candy matrix. This leads to candies with reduced flavor, in addition to the physical softening.

In cotton candy and certain hard candies, the enhanced mobility due to decreased T_g often leads to crystallization of the sucrose unless sufficient crystallization inhibitors are present in the formulation. Graining, or sugar recrystallization, causes substantial change in hard candy confections (Lees, 1965). As sugar crystals form, the water content of the liquid phase surrounding the crystal increases in water content due to the exclusionary process of forming the crystal lattice. This increased local moisture content causes a change in moisture dynamics. Moisture continues to penetrate into the candy matrix ahead of the crystallizing front. In the crystallizing region, however, the increased water activity causes moisture to migrate back out into the air, resulting in a net loss in weight. Makower and Dye (1956) and Palmer et al. (1956) documented the initial moisture uptake of a sugar glass followed by moisture loss after initiation of graining. Graining also leads to concentration of flavors in the crystallization zone followed by rapid flavor loss (Levi and Karel, 1995).

7 SHELF LIFE

Shelf life is the length of time that a food maintains an acceptable level of quality. The end of shelf life for a food product is characterized by the presence of undesirable physico-chemical qualities or microbial levels. As noted in the previous section, moisture affects both physical and chemical attributes that determine shelf life, including crystallization, glass transition, and rate of enzymatic or non-enzymatic reactions. Additionally, the water activity of a food system affects the growth of bacteria, mold, and yeasts that may cause spoilage or safety concerns.

Although Table 2 gives the general range of a_w values for various confectionery categories, whether a candy dries out or picks up moisture is determined by the relative values of a_w and storage conditions. Furthermore, the rate of moisture migration, which ultimately determines shelf life, depends on how easily water molecules move through the candy matrix and packaging system. Thus, it is important to understand how these factors affect the rate of moisture migration (see Section titled Moisture Transport). In this section, methods for measuring shelf life, including accelerated tests, will be discussed along with methods of enhancing shelf life.

Shelf Life Measurement

Although not the only mode of failure for confections, moisture migration is arguably the major determinant in the end of acceptable shelf life for many confections. Thus, shelf life testing in confections often evaluates changes in physico-chemical properties related to moisture changes. Shelf life testing may incorporate either sensory or analytical methods, or may combine multiple types of tests. Ultimately, shelf life is defined as the time when the consumer no longer finds the confection acceptable, so sensory testing is almost always incorporated into shelf life testing protocols.

Confections that tend to change in hardness can be tested during storage using texture profile analysis (TPA). This method uses a two-cycle compression test to compile force data during compression (Nielsen, 2003). The data can be correlated with hardness or the point where the product fractures. Baiano and Del Nobile (2005) studied hardness in almond paste products during storage. The study was conducted under accelerated conditions (37°C) meant to simulate worst-case conditions for storage. Hardening was the limiting factor in the shelf life of the almond paste products. A sensory panel test was used to determine maximum acceptable hardness. This correlated to a maximum force of 25 N on a texture analyzer. The length of acceptable shelf life was determined as the length of time in which the maximum compression force remained under 25 N (Baiano and Del Nobile, 2005). Hardness testing could also be used with confections that soften or lose crispness during storage.

Stickiness is a physical condition that is related to cohesive forces within the confection and adhesive forces between different materials such as a hard candy and its wrapper (Nowakowski, 2000). Stickiness can be measured by mechanical texture analysis as both adhesion from touching a material (tack) as well as from peeling two materials apart (peel) (Nowakowski, 2000). Results showed an increase in stickiness with increased moisture content to a maximum dependent on the corn syrup composition. Above the maximum, stickiness decreased as additional moisture reduced cohesion. Nowakowski (2000) also determined that peel force was higher in sugar glasses with a high ratio of corn syrup to sucrose.

Accelerated Shelf Life Studies

Accelerated shelf life studies are conducted by changing the storage conditions to hasten the deteriorative processes that occur during storage. In confections, elevated temperatures and humidities are often used to enhance product degradation in accelerated shelf life tests. A product with a one-year shelf life may be evaluated under accelerated storage conditions within perhaps a month in certain circumstances.

However, it is often difficult to extrapolate the results from an accelerated study to normal shelf life conditions. Empirical relationships are usually developed to correlate accelerated conditions with normal storage conditions. For example, one week at accelerated storage conditions may correlate to four weeks of

normal storage. However, these correlations are almost always product specific, and caution must be exercised when extrapolating from one product and formulation to another.

Increasing temperature is often used to change the rates of reactions in accelerated storage studies. A general rule of thumb is that an increase of 10°C generally causes a doubling of reaction rates (Taub and Singh, 1998); however, not all reactions follow this general rule. Fluctuating temperatures generally also enhance physico-chemical changes, including moisture migration. Since many rates of reactions and physical processes increase exponentially with temperature (e.g., the Arrhenius equation), the average reaction rate under cycling temperatures is slightly higher than the reaction rate at the equivalent average temperature of the thermal cycles. Thus, cycling temperatures promote more rapid degradation than holding at constant temperatures.

Rates of moisture migration also can be manipulated by changing the relative humidity at which the product is stored. For example, storage of hard candy at elevated humidity (75–80%) accelerates moisture migration through the package and significantly decreases shelf life, whereas storage at dry conditions (20–30% RH) promotes drying of candies like marshmallow and fudge. However, there is little public domain information regarding how well these studies correlate with shelf life under normal conditions.

A major caveat in all accelerated storage studies is that the mode of deterioration at the accelerated conditions must be the same as the mode of deterioration under normal conditions. It does little good, for example, to study shelf life of hard candy due to graining under accelerated conditions if it is loss of flavor that limits shelf life at normal conditions. Therefore, predictions from accelerated studies may not always be reliable for complex systems (Hough et al., 2006).

Extending Shelf Life of Confections

Equation (14) can provide a guide for designing strategies to reduce the rate of moisture migration and extend shelf life. The rate of moisture migration can be reduced, and shelf life extended, by either decreasing the driving force for water transport or increasing the resistance to migration.

Decreased Driving Force

One approach to reducing moisture migration is to remove the driving force, or difference in water activity between two regions in a multi-domain confection or between the candy and the air. However, since water content plays such an important role in textural properties of confections, it is often difficult to manipulate water activity to reduce the driving force for moisture migration. In the caramel covered cookie example used previously, it may not be possible to design a soft caramel with sufficiently low a_w and/or a crisp cookie with sufficiently high a_w to completely prevent moisture migration over time. However, through manipulation of formulation to change a_w of either

or both component, sufficient change in the driving force may be possible to extend shelf life, at least to some extent.

To manipulate a_w of a formulation, humectants are often employed. Addition of ingredients with a high affinity for water, such as invert sugar, organic acids, glycerol, etc., can reduce water activity, while maintaining product textural qualities. For example, replacement of a portion of the sucrose or corn syrup with a humectant in the caramel example above might reduce water activity without negatively affecting texture.

Increased Resistance to Moisture Migration

In the chocolate-covered caramel and cookie product depicted in Fig. 4, water migrates from caramel into cookie in addition to migrating through the chocolate coating and package layer into the surrounding air. The rate of moisture migration into and through each component of this confection depends on the diffusivity of water molecules through each matrix. The diffusivity of water molecules into the porous cookie structure will be different from diffusivity through the caramel.

One approach to increasing the resistance to moisture transport (decreasing diffusivity) is to manipulate the structure of each part of the candy matrix. Since diffusivity generally decreases with decreasing water content, a denser matrix at lower moisture content might be sufficient to reduce mass transfer rates and increase shelf life. Unfortunately, no methods to modify candy structure without negatively affecting textural properties have been published.

Another approach to reducing the rate of moisture migration is to protect hygroscopic elements within the candy matrix. For example, fruit acids such as citric and tartaric acids are hygroscopic and using high levels in a food to create a characteristic sour flavor can result in increased driving force for moisture migration. Corriveau et al. (2003) patented a process to minimize the effect of a high acid level in confections. The method involved completely or substantially encasing the hygroscopic ingredient by locating it between two layers of the confection itself. While this idea can be extrapolated to other hygroscopic ingredients, the confection must be significantly less hygroscopic than the entrapped component and the level of addition must be low enough that it is not detrimental to consumer acceptance.

Yet another method to reduce moisture migration is through use of appropriate barrier layers. This includes the packaging layer, which protects the candy from the ambient air, and edible barriers, which slow moisture migration between domains with different water activities. Edible barriers and packaging layers can extend shelf life by reducing the rate of moisture migration, but often cannot completely prevent moisture from moving between components and into the surrounding air. For example, in Table 10, both the caramel and cookie layers lost moisture despite being surrounded by a chocolate layer, which acts as a water barrier, and a packaging barrier.

Packaging. Packaging has many roles in determining the shelf life of a food. Physically, packaging acts as a barrier to

prevent contamination by undesirable microorganisms or dirt. Different packaging materials can also preserve the environment within the package by being selectively permeable to molecules such as oxygen or water. Other materials may be designed to keep light out, slowing the rates of some reactions in the food. Accordingly, packaging costs can range from low to greater than the cost of the food itself depending on the level of technology needed.

The ability of a packaging material to protect the food product against moisture migration is largely dependant on the material's permeability and the ability to seal it properly. Permeability involves dissolution and diffusion of the molecules through the package layer. Permeability is dependant on the type of vapor, packaging material, vapor pressure, temperature, and interactions of the vapor with the material itself (Sacharow, 1968). The degree of crystallinity and symmetry of the material also affect permeability. Greater degree of order and structure reduces the ability of a molecule to permeate the packaging material. While thickness is not a direct indicator of permeability when comparing different packaging materials, increasing thickness generally decreases permeability for any given packaging.

Although the type of packaging being used is important to moisture migration properties, how the confection is packaged is equally as important. The packaging should cover the entire surface of the candy and be completely sealed at all edges. Gaps at the edges of the packaging due to twist-wrapping or cutting the edges too short provide open areas for moisture migration or other contamination.

Polymer films and composites. Polymer films such as polyethylene, polypropylene, and polyvinyl chloride are common packaging materials for confectionery products. These films can be manufactured to be transparent, allowing consumers to see the product before purchase. Polymer films also are light weight, can be sandwiched with other packaging materials as laminates, and can be formed in many ranges of strength and flexibility. Permeability to moisture and gases is dependent on the chemical composition of the individual film as well as film thickness.

Baiano and Del Nobile (2005) compared moisture loss and hardening of almond paste (marzipan pastries) through two multi-layer polymer films containing either a layer of ethylene-vinyl alcohol (EVOH) or nylon. The EVOH film had better barrier properties for both moisture and oxygen, and shelf life of the almond paste was extended by 0.5 months by using EVOH rather than nylon.

Polymer-coated papers or films are becoming popular packaging materials due to their light weight and biodegradability. While aluminum foil has been the traditional wrapping material to protect chocolate bars, coated papers are being created with specific properties such as resistance to grease and low oxygen permeability (Anonymous, 1998). Chewing gum, chewy candy such as taffy, and chocolates are often packaged using coated papers.

Metal foils. Metal foils such as aluminum or tin have been a traditional wrapping material for chocolate and other con-

fections due to their low permeability in comparison to many plastic wrappings (for similar thicknesses). Foil has good barrier properties for water vapor and other gases as well as light. The main path of moisture transmission in foil is through pores—small holes that allow direct movement of moisture. Although no work has been published on confections, a study by Allinson et al. (2001) demonstrated foil's ability to preserve the activity of a moisture-sensitive pharmaceutical compound during storage. Aluminum foil blister packages (12 mil thick) were compared to polyvinyl chloride (PVC), Aclar (laminated PVC), and cyclic olefin blister packages as well as high-density polyethylene (HDPE) bottles. The foil maintained 100% assay of the active ingredient over a six-month period at 75% RH. However, aluminum foil is more expensive than polymer films and is generally reserved for purposes requiring a nearly complete barrier to moisture, gases, or light. Lack of strength at low thicknesses is also a disadvantage as small tears in the foil reduce the effectiveness of the barrier.

Edible coatings as moisture barriers. Edible coatings or films are often used as protective barriers against moisture migration in foods. The coatings can either be used on the surface of the product to prevent moisture uptake from the environment or placed between regions of varying water activities within the confection. Lipid-based films are often used due to their good water vapor barrier properties, however, protein and cellulose-derived coatings have also been developed as moisture barriers.

Lipid-based edible film technology. Lipid-based coatings or films may be used to prevent or slow transfer of moisture into or out of a confection or between two different domains (e.g., cookie and caramel). Coatings composed purely of lipids may be used, although composites containing both lipids and hydrocolloids may be formed to create more fracture-resistant films. Unfortunately, the hydrocolloids themselves may attract and bind moisture, reducing barrier effectiveness over time. Moisture adsorption is accelerated when the hydrophilic materials are in contact with product regions having water activity greater than 0.75 (Loh and Hansen, 2002).

Lipids containing saturated fatty acids (i.e., stearic and palmitic acid) are often used in composite films since the saturated fatty acid chains assemble in a more uniform crystal packing arrangement to make a better water barrier. Also, by increasing chain length, the melting point increases and molecular mobility decreases (Greener and Fennema, 1992). However, since pure fatty acid mixtures are difficult to obtain in nature, natural oils or animal fats are often used. Because of their fluidity, oils are generally hydrogenated or combined with other fatty acids to create coatings. Haynes et al. (2004) described a bakeable lipid-based film made up of a highly crystalline fat, a crystalline carbohydrate, and a crystalline food fiber. The crystalline fat was less able to migrate during baking or storage and its structure provided an effective moisture barrier. The carbohydrate reduces the amount of lipid needed to coat the surface of the food product, while the fiber increases flexibility and strength. Loh and Hansen (2002) formulated an oven-stable lipid barrier by milling a low-melting oil (melting point less than 35°C) with

a high melting fat (melting point about 70°C) at a temperature between their two melting points. The resulting cream-type mixture was then applied between two product regions of different water activities to form a continuous barrier approximately 10 μm thick. The crystalline structure was resistant to fracturing, but the thickness was found to be imperceptible to taste.

Waxes, shellacs, sucrose fatty acid esters, and acetoglycerides also may be used as lipid-based moisture barriers. Waxes contain many hydrophobic compounds and are often used to coat fruits, vegetables, or candies. Generally, waxes need to be applied using oil-in-water emulsions or petroleum solvent mixtures. Shellac, also known as confectioners' glaze, is often used to coat or provide shine on candies; however, the brittleness of shellac generally limits its use (e.g., panned candies). Sucrose fatty acid esters also have been used to reduce moisture migration in fruits, vegetables, and starchy snack foods, although have not been tried on confections (in the published literature). Acetoglycerides are created by acylating glycerol monostearates (Greener and Fennema, 1992). The resulting films are flexible and have been used to increase plasticity of wax coatings. Guillard et al. (2003) studied the effectiveness of acylated monoglyceride films for preventing moisture migration between higher and lower water activity food domains. Compared to dark chocolate and wheat gluten films, the acetoglycerides were more effective as moisture barriers by reducing water solubility. Additionally, by increasing the degree of acylation, the film's affinity for moisture decreased.

Chocolate or compound coatings are often used in the confectionery industry to coat candy centers and prevent moisture migration. Guillard et al. (2003) measured moisture migration through dark chocolate as an edible film. They formed films from a tempered mixture of dark chocolate and cocoa butter, and determined moisture sorption isotherms for the chocolate in an agar gel/sponge cake system. At water activity levels greater than 0.80, the moisture isotherm of dark chocolate increased sharply, perhaps indicating interactions between water and small nonlipid molecules (such as sugar) in the chocolate. Biquet and Labuza (1988) also studied the moisture permeability characteristics of chocolate films as edible moisture barriers. They produced films as thin as 0.6 mm and studied the moisture sorption and desorption isotherms. Their sorption curves displayed hysteresis, which may be attributed to the starch in the cocoa solids (Biquet and Labuza, 1988). Antunes and Antunes (2000) studied Biquet and Labuza's (1988) data and found that moisture adsorption of the chocolate films showed nonlinear behavior. The chocolate films showed maximum moisture content between 20 and 40 days of storage in the humid environment before decreasing and finally reaching equilibrium at 60 days. They suggested a concentration dependence of the diffusion coefficient and also determined that the concentration of moisture at the external film boundary was dependent on both the material and the relative humidity of the storage environment. However, these experiments were based on one-dimensional moisture migration. The chocolate films were placed horizontally on a nonabsorbent surface and moisture could only move in one direction, which may

not be applicable to multi-domain coated products such as a chocolate-coated candy centers or cookies.

Edible protein films. Protein films may also be used as edible and biodegradable coatings. Guillard et al. (2003) studied wheat gluten as a moisture migration barrier in their sponge-cake and agar gel system. Wheat gluten films had similar moisture sorption to the sponge-cake. However, the wheat gluten had decreasing effective diffusivity at increasing moisture content. Diffusivity decreased from $0.21 \times 10^{-11} \text{ m}^2/\text{s}$ to $0.01 \times 10^{-11} \text{ m}^2/\text{s}$ as moisture content increased from 17 g/100 g wet basis to 54 g/100 g wet basis. They were unable to explain this behavior and suggested the physical and chemical structure of wheat gluten needs further studying.

Milk whey protein films have also been studied for use as coatings. However, since whey proteins are hydrophilic, interactions with water decrease the effectiveness of these films as moisture barrier. Yoshida et al. (2002) studied moisture sorption of whey protein films over time. They found a linear diffusion model could be fitted to the adsorption of the whey protein films at 75% RH. The researchers suggested a possibility of nonlinear effects (similar to those seen in Biquet and Labuza's (1988) chocolate film experiments) during a long storage period.

Cellulose-derived coatings. Cellulose and its chemically-derived ethers and esters are becoming popular ingredients in edible film technologies. Methyl cellulose is often chosen for its solubility in water and good film-forming properties as well as moderate barrier properties to water and oxygen (Maftoonazad and Ramaswamy, 2005; Bravin et al., 2005). Plasticizers for softening methyl cellulose films include glycerol (Maftoonazad and Ramaswamy, 2005; Bravin et al., 2005) and polyethylene glycol (Debeaufort et al., 1994).

Methods of applying the film depend on the type of application. Bravin et al. (2005) formed methyl cellulose-starch and methyl cellulose-starch-lipid emulsions and applied the films to crackers by spray drying (2 and 3.5 bar pressure) and spreading. Spray drying at 2 bar produced the lowest permeability for the oil-free coating. Conversely, the addition of 20% oil statistically reduced ($p < 0.05$) water vapor permeability for both methods with spreading producing the lowest permeability. By observing environmental scanning electron microscopy images of coating cross-sections, the researchers observed large cavities within the structure of the spray-dried film at 3.5 bar. They hypothesized that the high surface tension of the droplets may have prevented proper aggregation on the surface of the cracker and created water vapor diffusion pathways. However, both types (oil and oil-free) of films and application methods (spreading and spray-drying) increased the shelf life of the crackers in comparison to uncoated samples at 65 to 85% relative humidity.

WATER IN CONFECTIONS

The nature of water in confections depends on many factors, including the ingredients used in the formulation and the conditions used in processing. These factors affect the physical

state of the matrix, the texture of the product and its stability during storage. In this section, the nature of water in a variety of candy products is discussed along with the effects of different ingredients used in these confections. Any recent studies on water-related properties are highlighted, although limited technical work has been published on many candy categories.

Hard and Candies

Hard candies are subcooled, highly supersaturated sugar solutions that have such a high viscosity they are in the glassy state (Kitt, 1993; Jeffery, 2001). Lollipops, candy canes, medicated confections (cough drops), soft-centered sweets, peanut brittle, and laminated or honeycombed sweets are examples of hard candy. They are made with glucose (corn) syrups, sucrose, and other sugars as well as colors, flavors, and acids (Jackson, 1995). Commonly used ratios of sugar to corn syrup are 70:30 for basic hard candies or 45:55 for center-filled co-extrusions (Jackson, 1995). The sugars and corn syrup are dissolved in water and boiled to very high temperatures (295–305°F; 147–152°C) to give very low moisture content. The syrup is allowed to cool until it reaches a plastic (amorphous) state. The flavors, colors, and acids are then added to the candy mass before it is formed into the desired shapes and cooled to room temperature (Minifie, 1999). Equilibrium relative humidity (ERH) values of hard candies are 26–32% (Jackson, 1995) and the moisture content is 1–3% (Kitt, 1993), although commercial products often have water content between 3 and 5%, depending on conditions and time of storage.

Table 11 shows the water content and water activity of a variety of commercial hard candies directly from the supermarket (Nowakowski, 2000). Exactly how long or under what conditions these products had been stored is not known; the data simply provide a snap shot of moisture content at the point at which these commercial samples were analyzed. Typically, water content was above 3%, and often well over 4%, with glass transition temperatures as low as 26°C (79°F). Despite the lack of details on these candies, Table 11 provides some interesting information regarding hard candy stability.

Stability of hard candy is related to its glass transition temperature, which is determined by the types of sweeteners used and the water content (Gabarra and Hartel, 1998; Nowakowski and Hartel, 2002; Smidova et al., 2004). Sweeteners with high

molecular weight, like 42 DE corn syrup, typically increase T_g , whereas those with lower molecular weight, like invert sugar, typically decrease T_g . Increasing moisture content also decreases T_g . Hard candy is in a stable glassy state as long as storage temperature is lower than T_g . If the storage temperature goes above T_g , the candy is no longer in the glassy state and stickiness or graining cause the end of shelf life. Candies with high corn syrup content, particularly if high DE corn syrups are used, readily pick up moisture due to their hygroscopic characteristic. The added moisture lowers T_g to the point where stickiness and loss of flavor can occur. When candies with low corn syrup content/high sucrose content are stored at a temperature higher than T_g , sucrose crystallization, or graining, can occur, leading to softer texture and rapid flavor loss. As clearly shown in Table 11, some of the commercial candies are dangerously close to leaving the glassy state, especially if ambient temperature is elevated for any reason (summer weather, warm storage conditions, etc.).

The specific saccharide composition in a hard candy product comes from a combination of what went into the formulation (ingredient addition) and what happens during processing (inversion and reversion). Smidova et al. (2004) recently analyzed the water content and saccharide composition (sucrose, fructose, glucose, maltose, and higher saccharides) of numerous commercial hard candies from Europe. Water content varied from 2.1 to 5.1%, sucrose from 31.7 to 87.7%, glucose from 1.1 to 12.4%, fructose from 0.2 to 8.5%, maltose from 0.7 to 33.1, and higher saccharides from 0 to 44.9%. Fructose content, indicating inversion of sucrose during cooking, varied from as low as 0.2% to as high as 8.5%. Since fructose has a very low T_g , the increased level of fructose led to a fairly low T_g in the candy (about 26°C, onset temperature), compared to the average of 35 to 40°C. However, other candies, with lower fructose content, were found to have even lower T_g , even as low as 22.4°C (onset temperature). In this study, T_g was also inversely correlated to water content (higher water content gives lower T_g) and positively correlated with the percentage of higher molecular weight saccharides (anything larger than sucrose and maltose). Due to the complex range of saccharide composition and water content in these commercial samples, however, no firm conclusions could be drawn about the correlations between T_g and composition.

Simply raising T_g of a hard candy might not be the best answer to increased shelf life since T_g also determines the hardness of the candy. If T_g is too high, the candy can be too hard, sharp, and brittle (Nowakowski, 2000), leading to dusting, slow dissolution, and flavor release, and sharp mouth feel. Hard candy manufacturers who have tested high maltose corn syrups in their formulations can attest to these problems. Thus, control of water content and optimization of T_g are two important requirements to produce hard candy with high quality and long shelf life.

Moisture Sorption of Amorphous Sugar Glasses

Sugar glasses are notoriously hygroscopic, and it is often the changes associated with moisture sorption that limits shelf

Table 11 Water content and glass transition temperatures (T_g) of commercial hard candies (Nowakowski, 2000)

Sample	Water content (%)	T_g (°C)
Brand 1 (5 flavors)	4.1 ± 1.0	26.6 ± 2.2
Brand 2 (5 flavors)	3.5 ± 1.0	40.3 ± 4.4
Brand 2 Sour Balls	2.8 ± 0.5	41.2 ± 1.6
Brand 2 Blue Mints	4.8 ± 0.9	33.2 ± 0.5
Brand 3 Wild Cherry	3.8	37.1
Brand 4 Cherry	1.7	40.2
Brand 5 Throat Lozenges	3.8 ± 2.5	36.3 ± 0.4

of hard candy. One of the first studies on moisture sorption and graining of sugar glasses was conducted by Makower and Dye (1956). They exposed sucrose and glucose glasses to air at different RH and characterized moisture uptake. The sugar glasses, initially at nearly zero water content, quickly picked up moisture to a level in equilibrium with the RH of the air on contact with the matrix. As expected, higher water content was observed for higher RH. Since no crystallization inhibitors were used in this study, once the water content rose above some minimum level, the supersaturated matrix began to crystallize. Upon crystal formation, the remaining liquid phase has higher water content and its water activity increases. Thus, the syrup layer near the surface has higher water activity now than the air and moisture transfer is from candy to air, resulting in a net loss of moisture of the piece after graining has started. Makower and Dye (1956) and Palmer et al. (1956) correlated the decrease in water content with the onset of crystallization, as characterized by X-ray diffraction studies. Lees (1965) provides a diagram of this event and the penetration of a crystallizing syrup layer.

Similar effects are expected in sugar-free hard candies, although fewer studies have been done to quantify glass transitions and graining of sugar-free hard candies. McPetridge et al. (2004) evaluated moisture sorption and graining in model sugar-free candy formulations. Two types of hydrogenated starch hydrolysate (HSH), with different polyol distributions, were mixed with both isomalt and lactitol to make hard candies. The glasses were exposed to high relative humidity (80%) and moisture sorption, glass transition temperature and onset of crystallization studied. Sorption of up to 40% water was observed, along with a rapid decrease in T_g with increasing moisture content. Interestingly, two glass transitions were observed after moisture uptake started, perhaps due to different surface and bulk conditions. Graining of the isomalt system was eventually observed, with the lower molecular weight HSH having more inhibition than the higher molecular weight HSH.

The effects of various HSH and polydextrose on moisture sorption and graining of isomalt or lactitol hard candies was also studied by Raudonus et al. (2000). Interestingly, they found that addition of HSH inhibited crystallization of lactitol, whereas it enhanced crystallization of isomalt hard candies. This may be attributed to the increased sorption rate of the isomalt matrix in the presence of HSH, as related to the decrease in T_g observed at low (<25%) levels of addition.

Studying the mechanisms and kinetics of moisture penetration into sugar glasses is an important area of research. Unfortunately, other than measuring total change in weight (bulk sorption), there are few methods to quantify moisture penetration into glassy systems. Magnetic resonance imaging (MRI) techniques, although useful in candies with higher moisture content, typically do not work at lower moisture contents of sugar glasses. Other methods are needed. Liang et al. (2007) utilized an infrared (FT-NIR) microspectrometer to quantify moisture penetration rates into various sugar glasses. Initial results clearly show a high moisture syrup layer at the interface of the candy

exposed to humid air. The rate of moisture penetration into the sugar glass was relatively slow compared to surface sorption, so penetration of a distinct boundary between the syrup layer and the glassy interior was readily observed. When insufficient corn syrup was present in the formulation, graining of sucrose was initiated at the surface, with the crystalline zone gradually moving into the interior. A spike of high moisture content material was seen to slowly penetrate into the sugar glass just in advance of the moving crystalline boundary. Understanding moisture dynamics in these commercial systems has the potential to lead to new ingredients that may minimize the effects of moisture penetration.

Flavor Loss

Flavor loss during storage is sometimes another concern for hard candy manufacturers. The ability of flavor molecules to escape the glassy matrix has also been related to the state of the sugars through the polymer science approach. Levi and Karel (1995) found that the loss of volatile markers from intact glasses (stored below T_g) was very slow, with only perhaps 10% of the flavor being lost over months of storage. However, if the glass was stored at temperatures above T_g , flavor mobility was significantly increased and flavor loss occurred rapidly, with a rate dependent on the difference between storage temperature and T_g . The largest and fastest flavor loss occurred, however, when the glassy matrix was allowed to crystallize. The concentration effect of sucrose crystallization on flavor led to a substantially increased driving force for diffusion, leading to a very rapid and nearly complete loss of flavors. Understanding the effects of hard candy composition, including water content, on T_g and flavor migration will allow hard candy manufacturers to better design products with higher quality and longer shelf life.

Cotton Candy

Cotton candy, or spun sugar, is made by melting colored and flavored sucrose crystals in a spinning device to form fine threads (or floss) of sugar glass. Rapid cooling of the molten sugar as it exits the spinning head results in formation of a glassy state with no crystallization. However, cotton candy, due to the high surface area of the fine floss, is inherently unstable and is prone to moisture uptake, collapse, and recrystallization.

In principle, moisture sorption of cotton candy is similar to that of hard candy, with the main difference being the lack of corn syrup in cotton candy. Prevention of crystallization in cotton candy is due entirely to the limited molecular mobility in the glassy state, whereas the corn syrup present in hard candy provides additional inhibition. Labuza and Labuza (2004) studied the moisture uptake of cotton candy stored at different relative humidity (RH). Cotton candy remained stable for over two years when held at 11% RH, but crystallized within three days when held at 33% RH. In this range of RH, the cotton candy had

picked up sufficient moisture that its T_g had been reduced to the storage temperature (22°C). As long as the T_g of the cotton candy remained above storage temperature, the candy retained its glassy nature. When T_g dropped below room temperature due to excessive pick-up of moisture, the candy grained, with a rate of graining dependent on the difference between candy T_g and room temperature. Graining occurred more rapidly during storage at higher RH because enhanced moisture uptake caused a greater reduction in T_g , which ultimately allowed the sucrose molecules sufficient mobility to organize into a crystal lattice.

Fondant and Creams

Fondants and creams are categorized as partially crystalline confectionery, containing about 50–60% crystalline sucrose in a saturated sugar solution (Lees, 1965; Minifie, 1999; Jeffery, 2001). The general formulation of fondant and cream includes 70–90% sucrose (dry solid basis), 10–30% corn syrup (dry solid basis) and 7.5–15% water (12 to 15% most common; Jeffery, 2001). The nature of both the crystals (number and size distribution) and the liquid phase (dissolved sugar composition, water content, etc.) significantly affect the texture and shelf life of fondants and creams, and both are significantly affected by the final water content.

Creams are similar to fondant, but are generally softer, with slightly higher water content. They have similar microstructure as fondant with numerous small sugar crystals held in a saturated sugar syrup. However, creams generally contain an aerated frappe to soften the finished texture (Jeffery, 2001). A usage level of 7 to 10 percent can lighten the texture of the cream without causing difficulties if the cream is to be deposited for molding (Minifie, 1999). Invertase may also be added to fondant to soften the confection over time to a cream texture (Jeffery, 2001).

Fondants are made by cooking the sugar syrup mixture to the appropriate temperature to yield the desired final water content (typically, 118–120°C). The supersaturated sugar mixture is carefully cooled without agitation (often on a cooling drum) to between 40 and 50°C (104 to 122°F) before being sent into a beating tube. Crystallization of sugar is initiated all at the same time through application of intense beating energy to promote nucleation. The product exiting the beating tube is highly crystallized (up to 50% crystals) and ready for further processing.

Water content has a large influence on the characteristics and texture of fondants and creams. Lower water content gives firmer products with higher crystallinity, whereas higher water content results in fewer crystals, more syrup phase, and softer products. Water activity of the product should be less than 0.65 to maintain stability and extend shelf life.

Water activity is lowered in fondants and creams by addition of corn syrup, invert sugar, and other components (i.e., sorbitol, glycerol, etc.) with humectant characteristics (Lees, 1965). The efficiency of different humectants in reducing a_w of fondant was given in the order of glycerol > sorbitol and invert sugar >

Table 12 Measured water activity values (a_w) of various fondants (from Bussiere and Serpollini, 1985)

Fondant	Sucrose (%)	Corn syrup solids (%)	Water (%)	a_w
1	50.0	25.0	25.0	0.810
2	57.2	28.5	14.3	0.764
3	60.0	30.0	10.0	0.705
4	61.6	30.8	7.6	0.638
5	62.5	31.2	6.3	0.560
6	28.1	59.9	12.0	0.580
7	21.5	65.3	13.2	0.585

sucrose > 42 DE glucose syrup (Lees, 1965). According to this ordering, sorbitol and invert sugar were found to have about the same effect on fondant.

Bussiere and Serpollini (1985) compared experimental measurements of water activity of various fondants with water activity values calculated from the Grover (1947), Money and Born (1951), Norrish (1966) and a modified Norrish equation based on the K values of Chirife et al. (1980). Table 12 shows the composition of each fondant formulation studied with the experimentally measured a_w values. Water activity varied from as high as 0.81 for fondant (ratio of sucrose to corn syrup solids of 2:1) with 25% water content to as low as 0.56 for fondant made with the same ratio of sucrose to corn syrup solids but with only 6.3% moisture. Fondants 1 through 5 show the effects of decreasing water content on a_w . At lower water content, there is more crystalline sucrose so the dissolved solids content in the liquid phase of the fondant increases, which drives down the water activity. Fondants 6 and 7 compare the effects of increasing corn syrup solids in the formulation. Higher corn syrup solids mean less sucrose crystallizes and dissolved solids in the liquid phase of the fondant is higher, and thus, a_w decreases.

Comparison of the different methods of predicting a_w showed that the modified Norrish equation based on the constants developed by Chirife et al. (1980) gave the best match to the experimental a_w values for the fondants studied by Bussiere and Serpollini (1985). In general, the modified Norrish equation predicted a_w values that were within about 1% of the experimental values, except for Fondant 5 where the deviation was 4.6%.

Bussiere and Serpollini (1985) also studied sugar-free fondants made with sorbitol and hydrogenated starch hydrolysate (HSH; in this case, Lycasin). Table 13 shows the fondant formulations and measured a_w values. As with the sugar-based fondants (Table 12), a_w decreased as water content decreased and HSH content increased (Table 13). Again, at lower water content, there was more crystalline sorbitol and higher dissolved solids in the remaining liquid phase of the fondant. The modified Norrish equation was again found to adequately predict a_w , with errors generally less than 5% from the experimental value. The K value used for the HSH syrup was determined by the authors to be -2.05 with an average molecular weight of the syrup taken to be 303.

The use of invertase in fondants and creams allows an initially firm product to soften over time due to the effect of the enzyme

Table 13 Measured water activity values (a_w) of various sugar-free fondants (from Bussiere and Serpollini, 1985)

Fondant	Sorbitol (%)	HSH ¹ (%)	Water (%)	a_w
1	75	16.25	8.75	0.691
2	75	17.5	7.5	0.683
3	75	18.75	6.25	0.621
4	75	20.0	5.0	0.575
5	75	21.25	3.75	0.496

¹HSH—hydrogenated starch hydrolysate.

on the state of sugar and the water content (Lees, 1965). Firm fondant or cream can be enrobed or panned with chocolate and then allowed to soften over time during storage. Manufacture of chocolate-covered cordial cherries typically relies on invertase softening, as does the slight softening of boxed chocolate-covered creams during storage. The invertase breaks down sucrose molecules in solution into the component monosaccharides, fructose and glucose, using up a mole of water for each mole of sucrose hydrolyzed (Silver and Karel, 1981). Thus, the water content of the fondant or cream decreases by 1 or 2%, depending on the amount of sucrose inverted. Despite this reduction in water content, the fondant still softens, primarily due to the change in state of sucrose from crystalline to liquid. For each mole of sucrose in solution hydrolyzed by invertase, about one mole of crystalline sucrose dissolves to maintain saturation equilibrium (between crystalline and dissolved sucrose). The reduction in crystalline sucrose is the primary cause of the softening effect of invertase in fondants and creams, whereas the production of invert sugar is the main factor that leads to a reduction in a_w .

Since a mole of water is consumed for each mole of sucrose hydrolyzed, water plays a critical role in controlling the enzymatic reaction (Silver and Karel, 1981). The reduction of water content and production of glucose and fructose both lead to a significant decrease in water activity of the cream as the enzyme reacts with sucrose. The rate of enzyme reaction decreased to zero over time due to the lack of available water; however, addition of water back into the system led to a rapid increase in enzyme activity (Silver and Karel, 1981; Wu, 2006). Thus, the enzyme still retains the ability to hydrolyze sucrose, but the environmental conditions (water activity, invert sugar, etc.) prevent it from being active after a certain amount of hydrolysis occurs.

Marshmallows

Marshmallows are simply described as air bubbles surrounded by sugar syrup (Minifie, 1971). The sugar syrup, made of sucrose, corn syrup, and water, is cooked to a temperature appropriate for the desired water content, after which air is whipped into the matrix through mechanical agitation (Jeffery, 2001). Proteins, such as gelatin, gum Arabic, egg albumen, agar-agar, pectin, milk or soy protein, are typically added to the sugar syrup to stabilize the foam (Minifie, 1971). During whipping,

Table 14 Water activity of various marshmallow products (unpublished data)

Sample	a_w
Fresh-made	0.733
Jet-puffed (store-bought)	0.658
Marshmallow chicks (store bought)	0.584
Circus peanuts, grained (store bought)	0.62
Marbits, cereal (store bought)	0.383

the density of the product decreases as the syrup and foam mixture expands into a light, fluffy marshmallow (Jeffery, 2001; Jackson, 1995; Minifie, 1971). Marshmallows may be either ungrained or grained, depending on the ratio of sucrose to corn syrup.

Water content affects marshmallow hardness and flow properties. Ungrained marshmallows typically have moisture content of 15–18% and lower density (0.5–0.7 g/ml), whereas grained marshmallows have moisture content of 5–10% and higher density. The ERH of marshmallows is typically around 60–70% (Minifie, 1999), although this depends on the type of marshmallow product and processing conditions. Water activities of a sampling of marshmallow products, both homemade and store-bought, are shown in Table 14 (unpublished data).

A fresh-made, ungrained marshmallow has fairly high a_w , above 0.7, dependent on moisture content and composition. During storage, water activity (and moisture content) decrease in this type of marshmallow, especially in regions where the average relative humidity is below 60%. Grained marshmallows, like circus peanuts, typically have slightly higher moisture content than ungrained marshmallow since the liquid phase has higher moisture content. Marbits, the small, hard marshmallows found in cereals, are grained and dried to low moisture content, so have very low a_w . Unfortunately, no published studies have investigated the relationships between composition and water activity in marshmallows.

Lim et al. (2006) studied hardening of marshmallow during storage at 25°C and 21% RH. The initial water content of the marshmallow was 19.5%, and although water activity was not measured, it was probably between 0.65 and 0.70, if not higher. As expected, storage at this low RH caused the marshmallow to lose water and harden over time. After 20 weeks of storage, the marshmallow water content had decreased to 7.9% and hardness had increased by greater than a factor of ten. Although water activity was not measured, it undoubtedly decreased substantially over this time (as seen in Table 11 for other marshmallow products). Lim et al. (2006) also correlated the increase in hardness during storage to an increase in the T_g of the product. Figure 7 shows that T_g was below -40°C initially (with higher moisture content and a_w) and increased to just above 0°C after 20 weeks, when the moisture content had decreased to 7.9%. This increase in T_g is directly responsible for the hardening since the amorphous sugar matrix was becoming closer to a brittle glassy state. Labuza (2006) presented similar results relating moisture loss and marshmallow hardening.

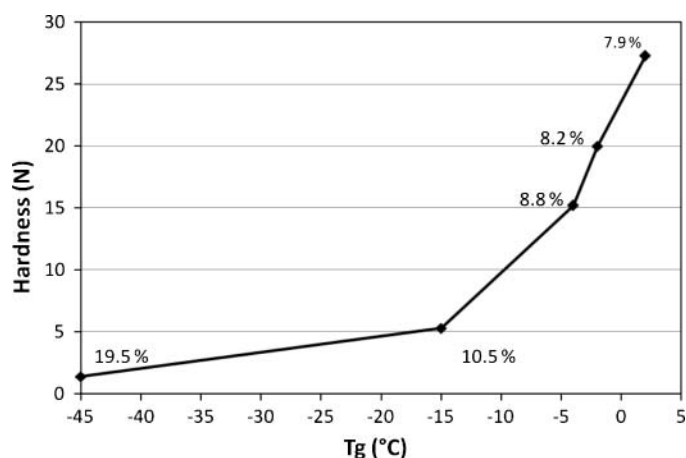


Figure 7 Change in hardness relative to glass transition temperature of marshmallow stored at 25°C and 21% relative humidity (numbers by each point represent percent water content) (redrawn from Lim et al., 2006).

Nougat

Nougat, like marshmallow, is made by whipping a sugar syrup into a foam (Minifie, 1999). Nougat can be crystallized or uncrystallized, with fat and flavor added to enhance eating characteristics (Jeffery, 2001; Jackson, 1995). The texture can vary in firmness depending on water content and state of the sugars (Jeffery, 2001). Soft nougats generally contain a syrup phase that is interspersed with the fat and other ingredients (Minifie, 1999). The fat affects texture and adds lubricity during cutting and eating (Jeffery, 2001). Moisture content ranges from 6% in hard nougats to 15–17% in soft nougats (Jeffery, 2001).

Both chewy and grained nougats are made by mixing egg albumen or another protein with water and sugar to produce a frappe. The sugar, corn syrup, and water are boiled to the desired moisture content and added slowly to the egg albumen mixture. Other ingredients (and graining agents, if desired) are added along with the melted fat. The fat is added last to minimize deflation of the foam. The finished nougat is then cooled and allowed to set before cutting (Minifie, 1999).

Nougats may be either chewy or grained/short nougats, depending on whether the sugar has crystallized or not. In chewy nougats, corn syrup content is higher than sucrose content so that the sugars are in the amorphous state (ungrained). The sucrose content in grained nougat is higher than corn syrup content so that the sugars are partially crystallized. Fine sugar may be added during production to promote or seed crystallization (Minifie, 1999). Typically, grained nougats have slightly higher a_w than chewy nougats at the same moisture content due to the influence of graining. If the nougat is grained, it has an ERH of 60–78% and if it is ungrained, it has an ERH of 40–55% (Minifie, 1999).

Hardening of nougat, both grained and ungrained, can be a problem if the confection is stored in a low relative humidity environment. However, no studies have been reported that document these effects.

Caramel and Fudge

Caramel and fudge generally consist of sugars, corn syrup, milk protein (often from sweetened condensed milk), fat (may be milk fat or vegetable fat), salt, and water. Fudge is typically considered a crystallized caramel (Jeffery, 2001; Jackson, 1995). The ingredients are cooked to drive off water, leaving anywhere from about 6 to 18% water content for caramels. During cooking, the Maillard reaction occurs between reducing sugars and proteins to give the desired caramel flavor and color (Jeffery, 2001). Caramels and toffees have an ERH between about 45 and 60%, depending on moisture content and formulation, with fudge often having a slightly higher value due to the sugar crystallization (Willis, 1998).

Caramel is a noncrystalline amorphous sugar candy, although commercial caramels may consist of some (<10%) small sugar crystals to modify texture and reduce stickiness. The organization of protein aggregates around fat globules contained within the amorphous sugar matrix provides stand-up properties and prevents cold flow. Due to the wide range of water content, between about 6 to 18%, caramel can have textures from soft and runny to very hard and firm. Texture may be “short” when slight graining occurs.

The final water content of caramel and fudge is critical to the texture, quality, and shelf stability. The water content of caramel varies from as low as 4–6% to as high as 18%, with texture ranging from very hard and brittle to soft and runny over that range. The glass transition temperature, governed by water content and composition, directly correlates to the texture. Chung et al. (1999) measured the glass transition temperatures of caramels made with different types of corn syrup and correlated these results with general textural attributes. Caramel formulations were all cooked to the same temperature (119°C, 246°F) so that the water content varied with the type of corn syrup used in the formulation. Caramel made with high fructose corn syrup had the highest water content of 9.6% (due to the highest boiling point elevation of the corn syrups studied) and the lowest T_g of 0°C (32°F). This caramel was softest and runniest, reflecting the very low T_g . On the other extreme, the caramel made with 26 DE corn syrup had the lowest water content (lowest boiling point elevation) of 8.4% and the highest T_g of 20°C (68°F). This caramel was quite hard, reflective of the fact that its T_g was only slightly below room temperature. The caramels made with 42 and 62 DE corn syrups had intermediate T_g values, as expected, of 9°C (48.2°F) and 5°C (42°F), respectively. As expected, their textures fell between those of the two extremes. This example clearly shows how simply changing the type of corn syrup in a caramel formulation can dramatically affect texture, in part through the effect on water content and T_g . For comparison, Foegeding and Steiner (2002) found a T_g of -14.8°C (5.4°F) for a caramel made with 63 DE corn syrup and cooked only to 115°C (239°F). The higher water content remaining in this caramel formulation led to the much lower T_g than found by Chung et al. (1999) for a similar caramel.

Dissolved sugars and salts lower water activity to help stabilize against microbial growth; however, some fudge products may have sufficiently high a_w (above 0.65) to support mold growth. Caramels and fudge with high water content (high a_w) may need added preservatives, like potassium sorbate, to stabilize against mold growth.

Besides mold growth, graining (moisture loss) and stickiness (moisture gain) are potential shelf life issues for caramel. High water content and/or high DE corn syrup content may cause stickiness, whereas inappropriate ratios of sucrose to corn syrup and sucrose to water can lead to graining (Lenz and Hartel, 2005).

Gum

Gum consists of gum base, which is made of natural or synthetic rubber or polymers, along with gum texturizers, sugars, flavors, and humectants. Bubble gum typically contains higher molecular weight polymers than chewing gum in order to provide elasticity for blowing bubbles. Sugars such as ground sucrose and dextrose are used in addition to 42 DE corn syrup (Jackson, 1995). Chewing gum is produced by first melting the gum base and then mixing in the sweeteners and other ingredients. The gum is then rolled and cut into the proper size pieces. Before being wrapped, the gum is conditioned in temperature-controlled rooms to guarantee proper consistency.

The main factors that affect water activity of gum are water content, corn syrup (both DE and specific gravity) and other sugars, and glycerin. Chewing gum usually has an ERH between 50–60% (Minifie, 1999).

Moisture loss is often the cause for the end of shelf life of gums, which is why gum may also contain humectants to retain softness and hold moisture. Since gum typically has a_w of about 0.55, if it is exposed to dry conditions, it typically loses moisture and becomes hard and crumbly.

Gum typically has a shelf life between six months and approximately one year depending on the type of product. Soft bubble gum has a shorter shelf life (approximately six to nine months), while coated pellet gum has a longer shelf life since the hard sugar shell provides protection from environmental conditions. However, moisture migration between the gum center and the hard sugar shell can lead to the end of shelf life as the shell softens and the gum hardens. No recent publications were found in the literature that documented the effects of moisture on shelf life of gum products.

Jelly and Gummy Candies

Jelly candies like jellybeans and gummy bears consist of a gelling agent (i.e., gelatin, pectin, or starch) added to relatively high moisture content (15–20%) sugar syrup (Jeffery, 2001; Jackson, 1995). The syrup, which is formulated not to grain by adding more corn syrup than sucrose, is immobilized in the

gel structure (Jeffery, 2001). Textural properties of this category of candy depend primarily on the water content and the type of gelling agent used. Regardless of the gelling agent, candies with higher water content are significantly softer than candies made with the same ingredients but with lower water content. The ERH for these types of candies is usually given to be around 60–70% (Minifie, 1999), although some hard jelly candies may have a_w as low as 0.5.

Jelly and gummy candies are often produced by molding in dried corn starch, where impressions in dried starch are filled with hot liquid candy, which is then cooled and allowed to set. The starch pulls moisture out of the candy piece and creates a “skin” on the surface of the jellies. The skin helps prevent deformation of the candies when removed from the starch (Lees, 1979). Drying time may vary from 24 to 72 hours depending on the candy and the desired final moisture content (Sudharsan et al., 2004). The speed at which drying occurs must be controlled. If skin formation occurs too rapidly, the surface may become too hard and trap moisture inside. This in turn can lead to “sweating” on the surface of the candy during storage (Sudharsan et al., 2004).

Ziegler et al. (2003) documented the rate and extent of moisture migration from the jelly candy into starch during setting. Magnetic Resonance Imaging (MRI) was used to follow the movement of moisture from the candy into the starch and air to assess the rate of moisture migration. Due to rapid initial moisture loss, a hard skin of dried candy was observed to form at the interface with the drying starch.

Jelly and gummy candies are likely to harden over time as the candy loses moisture to the atmosphere through the skin. Since gummy and jelly candies generally have finished a_w of 0.5–0.7, they tend to lose moisture and harden if stored at dry conditions.

Recent studies on physical (and sensory) properties of mixtures of biopolymers and sugars in low moisture systems are utilizing the polymer science approach (DeMars and Ziegler, 2001; Kasapis et al., 2004). The rheological/mechanical properties of these mixtures, either real jelly candies or simulated candies, are being studied from a fundamental approach based on understanding molecular mobility. The effects of mixed biopolymers (for example, gelatin and xanthan gum) on the glass transition, T_g , of such systems will lead to development of advanced options for new jelly candies with tailored physical properties. Control of water in these systems through gelation of the hydrocolloid is critical to control of product texture.

Compressed Tablets and Wafers

Various powdered base materials, such as sucrose, fructose, dextrose, sorbitol, mannitol, or xylitol, are used to manufacture compressed tablet candies. In addition to the base, binders such as gum arabic, gelatin, and alginates, along with lubricants, oils, fats, magnesium stearate or stearic acid, and color and flavor materials are used to make tablets. The ingredients are

mixed, wetted, and formed into a mass that is then granulated, sieved, and dried (Minifie, 1999). This ensures even mixture of the ingredients during the tableting process. The resulting powder or granules are compressed under pressure to produce hard sweet tablets, often with a rough surface (Minifie, 1999; Jackson, 1995). Compressed tablets have low moisture content and are shelf stable for a long time (years).

Wafer candies, sometimes called lozenges, are made by mixing powdered sugar with a binder made primarily of corn syrup and gelling agent. The resulting dough contains about 5 to 10% moisture, from which candy pieces are formed either by extrusion or by sheeting and cutting. The wafers are then dried to very low moisture content (<4%) and thus, have very low a_w values (<0.4).

The water content of the dough used to make wafers and lozenges plays an important role in the hardness of these candies. Higher moisture content promotes a greater extent of bonding between crystals during drying, which leads to a harder candy. The high crystallinity and low a_w of tablets and wafers make these candies stable to moisture changes even in the presence of fairly high relative humidity.

Sugar Panned Candies

Sugar panned candies are either soft panned or hard panned. Water content during manufacture and storage of sugar-panned candies is critical to product quality and shelf life.

Soft panned candies such as jellybeans are created by building up successive layers of coating materials on candy centers in a rotating pan. For example, jellybean centers (initial water content of 7 to 10%) are alternately layered with engrossing syrups and fine-grained sugar until the desired size is reached (Minifie, 1999). The shell, which may be up to several millimeters thick, makes up on average about 20 to 30% of the final product. Although the shell may have only 4 to 5% water content when applied, the high crystalline content means that the liquid phase of the shell has much higher water content (probably as high as 10%). The soft-panned sugar shell contains relatively large sugar crystals, dependent primarily on the size of the particles added in engrossing. These large crystals and the relatively high water content of the liquid phase of the shell provide the "soft" texture of these products. The coating must be applied evenly and each layer must be dried under controlled conditions to produce uniform confections.

Once the shell has been applied, the coating is then allowed to set as the product is stored in shallow trays in a dry environment. During this storage step, moisture can potentially move from the coating into the jelly center or be lost from the jellybean into the atmosphere. Troutman et al. (2002) studied moisture migration in a jelly bean during curing (at 50% RH and room temperature) by using MRI, in addition to measuring changes in water content and water activity of the different zones. Directly after the panning process, the shell had water content of 4 to 4.5% with a_w of 0.75, whereas the jelly candy center had initial

water content of 7 to 8% with a_w of 0.64. After 2 days of curing, the water content of the shell had decreased to 3.5 to 4.0% with a_w of 0.68 and the jelly candy center had also lost moisture to 6.5 to 7.0% with a_w of 0.60 to 0.62. The water content of the jelly bean decreased by about 0.03% and was still decreasing after 48 hours of curing.

Moisture loss often continues throughout storage even when the candies are kept in the package. Hardening of jelly beans over time is widely observed and probably is the main cause of the end of shelf life. Moisture loss and hardening are further exacerbated by storage in an open package.

In hard panning, a highly concentrated sucrose syrup (80–85% solids) is applied to a candy or nut center tumbling in a pan (Minifie, 1999). The syrup is allowed to spread over the piece and then drying air is applied to the pan to promote rapid drying and intense crystallization of the syrup. Extremely small and numerous crystals, possibly fused together, are desired in hard panning to give the hard, brittle shell characteristic of hard panned candies. Control of crystallization and drying is extremely important to obtain a high quality candy.

Ben-Yoseph et al. (2000) studied drying of thin sugar films similar to those formed during hard panning. Model films were dried on a microscope stage to allow visualization of sugar crystallization, and drying rates also predicted by computer simulation of drying and crystallization. The effects of initial solution concentration, drying air flow, temperature and relative humidity were studied. Of these parameters, temperature was found to have the greatest effect on drying and crystallization, with air flow and initial solution concentration having almost no effect. Relative humidity of the drying air had minimal effect on the rate of drying or crystallization, but influenced the amount of water remaining in the film at longer times, with higher relative humidity leading to higher moisture content, as expected. Additional studies are needed to quantify the relative rates of crystallization and drying in thin films similar to those found during hard panning.

SUMMARY

Moisture is one of the most critical factors that affects quality and the shelf life of confections. Texture, for example, of most candies is significantly affected by water content, with confections generally becoming harder as the moisture content decreases. Recently, the application of the state diagram approach to characterizing the properties of confections has provided a significant advance in our understanding of exactly how water content affects texture and quality.

In terms of shelf life, it is well known that the difference between water activity (a_w) of the candy and the RH of the surrounding environment determines whether a confection gains or loses moisture during storage. The closer a_w is to the RH during storage, the less potential for moisture migration to or from the environment. Similarly, in confections with multiple domains of different a_w , migration occurs between the domains until

equilibrium is reached (at equal a_w values). Methods to protect confections against moisture migration are continually being studied to preserve quality and extend shelf life. This includes approaches to retard migration to the environment through use of improved packaging materials and to retard migration within multi-domain candies through the use of edible films and/or reformulation to balance a_w of the different domains.

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