

# 1

## Quality Changes in Food Materials as Influenced by Drying Processes

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### 1.1

#### Introduction

Drying and dewatering plays a major role in food manufacturing or food processing activities worldwide. Often one of the last operations in the food processing, it controls to a large extent the quality of the final product. Drying is applied to a wide variety of food products, from cereals to finished goods, from raw materials to by-products. The processes used are numerous, according to the type and quantity of product to dry, the amount of water to eliminate, the final desired quality or functionality of the dried product (Tab. 1.1).

Drying and dewatering impact the mechanical, sensory and nutritional properties of food products, and can be used to create new functionalities (Bonazzi and Bimbenet, 2003, 2008). Drying is one of the main techniques for preserving agricultural and food products; it takes place in the processing of many products, as the main operation or as a consequence of other processing steps. Heat and mass transfer phenomena which are typical of drying also appear during other processes, as in cooking, baking, roasting, smoking, refrigeration, freezing, during storage, and during pneumatic transportation.

The main objective of drying is to decrease the water activity ( $a_w$ ) of various perishable materials to values  $<0.5$ , in order to enable their storage at ambient temperature. The importance of  $a_w$  in controlling the shelf-life of foods by suppressing the growth of micro-organisms, by reducing the rates of chemical reactions, and by inhibiting enzymatic deterioration is well established. The respective relationships have been summarized by Labuza *et al.* (1970) in a diagram similar to that of Fig. 1.1.

Water activity is more important to the stability of a food than the total amount of water present, and it makes it possible to develop generalized rules or limits for the stability of foods. For most foods, the critical point below which no micro-organism can grow is in the 0.6–0.7 water activity range. A food product is most stable at its monolayer moisture content, which varies with the chemical composition and structure. Water activity is also useful for predicting the final moisture content at equilibrium versus drying conditions (temperature and relative humidity), and for

Tab. 1.1 Diversity of drying equipment and products in the food industry.

Equipment	Products
Drum dryer	thick liquids, pulps, pastes or slurries: mashed potatoes, carrots, baby cereals, soups, starch
Rotary dryer	particulate solid foods: alfalfa, pasta, sugar beet pulp, pomace, starch, whey, pectin residues, lemon pulps, and so on.
Deep bed/dihedral dryer	cereals: malt, maize, sunflower grain, rice, wheat
Spray dryer	liquids: milk, whey, coffee, tea, yeast
Pneumatic dryer	for the finish drying of powders or granulated materials: starch, flour, proteins, distillery residues, aspartame, guar gum, methionine
Tunnel conveyor, belt or band dryer	pasta, vegetables, gelatin, fruits, nuts, breakfast flakes, extruded pet foods, soy proteins, tobacco, seeds, and so on.
Fluidized bed	powders and small particles: milk powder, whey, yeast, casein, extruded food, coffee beans, soy beans, sunflower beans, chocolate granules, lactose, L-lysine, nutmeg, tomato powder, soy proteins, salt, sugar, and so on.
Freeze-dryer	high added-value, heat-sensitive products: coffee extracts, fruits, vegetables, mushrooms, aromatic plants
Ventilated cabinets	sausage, ham

the selection of ingredients and packaging method. However, limitations of the water activity concept have also been identified. Water activity is defined at equilibrium, whereas foods with low and intermediate moisture content are often complicated, non-equilibrium (supercooled or supersaturated) systems showing time-dependent properties: changes towards equilibrium are observed, physical state and properties evolve during storage, composition and water activity may change with time.

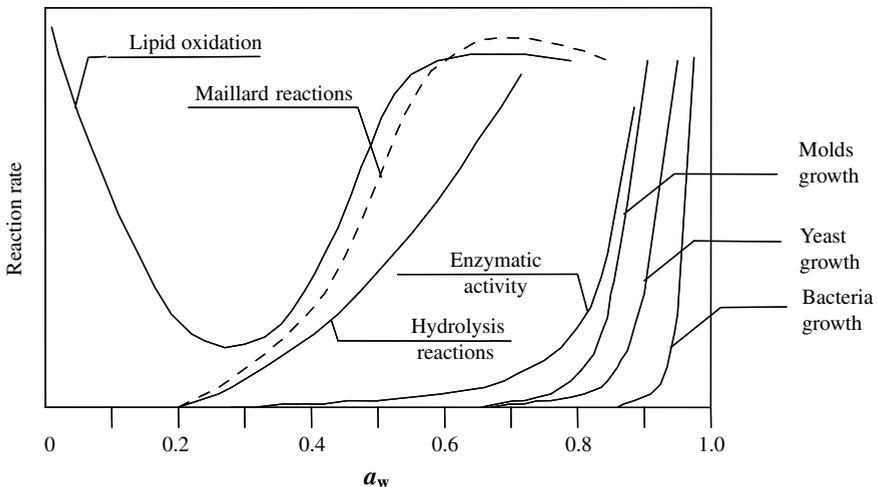


Fig. 1.1 Water activity and stability diagram of foods.

Many physical characteristics, such as crystallization, caking, stickiness, collapse, molecular mobility, and diffusivity cannot be fully explained with the water activity concept; corresponding relaxation times must also be taken into consideration.

Furthermore, drying leads to structures usually differing from those of the initial humid product. This can be a disadvantage, but it can also offer a new benefit, as for example the porous structure of mashed potato flakes, crispy granulates for breakfast cereals, instant dry milk powder, and so on. The drying process can, therefore, also be considered as a controlled texturing operation, a source of innovative and easy-to-use products.

In the food industry, drying is applied to many different types of products:

- Low hydrated agricultural products, as a complementary drying for stabilization (corn, rice, wheat, oil seeds etc.)
- Highly hydrated agricultural products, for weight reduction and stabilization, and for absorbing the seasonal character of some productions (milk and by-products, fruits and vegetables, aromatic and medicinal plants, tea leaves, meat, fish, eggs, etc.)
- Intermediate products from industrial processes, for stabilization and conditioning (coffee and tea extracts, pasta, sausages, sugar, etc.)
- Industrial by-products for feed (sugar beet pulps, brewery spent grains, meat or fish meal, whey, etc.)

and it has many purposes:

- Extend the shelf life of foods without the need for refrigerated storage
- Reduce weight and bulk volumes, for saving in the cost of transportation and storage
- Convert perishable products (surplus) to stable forms (e.g., milk powder)
- Produce ingredients and additives for industrial transformation (so-called intermediate food products (IFPs), like vegetables for soups, onions for cooked meats, fruits for cakes, binding agents, aroma, food coloring agents, gel-forming and emulsifying proteins, etc.)
- Obtain particular convenience foods (potato flakes, instant drinks, breakfast cereals, dried fruits for use as snacks, etc.), with rapid reconstitution characteristics and good sensorial qualities, for special use, such as in vending machines, or directly for consumers.

In the present economic context, trade and consumer impose their demand for supply chain, availability, habits, nutritional value, and so on. Dried foods must be processed with the goal of maintaining their quality, such as flavor, texture, convenience, and functionality, increasing their nutritional content, and reducing anti-nutritional factors or toxins. Frequently, there is an extreme focus of food processing on maintaining the bioactivity and structural functionality of the product (Rahman, 2005). This situation imposes constraints on the food industry with regard to the production and selection of raw materials, and the choice of equipment, depending on the products. As an example, the vending machines for hot drinks must deliver automatically powders with constant flowability and composition, good dosage properties, and good solubility. Quality is a relative property and it is,

**Tab. 1.2** Examples of different aspects of dried product quality from the consumer's point of view.

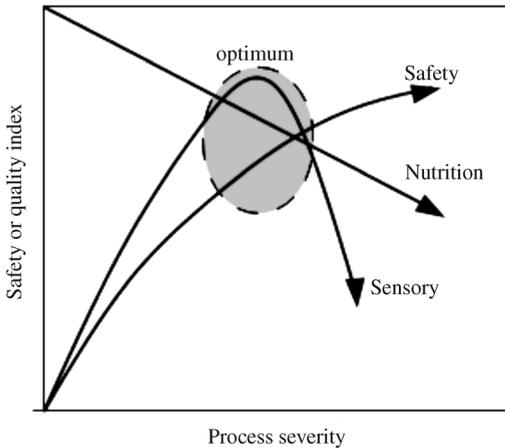
Appearance (dried/rehydrated)	Color, brightness Shape or aspect (big particles, powder) "Natural" looking
Taste (dried/rehydrated)	Taste itself Aroma Texture
Ease of use	Rehydration or dissolving rate (cold or hot water) Apparent density (variation for proportioning) Stability over time Packaging enabling use and re-use of the product without any quality loss No agglomeration or sticking to the packaging
Special properties Composition	For example, for pasta: no breakage during storage, short cooking time Reproducibility Additives: origin and concentration Energetic value (calories), fat content, vitamins, and so on. No allergens No nitrate or pesticide residuals Law, GMO, and so on.
Microbiology	Limited number of micro-organisms with absence of pathogens

therefore, important to define the expected properties from the consumer's point of view (Tab. 1.2) in order to be able to link possible spoiling or modifications to the relevant process parameters.

The quality of foods refers first to safety, and then to sensory and nutritional properties. But in many cases, the severity of processing is differently related to safety and to sensory or nutritional quality. Severe processing generally results in higher nutritional loss and in poorer quality, whereas it increases food safety (Fig. 1.2). An optimal drying time and the right level of severity of processing must, therefore, be designed in order to obtain the desired food characteristics.

The control of the mentioned properties relies, often in a complex way, on all the chemical and physical phenomena occurring during drying and subsequent storage. The chemical composition of foodstuff is variable and complex, including carbohydrates, proteins, lipids, minerals, vitamins, aromas, and so on. This complexity induces properties that change throughout drying and storage, and that must be controlled. Besides water content and water activity, many factors with positive and negative effects must be considered, such as

- the temperature and humidity conditions during processing,
- the changes in shape, structure, porosity, and mechanical properties,
- the sticking and crystallization phenomena linked with glass transition,
- the chemical reactions, specifically their nature and rate in relation to pH and temperature,
- the transfer conditions of heat and water related to diffusivity and conductivity



**Fig. 1.2** Effect of process severity on quality index (adapted from Rahman, 2005).

(Nadeau and Puiggali, 1995; Dumoulin and Bimbenet, 1998a, b; Nijhuis *et al.*, 1998). Many of these parameters are difficult to determine and/or to measure.

Interactions between water and other components depend on water and solute mobility, which are, therefore, responsible for biochemical reactions, physical transformations and mechanical phenomena during processing, storage and consumption (Le Meste *et al.*, 2001).

To optimize the quality of the final dried product, modeling tools are often used. Models are created to describe the history of the product during the drying process, using parameters such as time, temperature, water content and quality index. With computational fluid dynamics, progress has been made in understanding the circulation of gases around products, in predicting changes in the product, and, therefore, in improving the design of dryers. Process control coupled with on-line sensors, or with techniques like fuzzy logic, gives new approaches to drying control. From an industrial point of view, the first goal of drying process research in the food industry is to achieve a precise control of the product moisture content at the end of the drying process. More generally, drying as a part of a food process must follow the fundamental requirements of food production. This concerns nutritional and sensorial aspects, traceability and food safety; and also minimizing process losses, saving energy and water, and reducing the risk of pollution.

## 1.2

### Biochemical Reactions Induced by Drying

As a general rule, high drying temperatures tend to spoil the quality of food products. But it would be more precise to say that these quality changes are time- and temperature-related. Both parameters enhance the reaction rates, which also strongly depend on the water activity  $a_w$  of the products.

Many biochemical reactions can be induced by temperature increase in foods: Maillard reactions, vitamin degradation, fat oxidation, denaturation of thermally unstable proteins (resulting in variation of solubility or of the germinating power of grains, for example), enzyme reactions (which can either be promoted or inhibited), and so on. Some of these biochemical reactions generate components suitable, for example, for their sensory properties (flavor development); others may be more or less undesirable for nutritional or potential toxicity reasons (vitamin losses, changes in color, taste or aroma, formation of toxic compounds). All the reactions are linked to the simultaneous evolution of product composition, temperature and water content (or chemical potential, or water activity), these factors varying differently from one point to another, from the center to the surface of the products.

Vitamin C (ascorbic acid) is an important nutrient, and it is often taken as an index of the nutrient quality of processes. Ascorbic acid can be oxidized to dehydroascorbic acid under aerobic conditions, followed by hydrolysis and further oxidation. This degradation is influenced by water activity and temperature. In general, vitamin C retention after drying is relatively low, even if quite high contents (in  $\text{g (kg of product)}^{-1}$ ) can be reported for dry products, due to the evaporation of water and the concentration effect. As a general rule, the longer the drying period (low temperatures, high relative humidity, thick products), the lower the retention of ascorbic acid (Santos and Silva, 2008). Freeze-drying provides high retention of vitamin C, due to low temperatures, reduced mobility of reactants, and reduced partial pressure of  $\text{O}_2$ . Vitamin C retention is also improved by all drying processes under an inert atmosphere, which reduce the presence of  $\text{O}_2$ .

Color is one of the most relevant attributes with respect to the quality of dried foods, because it is part of their visual appearance and it is, therefore, most of the time one of the first criteria taken into account by consumers when choosing a new product. Color can change during drying due to chemical and biochemical reactions. The rates of such reactions depend strongly on the drying methods and the processing parameters. The color of fruit, vegetables, aromatic plants and spices is due to the presence of pigments (carotenoids, chlorophylls, anthocyanins, betalains) which are susceptible to degradation by enzymatic or non-enzymatic reactions, induced by drying and continuing during storage (Marty-Audouin *et al.*, 1992).

Chlorophylls are green lipid-soluble pigments with pathways for degradation in food systems that remain poorly understood. Chlorophyll can degrade to undesirable gray-brown compounds such as pheophorbide or pheophytin. Pheophorbide can be further metabolized to colorless compounds in metabolically active tissues. The formation of pheophytin is induced by heat and  $\text{H}^+$  ions. The initial step of chlorophyll degradation in processed foods is a disruption of the tissue, resulting in chemical, enzymatic, and possibly gene expression changes that bring about products of chlorophyll catabolism (Heaton and Marangoni, 1996).

Carotenoids are lipid-soluble orange and yellow pigments divided into two families: carotenes and xanthophylls. Among the carotenes can be cited  $\alpha$ - and  $\beta$ -carotene, the major pigments in carrots, and lycopene, the major pigment in tomatoes. Carotenoids are sensitive to light and temperature; high temperature, long processing time, light and oxygen have been shown to have effects on their

degradation.  $\beta$ -Carotene provides not only color, but also antioxidant capacity, provitamin A, and some other health benefits related to its intake. It can be degraded by thermo-oxidation, leading to the formation of low molecular weight colorless products, which generates losses of color and provitamin A levels as well as the development of off-flavors. Many studies have reported an initial stabilizing effect of blanching pre-treatment on carotenoids due to the inactivation of enzymatic (peroxidase and lipoxidase) activity. However, further dehydration conditions can cause degradation of carotenoids, not only due to chemical interactions but also to physical damage of tissues.  $\beta$ -Carotene is oxidized upon exposure to light and oxygen, and has been described as being labile to different drying techniques (convection, sun, vacuum or freeze-drying, see Soria *et al.* (2009)). Lycopene is a phenolic compound, almost exclusively found in tomatoes, with antioxidant activity renowned for contributing to reducing the risk of cancer in humans. Studying the effect of convective drying on semi-dried cherry tomatoes, Muratore *et al.* (2008) have measured that in non pre-treated samples the highest value of lycopene (for an identical water content reduction to 25% of the initial value) was found in tomatoes dehydrated at the highest temperature (80 °C, versus 60 or 40 °C), showing that in these samples lycopene was damaged by the length of the drying process (4 h versus 9 or 29 h, respectively). In pre-treated samples (by dipping in an aqueous solution of citric acid, sodium and calcium chloride), lycopene contents were preserved at low temperature with long process time (40 °C for 24 h), while for other temperatures this effect was less apparent or absent. The lower decrease in nutritional components in the pre-treated samples can be explained by a more rapid water loss in the presence of sodium chloride reducing the dehydration time, while citric acid provides secondary antioxidant activity.

Anthocyanins are water-soluble, pink, red, violet and blue pigments present in fruits. They are relatively stable in most technological processes, especially when the pH value is maintained low (Marty-Audouin *et al.*, 1992). They can be oxidized to colorless malvone in the presence of hydroperoxides. Betalains are purple red pigments, present in beetroot or cactus pear fruits, with a high antioxidant capacity. When heated in air at neutral pH, they are degraded to brown compounds. Betanin, or “beetroot red”, is a betalain pigment, a red glycosidic food dye obtained from beets and used as a food coloring agent. It degrades when subjected to light, heat, and oxygen; therefore, it is used in frozen products, products with short shelf-life, or products sold in the dry state.

Decrease of water activity in dry products generally leads to an increase in the half-life of these pigments. Maximum stability is observed for  $a_w = 0.12$ .

The biological value of dried proteins varies with the drying procedure. Prolonged exposures to high temperatures can affect the functional properties or render the protein less useful in the diet. Low temperature treatments of protein may in some cases increase the digestibility of protein over the native material.

Lipid oxidation is responsible for rancidity, development of off-flavors, and the loss of fat-soluble vitamins and pigments in dehydrated foods. Lipid oxidation is initiated by heat, light or free radicals and peroxides, activated by metal ions, and enhanced at higher dehydration temperatures. Moisture content also plays an important role in the rate of oxidation. At high moisture contents lipids can undergo enzymatic

hydrolysis, which may cause off-flavor formation, such as soapy tastes, depending on the type of lipids; at a low water activity of  $a_w < 0.2$ , auto-oxidation of unsaturated fatty acids causes off-flavors such as rancidity (Perera, 2005). The porosity of the dried product can have an impact on oxygen concentration and affect the susceptibility to oxygen, which is, for example, higher for freeze-dried products. In all cases the protection of fats with antioxidants (phenolic compounds like BHA<sup>1)</sup> or BHT,<sup>2)</sup> or tocopherols,<sup>3)</sup> for example) is an effective solution. Vacuum or inert gas packaging is also a complementary solution for protecting from atmospheric O<sub>2</sub> during subsequent storage.

Enzymatic activity in food products is inhibited at  $a_w < 0.75$ . Most of the time, enzymatic activity is not desirable, because it affects the amount of nutrients in food (e.g., hydrolysis of lecithin by phospholipase) or the color of the products (e.g., enzymatic browning of fruits and vegetables by polyphenoloxidase). It can be reduced prior to drying by a short heat treatment (vapor blanching), a light sulfitation, an addition of ascorbic acid, or an impregnation by soaking in concentrated salt and/or sugar solution.

A very common non-enzymatic reaction in food products is the browning reaction, either by caramelization or by Maillard reactions. The caramelization process is a complex series of chemical reactions promoted by the direct heating of sugars. It is followed by a condensation step, the isomerization of aldoses to ketoses, and a series of reactions that include both fragmentation reactions (flavor production) and polymerization reactions (color production). Maillard reaction occurs via a complex series of reaction steps between the free amino group of protein-bound lysine and/or other amino acids or proteins and the carbonyl groups of reducing sugars. It is classically described using five basic steps: a condensation step, the Amadori rearrangement reaction to yield aldoseamines or ketoseamines, the ketoseamine decomposition, the so-called Strecker degradation resulting in the formation of a series of volatile organic flavor compounds, and a final step leading to the formation of brown nitrogenous polymers and co-polymers, known as melanoidins (pigments).

Water content and water activity play an important role in the Maillard reaction. Labuza *et al.* (1970) studied the role of water as solvent and reactant in simple low-moisture model systems, and showed that water has a dominant influence on the rate of browning. For the first stage of the Maillard reaction to occur, water is essential. As depicted in Fig. 1.1, the Maillard reaction shows a classic max/min response to change in  $a_w$ , with a maximum in the range  $a_w$  0.65–0.70 under high temperature conditions of 80–130 °C (Labuza and Saltmarch, 1981). As the water content and humidity increase, the browning rate starts to decrease again. At this point the problem is no longer one of diffusion, but rather one of dilution of the reactants. The dual role of water as solvent and reactant in the kinetics of the Maillard reaction was also pointed out by van Boekel (2001). These reactions have nutritional effects (decreased availability of amino acids), and affect the color (browning), aroma and

1) Butylated hydroxyanisole.

2) Butylated hydroxytoluene.

3)  $\alpha$ -Tocopherol = vitamin E.

taste (aldehydes, ketones, pyrazine, furans, etc.) of food products. The rate of browning is high at relatively low water content, and this might explain the ease of browning in dried and concentrated foods. Temperature also has an effect on the browning rate. A two- to threefold increase for each 10 K rise has been reported on model systems; in foods containing fructose, the increase of browning may be five- to tenfold for each 10 K rise.

The control of the discussed reactions depends greatly on the dryer conception and on the control of processing conditions, which should allow one to respect limitations in product temperatures and residence times, and establish the homogeneity of treatment. The quality of process control automation is an important parameter, in particular to avoid over-drying, causing product quality spoilage due to too high final temperatures.

The concept and composition of packaging are the main factors for maintaining an oxygen-free atmosphere that will decrease possible oxidation during storage. The same objective may be reached in the case of powders by coating (i.e., with fat or sugar), or by encapsulation of reactive components or bioactive compounds, which are thus protected from oxygen, water or other conditions in order to improve their stability. Different types of encapsulating agents can be used for spray drying in the food industry: polysaccharides (starches, maltodextrins, corn syrups and arabic gum), lipids (stearic acid, mono and diglycerides), or proteins (gelatin, casein, milk serum, soy and wheat).

Sometimes the development of reactions is wanted, such as in semi-dried plums where a cooked taste is sought (prunes). Roasting of malt represents a case of positive over-drying that contributes to the development of colors and aromas.

### 1.3

#### Physical Transformations During Drying

Different phenomena linked to water loss and temperature variation with time are observed in the course of drying:

- decrease in water activity
- glass transition, crystallization
- melting of fat
- evaporation of volatile components
- migration or retention of components, volatile or not.

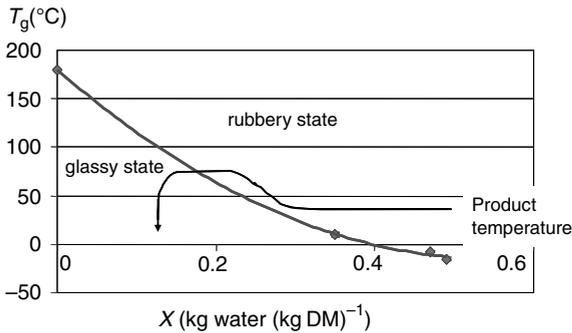
The consequences on product characteristics are complex and interconnected. For example, a decrease in  $a_w$  corresponds to a reduction of water availability and mobility in the medium, increasing biological and microbiological stability, which is the main aim. On the other hand, a decrease in water activity slows down the water transfer, and, therefore, the drying rate, increasing the time that the product must spend at relatively high temperature during which reactions may develop (Rocha Mier, 1993).

Aroma and flavor compounds are volatile chemicals that might evaporate during drying due to heating of the product and removal of water. However, it has been

widely observed that the release of aroma compounds during drying is much less than expected if considering only the volatility or vapor pressure of the molecules. Three explanations have been proposed: selective diffusion, entrapment within microregions, and interactions with the substrate. The first was proposed by Thijssen and Rulkens (1968). Retention is a process mainly controlled by diffusion, and diffusivity of aroma molecules decreases much faster than that of water when the moisture content decreases. As a result, the product evolves during drying as if its surface becomes virtually impermeable to aroma components. Rulkens (1973) also showed that the retention of volatile compounds increases with the dry matter content. The concept of microregions has been used to explain the retention of volatile compounds during freeze-drying (Flink and Karel, 1969). During freezing, sugars might create amorphous microregions entrapping the volatile molecules by hydrogen bonding. This is a description of the retention phenomenon at the microscopic level. It is also possible that retention is influenced by specific interactions with the substrate, such as covalent bonds (aldehydes with  $-\text{NH}_2$  and  $-\text{SH}$  groups), steric entrapment, or sorption (on proteins, lipids). However, the selective diffusion is often presented as the main and most general mechanism. Coumans *et al.* (1994) outlined that the concept of selective diffusion can be exploited to create high aroma retention conditions, by promoting a rapid decrease in water content at the surface of the product.

The retention or loss of aroma compounds is also influenced by the structure (amorphous or crystallized) of the dried product. Structural changes can be used for spray drying encapsulation processes (Bhandari *et al.*, 1992; Ré, 1998). Crystallization tends to increase the loss of aroma, because it rejects impurities, including volatiles. Senoussi *et al.* (1995) measured the loss of diacetyl as a function of the rate of crystallization of lactose during storage. They found that when the lactose was stored at 20 °C above the glass transition temperature  $T_g$ , the amorphous product immediately crystallized and practically all diacetyl was lost after 6 days. Levi and Karel (1995) also found increased rates of loss of volatile (1-*n*-propanol) as a result of crystallization in an initially amorphous sucrose system.

For a simple system of solute and solvent or macromolecular matrices, the glass transition curve (Fig. 1.3) represents a metastable transition from relatively low to very high viscosity, where the product no longer “flows”. In other words, the glass transition temperature,  $T_g$ , is the temperature at which an amorphous solid becomes brittle on cooling, or soft on heating. As the temperature increases above  $T_g$ , many of the physical properties of the material suddenly change. Among the most important changes are an increase in the free molecular volume, an increase in heat capacity, increases in the thermal expansion coefficient and dielectric coefficient, and changes in the viscoelastic properties (Genin and René, 1995). Below the glass transition curve, the food is stable to diffusion-limited processes for extremely long times (glassy state). Above  $T_g$ , the viscosity of the matrix is decreased; glasses and organic polymers become soft (rubbery state) and capable of plastic deformation without fracture. In this state, the molecular mobility is increased by two orders of magnitude, which results in an increased rate of physico-chemical changes in dried products, such as sticking, collapse, caking, agglomeration, crystallization, loss of volatiles,

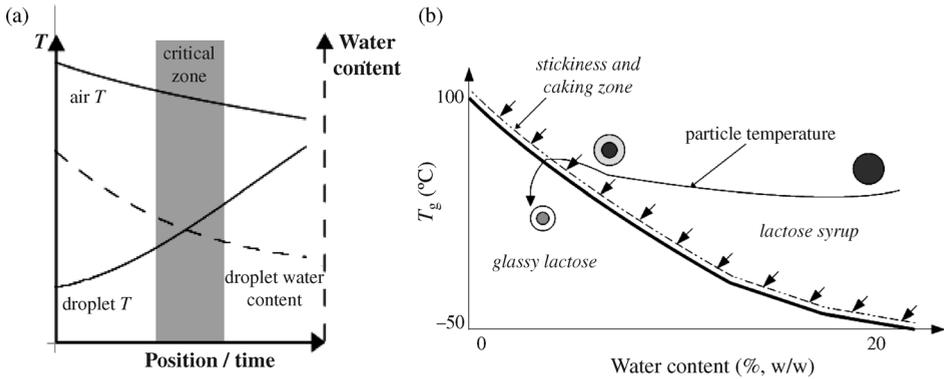


**Fig. 1.3** Typical glass transition curve and typical evolution of food product temperature during drying as a function of moisture content; (DM: dry matter).

browning, and oxidation. In general, biomaterials and foods form a complex, dehydrated mixture of amorphous compounds. Carbohydrates, proteins and minerals are miscible with water, and dehydration increases the solute concentration. Hence, dehydrated foods are supersaturated and non-crystalline amorphous solids, residual water acting as a plasticizer. Depending on their composition and molecular weight, food solids may exhibit a large variety of rheological properties, from brittle glassy solids, to sticky materials (like sugars just above  $T_g$ ) or elastic “rubbers” or leather-like materials (like high molecular weight carbohydrates or proteins over a large range of temperatures above  $T_g$ ). The control of phase and state transitions, and of time-dependent changes in these materials, is often the main requirement for dehydration and maintaining the product stability. Dehydrated food materials often remain in the metastable, non-equilibrium amorphous state for extended periods, but they can also exhibit time-dependent changes. At temperatures above  $T_g$ , sugars may crystallize from the amorphous state, with dramatic changes in the physical state; moisture distribution and migration between the remaining non-crystalline solids may change, affecting the stability of the products. According to a generally admitted rule, the higher the difference  $T - T_g$ , the higher the deterioration or reaction rates. In the glassy state, the water in the concentrated phase becomes kinetically immobilized and, therefore, does not participate in reactions; compounds involved in deterioration reactions may take many months or even years to diffuse over molecular distances and approach each other to react.

Some dehydrated foods (e.g., spray-dried powders or freeze-dried materials) are expected to form glassy structures, but the majority of traditionally dehydrated foods (cereals, fruits, fish and meat, vegetables, etc.) exist in the rubbery state (Alves-Filho and Roos, 2006).

For example, powdered milk products remain dry, free-flowing and stable when maintained below the glass transition temperature. However, if the powder picks up moisture from the air or experiences elevated storage temperatures, it may exceed the glass transition curve and become less stable (rubbery state). In this case, powdered milk would be likely to get sticky, and the powder would cake together. In a spray-dryer, operating parameters have to be chosen to ensure a rapid drying

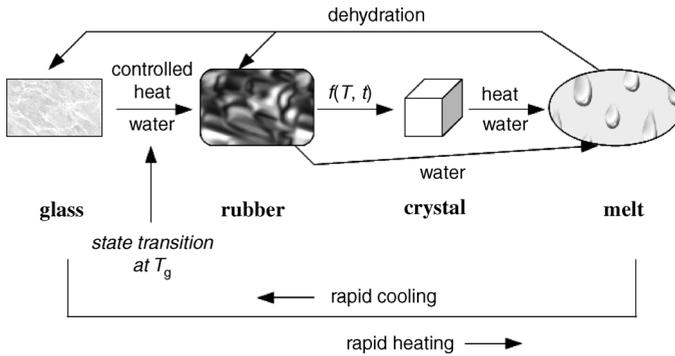


**Fig. 1.4** (a) Typical temperature and water content evolution in a co-current spray dryer, and (b) temperature–water relationship in spray-drying of lactose-based materials (adapted from Roos (2002)).

of the surface of the droplets so that the temperature rapidly passes below the glass transition temperature in order to avoid caking and to reduce the deposition rate and the adhesion of particles on the walls. The rapid removal of water results, within a short time, in the vitrification of liquid droplets and the formation of a solid particle surface, which prevents the formation of liquid bridges between particles or particle adhesion on the inner surfaces of the dryer. It is, therefore, very important to be able to predict the temperature and the moisture content at the surface of the powder versus processing time and state variables, as these govern the fouling of spray dryer walls (Fig. 1.4).

A combination of the calculation of local moisture content within particles with computational fluid dynamics (CFD) for transient, three-dimensional flow patterns in spray dryers is nowadays possible, as discussed in Chapter 5 of Vol. 1 of this series. Such CFD can indeed give precise information with regard to particle characteristics (temperature, water content) and trajectories in the dryer on a local scale, but it requires simplifications of the product and process (density, porosity, heat and mass transfer), and many experiments to determine unknown model parameters and to verify assumptions about, for example, the boundary conditions. Langrish and Kockel (2001) have postulated that the short drying times shown for particles of the size typically encountered in spray dryers, compared with the residence times of such particles in the dryer, mean that the particles are essentially in equilibrium with the gas, so that, for the purpose of estimating wall deposition, the moisture gradients are likely to be small. They concluded that a linear falling-rate curve (which involves only the average moisture content) is an acceptable approximation for the drying of milk powders.

A slow decrease in water content and water activity,  $a_w$ , would correspond to the concentration of solutions reaching the solubility limit with crystallization (sugars, salts). If drying is fast, some components may reach the amorphous state without crystallization, with a transition through the rubbery state, which is soft and sticky,



**Fig. 1.5** Change of physical state of an amorphous glass through rubbery to crystalline state;  $T$ : temperature,  $t$ : time (adapted from Bhandari and Howes (1999) and Roos (2002)).

before reaching the glass state, which is chemically more stable (low molecular mobility). On the contrary, heating may have the inverse effect (Fig. 1.5).

The described phenomena are also strongly related to the product composition. For example, during spray drying of milk or whey, the crystallization of lactose is promoted by small crystalline seeds. In general, food solids with low  $T_g$  cannot be successfully dehydrated into free-flowing powders which can easily be handled, packaged and stored. For example, sugar-containing materials such as fruit juices are extremely difficult to dehydrate, as the solids tend to adhere to dryer surfaces and cake inside other processing equipment. For such products, the addition of polysaccharides with high molecular weight (so-called “ $T_g$ -depressing agents”, such as, especially, dextrans) enhance the glass transition temperature, allowing passage to the glassy state, and avoiding sticking of particles on the dryer walls (Tab. 1.3).

**Tab. 1.3** Glass transition temperature of anhydrous sugars and carbohydrate polymers (adapted from Bhandari and Howes (1999)).

Food Materials	Molecular Weight	$T_g$ (°C)
Fructose	180	5
Glucose	180	31
Galactose	180	32
Sucrose	342	62
Maltose	342	87
Lactose	342	101
<i>Maltodextrins</i>		
DEc 36	500	100
DE 25	720	121
DE 20	900	141
DE 10	1800	160
DE 5	3600	188
Starch		243

The different states and transitions for the lactose component in milk were described by Vuataz (2002) and can be used for better control of drying and storage.

Further changes in physical state can also be observed under temperature elevation, like the melting of fat in cooked meats (“charcuteries”), for example. Migration of molten fat can lead to deterioration in several product quality aspects. More frequently, volatile substances are lost by evaporation. Thermodynamically, components with a low affinity for water may evaporate at temperatures largely below their boiling temperature.

#### 1.4

#### Mechanical Transformations Induced by Drying

The physical transformations that may appear in foods are different according to the different drying modes. When the product temperature is high enough for the product water vapor pressure to be equal to the total ambient pressure, the drying mode is ebullition. For example with a product with  $a_w = 0.3$ , the boiling temperature will be 114 °C under 0.5 bar, and 137 °C at atmospheric pressure. The boiling temperature depends on both ambient pressure and product water activity. This type of drying can be conducted at the surface of rotating drums, internally heated to 200 °C by steam, and is used, for example, for mashed potatoes, baby cereals, soups, or starch. It leads to a dry product in the shape of flakes, which shows a porous structure and is easy to dissolve. As the partial pressure of vapor is equal to the total pressure at the surface of the product, there is no oxidative reaction during drying by ebullition, and hence a better quality of O<sub>2</sub>-sensitive products can be obtained. The product is then milled after drying to a finished flake or powder form. Drum-dried ingredients reconstitute immediately and retain much of their original flavors, color and nutritional value, at an economical price.

Freeze-drying also leads to a porous structure created by sublimation of frozen water, that is, by direct moisture removal without melting in the liquid state. Moisture is typically removed in two stages:

- a primary drying, which refers to the removal of ice by sublimation
- a secondary drying, corresponding to the desorption of the unfrozen remaining water.

Freeze-drying is the drying method that gives final products of the highest quality compared to other drying methods. Due to the absence of liquid water and to the low temperatures required for the process, most deterioration reaction rates are very low, which gives a final product of excellent quality. The solid state of water during freeze-drying, with restricted movement in comparison to liquid water, protects the primary structure, and preserves the original structure and the shape of the food material with minimal reduction in volume. However, it requires a rigorous control of phase and state transitions of both water and solids during dehydration and of dried solids during storage. Collapse of structure during processing or storage results from passing above the melting temperature of ice or above the glass

transition temperature of the dry region of the solid, with subsequent flow due to thermal or water plasticization. Damage to the plant microstructure has also been observed on freeze-dried fruits and vegetables, but result from the freezing process *per se* (Lewicki and Pawlak, 2005). Growing ice crystals can injure the cell walls, creating cavities and disrupting the continuity of the cellular structure in the freeze-dried material. This phenomenon depends on both the freezing rate and the storage temperature of the frozen material, which govern crystal size, and on the nature of the plant materials, which differ in terms of the size of their cells.

Convective hot air drying is the most frequently used drying mode. If water migrates in the liquid state from the center of a solid product towards the surface, some shrinkage will be observed as a function of evaporated water volume. The consequences will appear as mechanical effects, and changes in shape and structure, especially if the product is malleable (e.g., fruits, vegetables, meat). These changes will only partially disappear during rehydration, because most of the physico-chemical changes that occur during drying, like disruption of cellular integrity, starch gelatinization or protein denaturation, are not reversible. Another important consequence of shrinkage is the decrease in the rehydration capability of the dried products.

The theoretical basis for predicting shrinkage should involve mechanical laws which take into account material stresses and deformations during dehydration. However, such an analysis is extremely complicated for foods because of the multiphase and cellular nature of the materials and because the variation of the mechanical properties with water content and temperature is generally not available. Therefore, most studies of food shrinkage are experimentally based. Many authors have evaluated the shrinkage on the basis of a bulk shrinkage coefficient, defined as the ratio of sample volume at time  $t$  to the initial volume. Khraisheh *et al.* (2004) showed that the volumetric shrinkage of potato samples follows a linear relation with moisture content at varying drying air temperatures, which suggests that the shrinkage is predominantly due to the volume of water removed. Such a linear shrinkage behavior of food materials has been reported by many researchers, whereas others reported a two-period phenomenon. In this case, the volume of water removed during the final stages of drying is larger than the reduction in sample volume. This behavior can be explained by the decrease in the mobility of the solid matrix of the material at low moisture contents. At lower drying temperatures a more uniform moisture distribution exists, inducing less internal stresses that allow the sample to continue to shrink until the last stages of drying. Such a substantial shrinkage results in a low porosity. On the contrary, at higher air temperatures, case hardening of the surface may occur and the volume of the sample becomes fixed at an earlier stage, inducing less shrinkage and a more intensive pore formation. Such a phenomenon also depends on the amorphous state of the sample. As previously stated, a significant change in volume can only be noticed if the solids remain in the rubbery state, at a temperature above  $T_g$  for the particular moisture content. Above  $T_g$ , the viscosity of the material drops considerably, to a level that facilitates deformation. During drying of pasta, Willis *et al.* (1999) observed a higher shrinkage when samples were dehydrated at 100 °C and 50% relative humidity than in samples dehydrated

at 40 °C at the same air relative humidity. In the first case, the temperature of the pasta was higher than the glass transition temperature, and the product remained in the rubbery state and shrank uniformly during the whole drying process. In the second case, the surface of the material became glassy, decreasing shrinkage and increasing residual stresses in the dried material, which underwent cracking and breakage during storage.

Surface cracking is another phenomenon that may occur during drying. The presence of fissures in pasta or grains decreases their quality and commercial value as well as the yield of the drying process. This happens when shrinkage is not uniform during the drying process, leading to the formation of unbalanced stresses and failure of the product. When water is removed from the material, a moisture gradient appears between the inside of the material and the external parts, generating a differential shrinkage and mechanical stresses in the product that occasionally lead to cracking of the product. Cracks appear if the stress locally exceeds the failure strength of the material. For many food materials, the tensile strength is significantly lower than the compressive strength, and fissures are therefore caused by tensile failure within the region of the product under tension, which is not always the surface (Kamst *et al.*, 2002). High stresses are generally induced by rapid drying at high temperature and low relative humidity. Increasing the relative humidity allows reduction in crack formation, even at high drying temperatures with high drying rates.

## 1.5

### Storage and Rehydration of Food Products

Drying is not an isolated operation. In addition to the frequently necessary pre-treatments, other post operations may affect the quality of the dry product, from storage to final use.

The main problem during handling and storage is moisture adsorption by the product surface in contact with the surrounding atmosphere. Moisture adsorption depends on the ambient relative humidity and temperature, and on the water activity of the surface of the product. The adsorbed water diffuses inside the product and increases the mobility of water and solutes, promoting reactions and modifying physical and mechanical properties (e.g., loss of crispiness). The retention of volatile components encapsulated in a dry matrix (freeze or spray dried) decreases upon structure collapse or crystallization of amorphous components. For example, diacetyl encapsulated in lactose or skimmed milk powders is protected as long as the storage conditions are suitable to keep the lactose in an amorphous state (low water activity and temperature close to  $T_g$ ). As soon as crystallization occurs, aroma losses are observed. However, the presence of proteins (as in milk) may contribute to retention of the volatile component (Senoussi *et al.*, 1995).

During the storage of amorphous lactose powder, no crystallization is observed for  $a_w < 0.35$ . Above 0.35, the glass transition temperature  $T_g$  decreases to values below the ambient temperature, leading to crystallization at a rate depending on

temperature  $T$ , or, more precisely, on the difference between  $T$  and  $T_g$ . At a fixed water content, local crystallization is accompanied by water release; moisture can be absorbed by the rest of the amorphous phase, resulting in a decrease in  $T_g$  and an increase in the crystallization rate ( $T - T_g$  increase). During milk powder storage, crystallization of amorphous lactose may also lead to agglomeration and caking.

Additional phenomena likely to appear during storage are similar to those observed during drying: Maillard reactions, oxidations (enhanced by UV radiation), breakage when handling, especially for fragile, fissured products. The role of packaging is to create an additional barrier against moisture, oxygen, radiation, and even mechanical impact. A controlled atmosphere associated with a low gas permeability by appropriate packaging can ensure good protection.

Dry products are very often used after their rehydration, in different conditions and contexts, involving various mechanisms. For example, for breakfast cereals, crispiness must be preserved for some time, even after adding milk; in contrast, soups are prepared from powder mixtures which must dissolve quasi-instantaneously in hot water.

Several aspects must be taken into account concerning rehydration (Bimbenet *et al.*, 2002). For powders, the dispersion in water depends on the size (agglomeration favors the dispersion), the composition (surface wettability i.e., composition in fat and non-soluble components), or the sinkability linked with structure (porosity, capillarity), leading to formation of lumps or precipitates.

Rehydration will usually not lead to recovery of the initial product, but to a different product. Drying creates irreversible transformations such as protein denaturation (insoluble), modified aroma and color, loss of firmness and shape. In order to compare the rehydration capacities, different criteria and standards, like temperature or stirring, have been defined according to product specificity and final use (Lewicki, 1998; Pisecky, 1997).

## 1.6

### Conclusion

New technological tendencies in the drying of foods are mainly quality oriented, and they refer to:

- well adapted pre-treatments
- formulation with natural additives, functional molecules, encapsulation and coating
- optimization and control of process parameters, especially temperature and humidity
- combined drying modes (simultaneous or successive) during the drying period, with pulsed or intermittent drying for a better control of moisture diffusion.

Significant progress has been achieved in the drying of food solids. In order to avoid a substantial shrinkage, convective drying can be associated with a short treatment at reduced pressure, which gives a nice texture to fruit or vegetable pieces

for breakfast cereals or instant soups. Another similar idea is based on the concept of drying with sudden expansion. The solid is heated under pressure by vapor at high temperature, and then suddenly expanded to a pressure at which water boils by auto-vaporization, creating a high porosity in the solid. Two batch processes of this kind have been described in the literature:

- “Explosion puffing”, developed by American researchers in the 1960s and applied to fruit and vegetable pieces (mushroom, celery, onion, pepper, pear, pineapple, strawberry, and cranberry) (Kozempel *et al.*, 1989; Jayaraman and Das Gupta, 1992). The product is heated to 150–200 °C under pressure, and then suddenly expanded to atmospheric pressure.
- “Controlled sudden decompression”, developed by French researchers in the 2000s, based on a similar principle, but with a lighter heating (100–165 °C) and a sudden decompression under vacuum (Louka and Allaf, 2004; Louka *et al.*, 2004). The process is applicable to very thermosensible foods (raspberry, kiwi fruit, etc.); it allows one to obtain dried product of a quality similar to freeze-dried products, at lower cost and with a decontamination effect.

More profound knowledge of the changes in the properties of foods that occur with processing is needed for the design of better drying methods that preserve desirable characteristics and minimize or eliminate undesirable ones. A larger amount of quantitative data on sensory and textural properties and on kinetics, as a function of food composition and moisture content, needs to be gained in the future. Simple model systems must be used to develop relevant data. At the present time, the information available on nutritional and functional component stability in foods during drying is still limited.

### Additional Notation Used in Chapter 1

$T_g$  glass transition temperature, °C

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