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Porosity

Establishing the Relationship between Drying Parameters and Dried Food Quality

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This book is dedicated to those individuals
who dedicate their lives to exploring
the benefits of nature's repository
in service to humanity.

Preface

The preservation technique of drying provides a significant increase in the shelf life of food materials, along with modification to quality attributes as a result of simultaneous heat and mass transfer. Variations in porosity are just one of the microstructural changes that take place during the drying of most food materials. Some studies have found a possible relationship between porosity and the properties of dried foods. However, no conclusive relationship has yet been established in the literature. This book provides an overview of the factors that affect porosity, as well as the effects of porosity on dried food quality attributes. The effect of heat and mass transfer on porosity is also discussed, along with porosity development under various drying methods. After an extensive review of the literature concerning the study of porosity, it emerges that a relationship among process parameters, food qualities, and sample properties can be established. Finally, hypothesized relationships among process parameters, product quality attributes, and porosity is discussed in detail.

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Contents

Nomenclature

D	Mass diffusivity (m^2/s)
k_i	Permeability of fluid (m^2)
$k_{i,i}$	Intrinsic permeability of fluid (m^2)
$k_{i,r}$	Relative permeability of fluid (m^2)
k_{th}	Thermal conductivity (W/m/K)
$k_{th,air}$	Thermal conductivity of air (W/m/K)
X	Moisture content dry basis (kg/kg, solid)
M	Mass fraction (kg/kg, total)
P	Total gas pressure (Pa)
T	Temperature of product (°C)
T_{air}	Drying air temperature (°C)
T_g	Glass transition temperature (°C)
ΔT	Solid mobility temperature (°C)
V	Total volume (m^3)
ε	Apparent porosity
τ	Tortuosity
ε_0	Initial equivalent porosity
μ	Viscosity (Pa s)
χ	Volume fraction of water (m^3/m^3)
ρ	Solid (kg/m^3)
r	Radius of pores (m)
$N(r)$	Number of pores between maximum and minimum radii of pores
N_T	Total number of pores
$f(r)$	Diameter probability function

Subscript

cw	Cell wall material
sg	Sugar
st	Starch
w	Water
ex	Excess volume
i	Component
n	Number of components
s	Solid
0	Initial
g	Gas
min	Minimum
max	Maximum
p	Particle
b	Bulk
eff	Effective
A	Binary molecular

Chapter 1
Introduction

1.1 Background

Porosity is defined as the ratio of free spaces occupied within a material to the total volume of the material. What defines a material as porous or a nonporous remains to be determined, although a few studies suggest that a nonporous material is one that has a porosity of less than 0.25, with a porous material having a porosity greater than 0.4 (Karathanos et al. 1996; Goedeken and Tong 1993; Waananen and Okos 1996; Lozano et al. 1983; Zogzas et al. 1994; Krokida and Maroulis 1997).

Knowledge of pore formation in food during the drying process can be useful in predicting transport properties, such as thermal conductivity, thermal diffusivity, and mass diffusivity (Rahman 2001), as well as dried-food quality (Xiong et al. 1992; Mayor and Sereno 2004; Mavroudis et al. 1998). This is because most of the factors that contribute to transport properties are significantly affected by the structure of the food material.

Drying methods and drying conditions affect the porosity of the final dried product. Thus, the same raw material may possess different pore characteristics at the conclusion of the drying process, depending on the drying method and conditions (Sablani et al. 2007). There is a scarcity of thorough research in the literature concerning the characteristics of pores in food products. Depending on the end use of the dried food materials, high porosity may be either desirable or undesirable. For example, if a long bowl life is required for a cereal product, a crust (lower porosity) product that prevents moisture absorption may be preferred. On the other hand, dehydrated foods, such as fruits, vegetables, and instant noodles, should possess high porosity to facilitate their fast rehydration.

In addition, porosity also gives an indication of the extent of shrinkage that a food material undergoes during drying, which in turn determines the size and shape of the finished product (Ayrosa and Pitombo 2003). Furthermore, it is well established that a more porous structure of the final product is an indication that less

M.U.H. Joardder et al., *Porosity*, SpringerBriefs in Food, Health, and Nutrition, DOI 10.1007/978-3-319-23045-0_1

structural damage took place over the time of drying. Finally, knowledge of the porous structure of dehydrated materials may help in the accurate modeling of mass and heat transfer processes, including the prediction of water diffusivity in various foods (Datta 2007).

It has also been found that porosity has a direct effect on other physical properties, such as the mass diffusion coefficient, thermal conductivity, and thermal diffusivity. The mechanical and textural properties of food are also correlated to porosity. Vincent (1989) found that torsional stiffness (0.5–7 MPa) varied with porosity (0.83–0.54) in the case of fresh apples. In addition to these, porosity plays a significant role in the agglomeration of cell strength in dried foods. Furthermore, variations in pore characteristics have a significant effect on the textural and sensory properties of foods (Vickers and Bourne 1976; Christensen 1984). Despite the importance of the effects of porosity on food properties, little work has been done to establish a relationship between porosity and dried-food qualities.

In brief, the prediction and control of porosity are complex tasks faced by food scientists and engineers. Porosity is one of those physical parameters that is required to build food behavior models; it is particularly relevant in the case of porous solid materials and as such plays a paramount role in the modeling and understanding of drying operations, cold and controlled-atmosphere storage, and other food-treatment processes (Lozano et al. 1983).

The outline of this book is as follows. The pore formation mechanism is described first, followed by a discussion of the factors that affect porosity during drying and a description of heat and mass transfer mechanisms through porous media. Pore development in various drying processes is then discussed. The effects of porosity on the other physicochemical properties of dried food materials are then reviewed. Finally, a hypothesis is proposed concerning the relationship between process parameters and product quality through an examination of pore characteristics.

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Chapter 2
Food as a Material

2.1 Introduction

Most materials subjected to a drying process can be treated as hygroscopic porous and amorphous media with multiphase transport of heat and mass. Food can be classified according to its water-binding properties, for example, whether it is nonhygroscopic or hygroscopic. In addition, it can also be classified as porous or nonporous according to its void-containing features. Overall, foods are more complex materials than pure solid crystalline in terms of physical properties. In the following sections, various material-related properties of plant-based foodstuffs are discussed in detail.

2.2 Water-Binding Properties

The chemical composition and physical structure of food materials affect both heat and mass transfer mechanisms (Rosselló 1992). If food is treated as a material, it can be classified according to its water-binding properties, such as whether it is nonhygroscopic or hygroscopic. In addition, it can also be classified as porous or nonporous based on its void-containing features. On the other hand, most food materials behave as if they were of an amorphous rather than crystalline nature. Overall, foods are more complex materials than pure solid crystalline in terms of physical properties than solid crystalline materials.

M.U.H. Joardder et al., *Porosity*, SpringerBriefs in Food, Health, and Nutrition, DOI 10.1007/978-3-319-23045-0_2

2.2.1 Hygroscopic

A material can be said to be hygroscopic when it possesses a large amount of water physically bound by a solid matrix, as shown in Fig. 2.1. Because of the presence of bound water, most of the time, hygroscopic materials deform during the drying process. These materials have equilibrium moisture isothermal relations. In general, foods can be considered hygroscopic, although there are some exceptions. The vapor pressure in hygroscopic materials differs from that in pure water (Karel and Lund 2003). This pressure depends on the water activity of hygroscopic materials. At a given temperature, water activity represents the ratio of vapor pressure due to the water in hygroscopic materials to the vapor pressure of pure water (Mathlouthi 2001). The bond of water with a solid matrix determines the degree of hygroscopicity. This can be expressed by the water activity given a certain moisture content of food materials (Chen and Mujumdar 2008).

2.2.2 Nonhygroscopic

The term *nonhygroscopic* does not encompass bound water, where the partial pressure of the water in the material is equal to the vapor pressure. Pore spaces in nonhygroscopic materials are filled with fluid when the material is completely saturated, or air if the materials are completely dried, as shown in Fig. 2.1. In nonhygroscopic

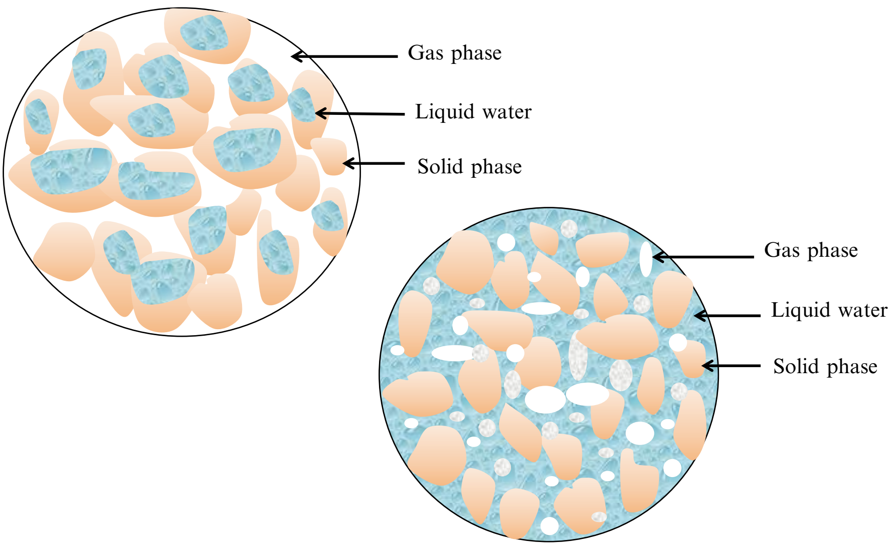

Fig. 2.1 Hygroscopic (*left*) and nonhygroscopic (*right*) materials

materials, the quantity of physically bound water is insignificant. When material of this kind undergoes drying, its shrinkage is not noticeable. In nonhygroscopic materials, temperature is the only parameter that controls vapor pressure. Moisture movement in nonhygroscopic materials creates no further complications because it is found in hygroscopic materials (Geankoplis 1993). Because of the insignificant amount of bound water, nonhygroscopic materials generally do not shrink during the drying process.

2.3 Structure Homogeneity

Regarding the arrangement of atoms or molecules, a material can be classified as amorphous and crystalline. The proportion of these two states dominates the functional and physical properties of the material, as shown in Table 2.1. Some food processing cause crystallization of food materials, such as the freezing of foods by crystallization of water, sugar, and salt. Consequently, the shelf life of food materials is prolonged significantly. On the other hand, to retain the flavor, taste, and color of food materials, the amorphous state of food microstructure is essential (Roos 1995).

2.3.1 Crystalline and Polycrystalline

Crystalline materials have a periodically repeated lattice of atoms or molecules. In this type of material, molecules are packed tightly (Bhandari 2012). Thermodynamically, crystals are found in a stable equilibrium state (Hartel 2001). Adding heat to a material up to a certain level will cause the material to melt. In addition, crystalline materials follow the heat capacity concept, which means that the temperature increases

Table 2.1 Differences in physical properties between crystalline and amorphous states of materials

Property	Crystalline state	Amorphous state
Density	High	Low
Mechanical strength	Strong (ductile)	Brittle
Compressibility	Poor	Good
Internal porosity	Low	High
Hygroscopicity	Low	High
Softening temperature	High (melting)	Low (glass transition)
Chemical reactivity	Low	High
Interaction with solvent	Slow	Rapid
Heat of solution	Endothermic	Exothermic

Adapted from Bhandari (2012)

proportionally in response to heating. When crystalline materials reach their melting temperature, they use the latent heat from melting without increasing the temperature until they reach their melting point. In general, melted liquid has a greater heat capacity because the liquid phase demonstrates slower rising temperature as a result of heating.

2.3.2 Amorphous Materials

Amorphous materials have a disordered molecular structure, for example, atoms or molecules arranged in a lattice that is duplicated periodically in space. Examples included all amorphous solids, water glasses, organic polymers, or even metals. Because molecules in an amorphous state have a more open and porous arrangement, individual molecules easily interact with external materials. An example of this is water, which is easily absorbed by amorphous food materials. Amorphous solids have higher entropy than crystalline materials because the microstructure of amorphous materials may consist of a short range array and regions of high and low density (Lian 2001).

The glass transition temperature (T_g) is the critical temperature at which a material changes from being "glassy" to "rubbery" (Roos 1998, 2003). Glassy here means hard and brittle, allowing for easy breakage, while rubbery means elastic and flexible. In contrast to melting, when an amorphous material undergoes a glass transition heat capacity change, it has no latent heat.

Slade and Levine (1991) first introduced the concept of a glass transition to explain or identify the physicochemical modifications in food materials during food processing and storage. In addition, this theory was proposed in order to explain the processes of shrinkage, collapse, fissuring, and cracking during drying (Cnossen and Siebenmorgen 2000; Karathanos et al. 1993, 1996a). Contrary to these findings, Rahman (2001) asserted that the glass transition theory does not always hold true for all products or processes.

Therefore, the heterogeneous nature of plant-based food materials, including fruits and vegetables, at the microstructural level could be one of the causes of the differences in porosity of dried foods of the same materials (Aguilera and Stanley 1999).

2.4 Pore Characteristics

Most parenchyma tissue contains intercellular spaces, generally filled with water and air. This initial volume of air is known as the initial porosity. Reeve (1953) showed that the width of the intercellular space varies from 210 to 350 μm, whereas the length ranges between 438 and 2000 μm. The initial porosity in fruits and vegetables varies between 0.02 and 0.34 (Boukouvalas et al. 2006; Ting et al. 2013). However, the distribution of these intercellular spaces is anisotropic in nature. They has a significant role in overall shrinkage during drying. The same material with a different initial porosity ends up undergoing different amounts of volumetric shrinkage. This is because the amount of initial porosity affects the rigidity of the tissue.

It has been found that a material with higher initial porosity shows higher shrinkage than the same material with lower initial porosity. In addition, the initial intercellular spaces govern the transport of mass and heat over the course of drying. Therefore, most macroscopic properties are affected directly or indirectly by the corresponding microstructural properties (Mebatsion et al. 2008; Aguilera 2005).

A large body of literature has been published on many food materials that behave like porous media because they contain porous structures. Many food materials are highly porous, for example, white bread and butter cookies, which have porosities of 0.90 and 0.55, respectively. Powder-based materials, such as milk powder, flour, and chocolate pudding, have porosities of 0.454–0.61, 0.69, and 0.5, respectively (Rassis et al. 1997). The minimum and maximum porosity values of a wide range of food categories have been compiled in the review works of Boukouvalas et al. (2006).

Difficulties arise when an attempt is made to classify a material as porous or nonporous. In this connection, Goedeken and Tong (1993) investigated measurements of permeability on pregelatinized flour dough, where they took porosity as a function in the range of 0.10–0.60. A significant correlation was found between permeability and porosity. The results revealed, for a porosity range of 0.1–0.6, permeability values ranging from 1.97×10^{-14} to 2.27×10^{-11} m^2. For a porosity of less than 0.4, more resistance to air flow through samples was allowed because the permeability was low (7.9×10^{-13} m^2). From this finding the authors concluded that a material can be defined as porous when it possesses a porosity of at least 0.4. However, Waananen and Okos (1996) proposed that a material having a porosity greater than 0.25 can be classified as porous.

In light of the findings in the literature, materials having a porosity of less than 0.25 can be classified as nonporous, while intermediate porous materials are those having a porosity between 0.25 and 0.4, and highly porous structures have a porosity above 0.4 (Karathanos et al. 1996b; Waananen and Okos 1996; Rahman et al. 1996; Krokida and Maroulis 1997).

Most pores in the fresh and dried porous samples are nonuniform in size and irregular in geometry (Yao and Lenhoff 2004). Therefore, to interpret the complex nature of pore geometry, some structural parameters are used, including pore type, pore size, pore size distribution, tortuosity, and specific surface area.

2.4.1 Pore Types

In general, most food materials are the combination of solid, liquid, and gases. Porosity is the volume of void or gas to the total volume and refers to the ratio of the free space that exists in the material to the total volume of the material. It can be obtained from the following relationship:

$$\text{Porosity} = \frac{V_{\text{Void}}}{V_{\text{Total}}},$$

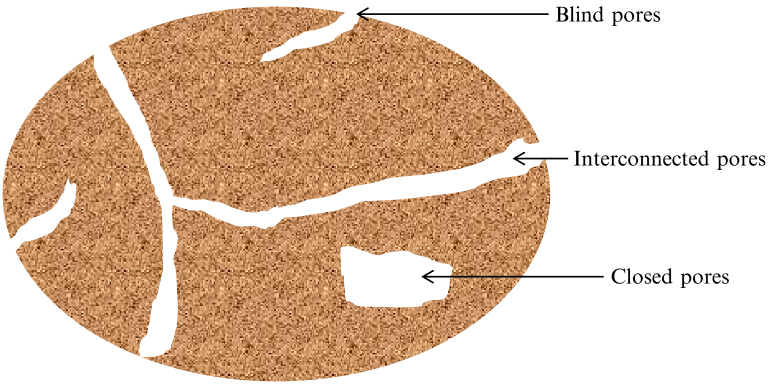

Fig. 2.2 Different types of pores in food sample

$$\varepsilon = \frac{V_g}{V_s + V_w + V_g} = 1 - \frac{V_s + V_w}{V}, \tag{2.1}$$

where V_a, V_w, V_s, and V are the gas, water, solid, and total volume, respectively.

Porosity can be alternatively expressed according to the following equation because it is usually estimated from the apparent density and the true density of the material:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p}. \tag{2.2}$$

Depending on the nature of the pores, three types of pore (Fig. 2.2) can develop during drying: blind pores, closed pores, and interconnected pores. It can be seen from Fig. 2.2 that blind pores are those that have one end closed, while interconnected pores are those that allow for the flow of fluids, and closed pores refer to pores that are closed on all sides.

Taking into account all types of pores, an apparent porosity of food material can be determined by the following relationship:

$$\varepsilon_{app} = \varepsilon_{close} + \varepsilon_{open} + \varepsilon_{blind}. \tag{2.3}$$

2.4.2 Pore Size

Pore size is important in both water transport and the mechanical properties of the plant tissue during drying. The size of a pore determines the pattern of internal water transport over the course of drying.

On the basis of pore size, pores in porous materials can be classified as macro-, micro-, and mesopores. Micropores have a width greater than 2 nm, pores with a width greater than 50 nm are called macropores, and pores between these two sizes are called mesopores.

In terms of porosity, materials can be divided into two groups, porous and capillary-porous materials. This classification is based on pore sizes. Porous materials are defined as those having a pore diameter greater than or equal to 10^{-7} m, while materials with pore diameters of less than 10^{-7} are called capillary-porous materials (Datta 2007). However, most food materials are treated as capillary- porous materials.

2.4.3 Pore Size Distribution

Pore size distribution serves as a descriptor of the size features of pores and represents the pore distribution density within a particular dimension of a sample (Yao and Lenhoff 2004). Pore size distribution is an important parameter in both the quality and transport of moisture during drying (Rahman et al. 2002). It can be described as the number diameter probability density function given as follows (Rahman et al. 2002; Prachayawarakorn et al. 2008):

$$f\left(r\right)=\frac{\mathrm{d}\left(\frac{N\left(r\right)}{N_{\mathrm{T}}}\right)}{\mathrm{d}r},\quad r_{\min}<r<r_{\max} \tag{2.4}$$

where $r_{\min}$ and $r_{\max}$ are the minimum and maximum radii, respectively. $N(r)$ is the number of pores between the pore radii r and $r+\mathrm{d}r$, and N_{T} is the total number of pores in the network.

Analyzing a scanning electron microscope image of a dried sample for a small area of a dried apple, we found (Fig. 2.3) that a large number of open pores were present on the surface of the dried apple.

In Fig. 2.3a, the selected area was 9.8 mm^2, in which the exposed area of the open pores was found to be 4.8 mm^2, which is approximately half the exposed surface area. In addition, the sizes of the investigated pores were in the range of 50–260 μm. This distribution also shows that many pores have diameters of even more than 50–200 μm diameter, as shown in Fig. 2.3b.

2.4.4 Specific Surface Area

Specific surface area refers to the accessible area of solid materials per unit of a porous material. In other words, the specific surface area is defined as the area of solid matrix per unit of porous material. In addition, the specific surface area of porous food

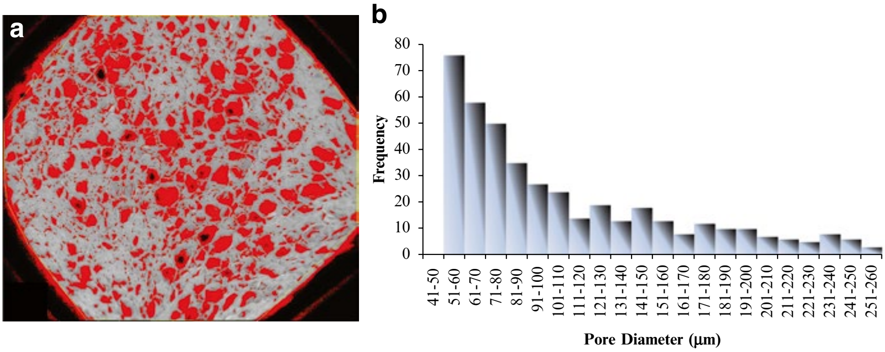

Fig. 2.3 (**a**) Surface pores in an apple sample (obtained by image analysis) and (**b**) pore distribution

materials is directly related to the binding capacity of water with a solid matrix. In other words, hygroscopic porous materials with higher specific surface areas possess more bound water than porous materials with lower specific surface areas (Jones and Or 2002). It is worth noting that even porous materials with the same porosity with different pore sizes have different values of specific surface area. The specific surface area is determined through accurate application of BET analysis.

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Chapter 3
Pore Formation and Evolution During Drying

3.1 Introduction

Water in fresh fruits and vegetables remains contained primarily in the cells (intracellular) and stays intact before any type of processing. A small amount of water exists within the intercellular spaces. Halder et al. (2011b) found that more than 85–95 % of the water within selected fresh fruit and vegetable tissues is intracellular and the remaining water is present in the intercellular spaces.

Internal moisture transport takes place by means of three mechanisms: (1) transport of free water, (2) transport of bound water, and (3) transport of water vapor. Liquid may flow owing to capillary and gravitational force, the transport of water vapor by diffusion, and the transport of bound water by desorption and diffusion. Crapiste et al. (1988) divided water flux inside plant tissue into three types of transport during drying: *intercellular* flow refers to the movement of water vapor through intercellular spaces, *wall-to-wall* flow refers to capillary water flow through cell wall tubes, and *cell-to-cell* flow refers to water flux through vacuoles, cytoplasm, and cell membranes.

In general, at high moisture contents, liquids flow as a result of dominating capillary forces. As the moisture content decreases, the amount of liquid in the pores also decreases, and a gas phase is built up, causing a decrease in liquid permeability. Gradually, the mass transfer is taken over by vapor diffusion in a porous structure, with increasing vapor diffusion (Datta and Rakesh 2009).

The evolution of porosity during drying is mainly caused by the void space left by the migrated water. However, the shrinkage of the solid matrix toward the center of a sample compensates for the void volume. Therefore, insight into heat and transfer mechanisms and the structural deformation phenomenon are essential to an understanding of the evolution of porosity in the course of the drying process. On the other hand, these transfer mechanisms and structural changes are significantly influenced by both material properties and process parameters.

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In particular, moisture content, solid density, initial density, particle density, and glass transition temperature are the important material properties that must be taken into consideration. Air temperature is the primary process factor that significantly influences the structural modification of food material. An improved interpretation of pore formation and evolution based on those material properties and process conditions is discussed in what follows.

3.2 Water Distribution Concept

Pore formation is prevented by the shrinkage, collapse, or expansion of food material during drying. The degree of these structural changes depends on the distribution of water within the food tissue. In broad classification terms, water in food materials can be grouped as free or bound water. In addition, on the basis of the spatial position of water, it can be referred to as intercellular and intracellular water and cell wall water, as shown in Fig. 3.1. The term *intercellular* refers to any water found inside a cell of any material, whereas *intercellular* water is water present in capillaries. Intracellular water varies between 78 and 97 % (wet basis) in different fruits and vegetables (Halder et al. 2011a), and the remaining water exists as intercellular water.

However, intracellular water encompasses water in cells and cell walls. Though it is hard to determine the proportion of water within cells and cell walls, attempts have been made to do so (Joardder et al. 2013, 2015a).

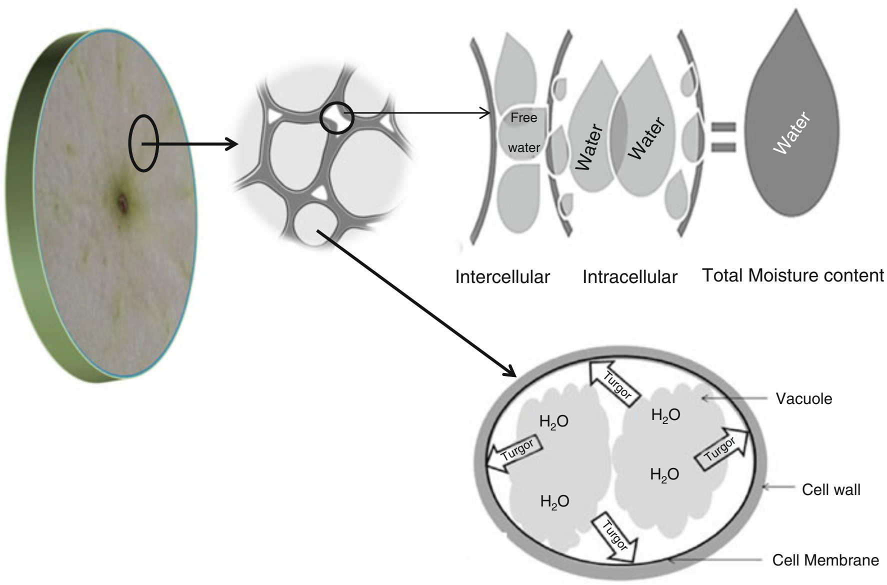

Fig. 3.1 Water distribution within plant based cellular tissue

In general, plant tissues undergoing drying are subjected to stresses leading to shape modification and deformation (Mayor and Sereno 2004). These stresses develop owing to simultaneous thermal and moisture gradients. The stresses generated by moisture gradients take place during the entire period of the drying process, while thermal stress is significant at the earlier stages of the drying (Lewicki and Pawlak 2003; Jayaraman et al. 1990). Therefore, the stress generated by the moisture gradient is the dominant cause of the shrinkage of plant tissue during drying.

It is essential to know the mechanisms and pathways of water migration from plant tissues during drying in order to understand the nature of collapse of tissue, which is a consequence of moisture transfer.

Studies dealing with the classification of water migration from samples during drying are common. For example, Le Maguer and Yao (1995) proposed three possible methods of water transport: apoplastic transport (cell wall to free space), symplastic transport (movement of water between two neighboring cells), and transmembrane transport (across cell membranes). In addition to these methods, Crapiste et al. (1988) presented different forms of water flux inside plant tissues during drying: intercellular (vapor movement through intercellular spaces), wall-to-wall (capillary flux across cell walls), and cell-to-cell (water flux through vacuoles, cytoplasm, and cell membranes).

Overall, water from three different spaces—cells, cell walls, and intercellular zones—takes various pathways to migrate to the atmosphere during drying. However, there are different pathways of water flux depending on the structure and composition of the food and on the drying conditions (Joardder et al. 2015b). Consideration of these factors will allow for the description of a conceptual map of the different pathways of water migration from plant tissue, as shown in Fig. 3.2.

Figure 3.2 shows that water from different spaces of a plant tissue can migrate through different pathways. For example, water from cells migrates through cell

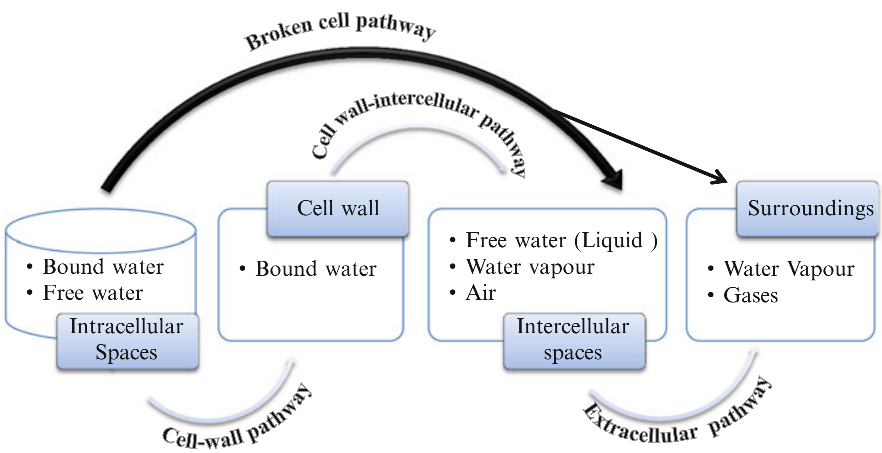

Fig. 3.2 Conceptual maps of different pathways of water migration from plant tissue

walls, including cell membranes, to intercellular spaces before finally ending up in the atmosphere. However, this phenomenon continues until the cell walls remain intact owing to a lower drying temperature.

At higher temperatures, in contrast, the cell membrane and walls are ruptured, resulting in some of the water traveling directly to its surroundings when the remaining water migrates through intercellular spaces to the atmosphere. Cell wall water migration requires relatively higher energy as it passes through intermicrofibrillar spaces, which are approximately 10 nm in cross section and many times longer in length (Lewicki and Lenart 1995). The intermicrofibrillar spaces are built up as a result of the gap between microfibrils, which are unbranched and fine threads, measuring roughly 10–25 nm in diameter (Lewicki 1998a; Gibson 2012).

At this point, a theoretical interpretation of pore formation can be put forth on the basis of water distribution, including free and bound water, as shown in Fig. 2.3. As discussed earlier, structural modifications are caused mainly by water migration from tissues. However, the bulk moisture content at different times cannot describe the structural modifications at those times. Water contents in terms of the bound and cell water can represent structural changes during drying. Based on microstructure studies and water migration analysis, a step-by-step pore formation mechanism is presented in Fig. 3.3.

1. At the very beginning of drying, only intercellular (free) water migrates from tissues, which causes no shrinkage of the sample.
2. After migration of the intercellular water, generally known as the falling rate stage of drying, intracellular water starts migrating from the cells, causing pore shrinkage. In addition, in the early stages of intracellular water migration, volumetric shrinkage is generally very close to the amount of removed water.
3. Following migration of the intercellular water, cell shrinkage happens as a result of a lower turgor pressure, which is caused by the migration of a significant

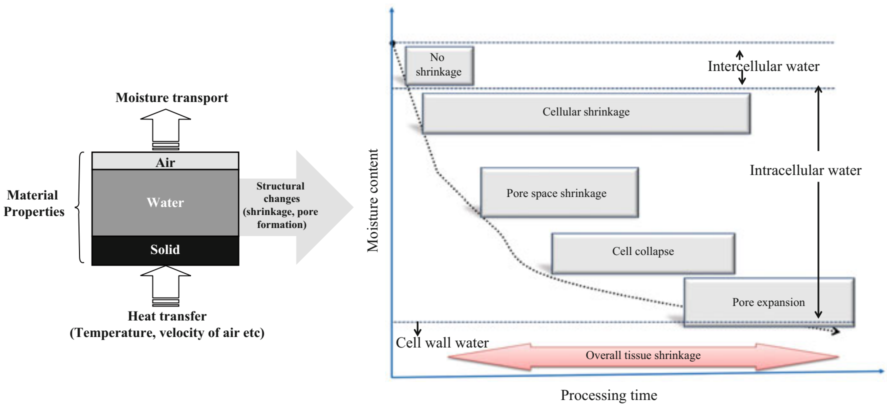

Fig. 3.3 Physical interpretation of pore evolution during the time of drying

amount of cellular water. It is expected that the shrinkage resulting from this water migration reduces cells to the proportion of the ratio of the water density and particle density. This means that a portion of voids that developed as a result of the water migration remains unshrunk and increases the porosity of the dried product. It is assumed that the particle density, in general, will fall within the ranges between the density of the solid materials and water (Ramos et al. 2003).

4. Initially, in most cases, food material encounters shrinkage without cell collapse. However, cell breakage is generally observed owing to longer drying times, but this does not cause a severe collapse of the cell. Cell collapse mainly occurs during migration of cell wall water. Among the different types of plant cells, parenchyma cells, as shown in Fig. 3.2, are typically thin-walled and are present abundantly in plant food materials. Vacuoles, which serve as cell water storage containers, are located inside these cells. Vascular solutes are usually osmotically active, which means they push cell membranes against cell walls. Consequently, the turgor pressure increases, which keeps the cells in a state of elastic stress and maintains the shape, firmness, and crispness of tissue (Ilker and Szczesniak 1990). If the turgor pressure is lost, the structure of the fruit collapses. Once the natural turgidity is lost, it cannot be restored (Reeve 1970).
5. Pore expansion: At the later stages of drying, the food solid matrix becomes sufficiently dry and achieves a higher viscosity (Del Valle et al. 1998), which hinders both shrinkage and collapse (Karathanos et al. 1996). In addition, further drying causes enlargement of intercellular spaces in food tissues.

Moreover, in general, cell wall solid matrixes of plant-based cellular tissue are flexible enough to allow for the migration of water from vacuoles. Consequently, shrinkage of the entire tissue occurs rather than increasing only the volume of intercellular spaces (Hills and Remigereau 1997).

Some of the possible sequences of no shrinkage, shrinkage, and collapse of a food structure are demonstrated in Fig. 2.3, although many of the possibilities have been left out. Owing to the diverse nature of different plant tissues, it is impossible to accommodate all the physics involved in pore formation and evolution during drying. In addition, some realistic phenomena, such as case hardening, are not taken into account. However, many variations exist in terms of the combination of shrinkage and collapse phenomenon.

3.3 Structural Mobility

To explain these physicochemical changes, Slade and Levine (1991) first introduced the glass transition concept in food materials during storage and drying. The glass transition temperature (T_g) is defined as the temperature at and above which an amorphous material changes from a glassy state to a rubbery state (Champion et al. 2000).

In the glassy state, the material matrix has a very high viscosity, in a range of 10^{12} to 10^{13} Pa s. Effectively, the matrix behaves like a solid because it is able to retain the rigidity of the structure by supporting its own body weight against the flow of the solid matrix owing to gravity (Angell 1988; Lewicki 1998b). Therefore, $\Delta T = \left(T - T_g\right)$ can be treated as the driving force of structural collapse (Del Valle et al. 1998), where T is the temperature of the sample undergoing drying. In this paper, *mobility temperature* will be used to refer to ΔT.

The glass transition theory is proposed in order to gain insight into the process of shrinkage, collapse, and cracking during drying (Rahman 2001; Cnossen and Siebenmorgen 2000; Karathanos et al. 1993, 1996; Krokida et al. 1998). Once the temperature of a cell membrane it exceeds the glass transition temperature, the cell membrane collapses significantly. At higher temperatures, cell walls cannot retain their structures intact, and rupturing begins. Subsequently, water from the cells migrates into extracellular spaces. Later, the water mostly migrates from these extracellular spaces to outside the material.

The effect of the glass transition temperature on the rate of shrinkage and pore formation can be described as follows:

(a) The kinetics of shrinkage are closely related to a material's physical state (Levi and Karel 1995). In other words, a rubbery state of a material shows high mobility of a solid matrix, whereas low mobility is caused when the sample reaches a glassy state. Consequently, volume shrinkage compensates almost entirely for the void volume that develops owing to water migration (Achanta and Okos 1996). At low temperatures, cell membranes remain intact and the transport of water out of the tissue involves migration through both cells and extracellular space. In addition to this, collapse can happen in the rubbery state only when the matrix is unable to support itself (White and Bell 1999). This collapse subsequently reduces the degree of porosity of the food sample.

(b) Shrinkage kinetics is highly dependent on the value of the mobility temperature. Generally, a high rate of shrinkage is caused by the higher mobility temperatures that can be observed in the early stages of drying. As drying progresses, the mobility temperature decreases, sharply reducing the shrinkage rate owing to the increase in the collapse resistance of dried materials (Karathanos et al. 1993; Katekawaa and Silvaa 2007). This is due to the decline in the moisture content and because the overall glass transition temperature of the sample rises above the drying temperature, decreasing the shrinkage rate as a consequence.

(c) The sample undergoes shrinkage until the mobility temperatures reaches zero or close to 0°. In other words, drying at higher temperatures causes shrinkage even at very low moisture contents (Kurozawa et al. 2012).

Although the glass transition concept can be applied to explain or identify physicochemical changes that occur during food processing, many experimental studies have been unable to establish the relevant relationship to support this concept (Wang and Brennan 1995; Del Valle et al. 1998).

3.4 Phase Transition (Multiphase)

Plant-based porous food materials, in general, encompass three phases during drying: solid, liquid, and gas (Chen and Pie 1989). In addition, voids spaces are filled by multiple phases, including water, vapor, and air materials. The pores change with the transport of those phases.

Phase change from liquid water to vapor is an important phenomenon because vapor phase diffusion is a significant mass transfer mechanism in porous foods. Therefore, the multiphase mass transfer phenomenon (Fig. 3.4) occurs during drying. In many cases, vapor diffusion accounts for 10–34 % of the moisture flux in convective drying at 55–71 °C (Waananen and Okos 1996). In addition, vapor diffusion is faster than liquid water diffusion in porous media during drying. The crust-formation effect can be observed if drying conditions allow for a phase transition (liquid water to vapor) in the outer zone material, even at high drying rates (Mayor and Sereno 2004). Another remarkable phenomenon, crust formation, occurs owing to the precipitation of nonvolatile compounds on the surface of materials (Ramos et al. 2003).

The evaporation rate has a significant effect on pore formation during drying. In particular, over the course of drying under microwave energy, higher microwave power leads to an increased evaporation rate; consequently, a more-porous structure develops in comparison with drying at lower-power microwave drying. Therefore, quick evaporation of water retains the porous structure and causes less severe collapse of the solid matrix.

In brief, the microstructure and solid matrix architecture of plant tissue varies so much that there are many exceptions to these explanations of pore formation. Therefore, various concepts, such as water-holding capacity, ratio of extracellular and intracellular water content, glass transition temperature, exchange surface area of the sample, phase change of liquid water, gas pressure, and internal moisture transport mechanisms, need to be taken into consideration to explain pore formation clearly for a particular material in given drying conditions.

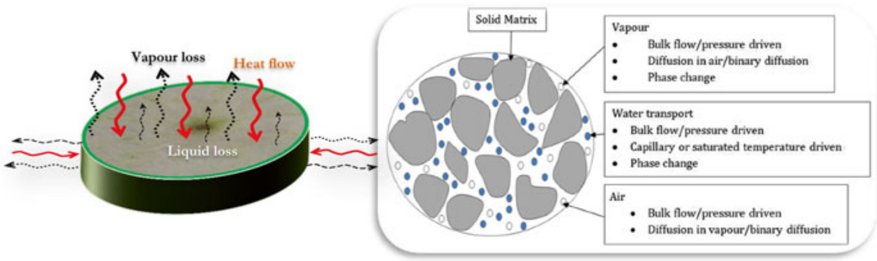

Fig. 3.4 Multiphase mass flow in food materials during drying

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Chapter 4
Factors Affecting Porosity

4.1 Introduction

The properties and structures of a dried product are generally are by the type of drying, its associated variables, and the raw structure and components of the food material (Aguilera and Chiralt 2003). Similarly, the properties of food material, drying methods, and their conditions have pronounced effects on the porosity of the final product. Even the same types of raw materials demonstrate different pore characteristics depending on the drying method and conditions (Sablani et al. 2007). On the whole, porosity is directly dependent on the initial water content, temperature, pressure, relative humidity, air velocity, electromagnetic radiation, food material size, composition, and initial microstructure and viscoelastic properties of the biomaterial, as shown in Fig. 4.1 (Saravacos 1967; Krokida et al. 1997; Guiné 2006).

Moreover, different food materials demonstrate different values of porosity owing to their diverse structures. For example, an apple develops the highest porosity, whereas bananas and carrots show less porosity in the same drying conditions. This could be due to their initial structures and compositions. Therefore, to control or predict food porosity, both the process conditions and product properties must be taken into consideration.

An extensive review of the literature reveals that changes in the porosity of food materials over the course of drying mainly depend on volume change and void formation owing to water migration. Actually, both phenomena occur simultaneously depending on the material properties and drying conditions. However, what follows are the significant factors that must be considered in predicting porosity in dried products.

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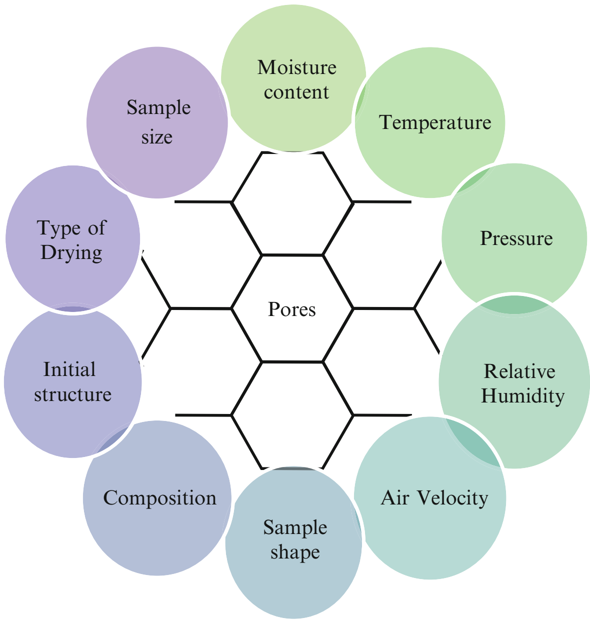


Fig. 4.1 Factors that affect pore formation and evolution

4.2 Drying Time

Drying time is a vital factor that significantly influences the collapse of cells in the course of drying. Therefore, a lower drying temperature (i.e., longer drying time) could cause structural damage to the food product because most of the food materials show qualities of a rubbery state during drying. Because of this, a longer drying time causes the collapse of plant tissues even when dried at a low temperature because plant tissues have a very low glass transition temperature (Karathanos et al. 1993). This phenomenon is more pronounced in hot air drying. To prevent this structural collapse for a longer time of air drying, a different level of volumetric heating is used.

4.3 Effect of Food Material Properties

Material properties play a vital role in the retention of the fresh structure of a sample by opposing the external forces due to heat and mass transfer. However, such material properties should be retained in a porosity prediction model because they do not vary with changes in drying conditions. Temperature, water content and distribution, and pressure are parameters that should be taken into consideration in this regard.

4.3.1 Moisture Content

Moisture content is the distinctive factor that causes porosity to vary significantly. Porosity in general increases with the removal of water. However, a food sample also shrinks more with the removal of water volume owing to the higher contraction stresses developed within the material. These two opposite physical changes determine the different patterns of pore formation and evolution. Under such circumstances, it becomes difficult to predict the nature of pore formation. To relate the relationship between water content and porosity, two experiment-based generic trends have been presented in the literature, as shown in Fig. 4.2 (Rahman 2001). One of the generic trends has an inversion point (A and B), while the other does not (C and D). In most cases, inversion begins at a critical moisture point. Actually, the two generic trends cover all manner of possible changes in porosity.

Relevant here is a study by Lozano et al. (1983b) in which all four types of porosity trends for selected agricultural products were investigated. In that study, the porosity of pears and carrots were found to change as a function of water with an inversion. Pears showed an upward inversion, while a downward inversion trend was reported in the case of carrots.

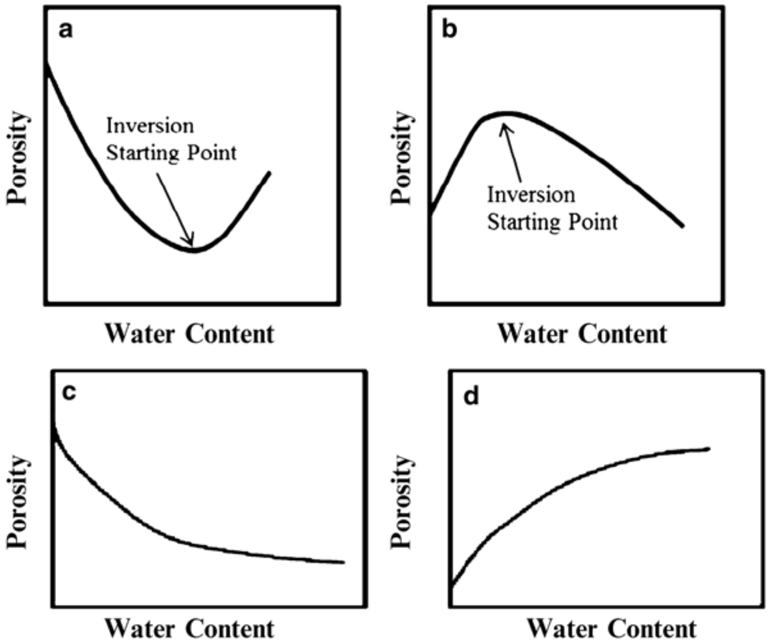
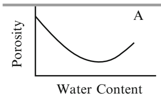
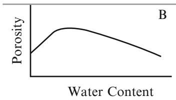
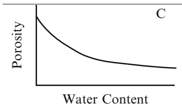
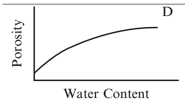


Fig. 4.2 Change in porosity as a function of water content (**a**, **b**: with inversion; **c**, **d**: no inversion point). Adapted from Rahman (2001)

Table 4.1 Changes in porosity with decrease in moisture content during drying of various fruits and vegetables

Porosity relationship with moisture content		Food stuff	References
	Upward inversion	Pear	Lozano et al. (1983b)
	Downward inversion	Carrot, pineapple, ginseng	Lozano et al. (1983b), Martí et al. (2009), Yan et al. (2008), and Martynenko (2011)
	Increasing without inversion	Sliced and whole pear, carrot, whole garlic, cube-shaped garlic, potato, mango, avocado, strawberry, banana, apple, prune	Guiné (2006), Liu et al. (2012), Karathanos et al. (1996), Sablani et al. (2007), Vincent (2008), Lozano et al. (1983b), Wang and Brennan (1995), Martí et al. (2009), Yan et al. (2008), Tsami and Katsioti (2000), Boukouvalas et al. (2006), Krokida et al. (1997), Katekawa and Silva (2004), and Djendoubi Mrad et al. (2012)
	Decreasing without inversion	Sliced garlic	Sablani et al. (2007) and Lozano et al. (1983b)

On the other hand, some other food materials show porosity without inversion. For example, sliced garlic was found to have decreased porosity with a decrease in the moisture content, whereas an increase in porosity and a decrease in moisture content were found for potatoes. On the basis of an extensive literature review, changing patterns of porosity with moisture content for various food materials are presented in Table 4.1.

In light of the aforementioned discussion, moisture content represents the only factor about which there is insufficient information for an accurate prediction of porosity. However, the water content of food materials is of paramount importance in the degree of collapse and expansion within food materials during drying, and so designers should pay particular attention to retaining the maximum safe water content.

4.4 Food Composition

Different types of food materials, different varieties of the same species, and different degrees of maturity of the same variety have all been observed to give considerably different responses under identical drying conditions. Eventually, varying final food structures are found after the drying process. Food compositions directly affect the mechanical properties of food materials. In other words, structural stability varies with the presence of heat and mass transfer through the food materials and causes tissue damage according to food structure and composition. For example, Joardder et al. (2014) found that, owing to different proportions of dietary fibers in the cell wall of two types of apple, there was different porosity under the same drying conditions. Moreover, the porosity was found to be within a range of 0.00–0.98 for a variety of food materials.

In addition, the stability in the composition of food samples also affects the pore formation pattern. For example, the food composition pectin methylesterase (enzyme) shows its highest activity between 20 and 60 °C and increases cell wall firmness. An illustration of this can be found in Mavroudis et al. (1998b), who performed the osmotic dehydration of an apple. A more porous structure was found at a drying temperature of 40 °C owing to higher cell wall firmness compared with dried food at 5 and 20 °C. In addition, porosity can also be controlled by incorporating additives into the food. An alginate gel resulting from freeze drying, for instance, will develop a cellular solid with a porosity of 0.96. It is possible to achieve almost zero porosity for the same cellular solid by including additives like starch or oil or by immersion in sugar solution (Rassis et al. 1997).

4.4.1 Original Structure of Raw Material

Different food materials possess various types of solid structural matrix along with different compositions. Because of this variation in structure and components, different plant-based food materials respond differently during simultaneous heat and mass transfer. For this reason, the porosity of processed food is also influenced significantly by the pattern of the solid matrix, the proportion of intercellular and extracellular spaces, cell dimension, and cell orientation.

Intercellular spaces in general contain air and form channels or voids. These spaces are the cause of initial porosity and occupy less than 1 % of the tissue volume of fruits and vegetables, such as carrots and potatoes, but up to 25 % in apples (Prothon et al. 2003). An enormous diversity of raw material structure can be found in terms of the moisture content, architecture of the solid matrix, and composition of food materials (Aguilera and Stanley 1999). A typical hierarchical structure of plant-based cellular materials is presented in Fig. 4.3.

From Fig. 4.3 it can be observed that from the nano level to the macro scale, food materials possess different structural and architectural patterns. For example, consider the magnitude of the nano–macro scale for cellular materials when organized from glucose to the tissue level. However, the same fruits of different types possess different raw structures in terms of cell dimension, cell anisotropy, and cell wall characteristics, which causes variation in porosity in the same drying conditions (Joardder et al. 2014; Yong et al. 2006).

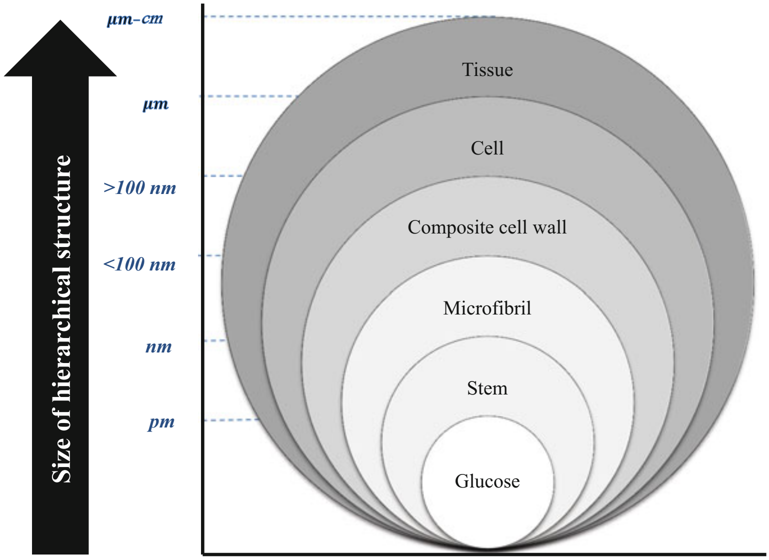


Fig. 4.3 Demonstration of hierarchical structure of different food materials

4.4.2 Anisotropy

An anisotropic structure is one that displays the different properties or structures of tissue when observed from different directions. In general, fruit flesh or cortex is comprised of parenchyma-type cells. Cell sizes vary across the apple fruit, with cells under the skin being smaller (70 µM), increasing in size (to approx. 250 µM) toward the center of the flesh (Bain and Robertson 1950; Reeve 1953). Toward the inner cortex, apple cells become more elongated, spreading out in a radial pattern, lying alongside air gaps (Khan and Vincent 1990). Growth within plant-based tissue varies according to position, with more rapid growth occurring at the calyx than at the stalk. There is a strong possibility that the water distribution and water holding capacity vary with this cell size variation.

Variation in cell size significantly affects the amount of collapse that occurs during drying, which leads to nonuniform porosity (Fito and Chiralt 2003). Large cells with comparatively less cell wall thickness actually weaken the tissue of plant-based food materials (Zdunek and Umeda 2005). For this reason, nonuniform porosity is observed in dried products with less porosity where larger cells exist in the sample. Therefore, the anisotropic geometrical nature of the cells of plant tissues should be taken into consideration because it is an important parameter that determines the structural properties in the course of drying.

4.4.3 Turgor Pressure

Among the different types of cells in plant cells, parenchyma cells are typically thin-walled and are present abundantly in plant food materials. Vacuoles, which serve as cell water storage containers, are located inside these cells. Vascular solutes are usually osmotically active, which pushes the cell membrane against the cell wall. Consequently, turgor pressure develops, which keeps the cells in a state of elastic stress and maintains the shape, firmness, and crispness of the tissue (Ilker and Szczesniak 1990). If the turgor pressure is in a range of 0.3-1 MPa is lost, the structure of the fruit collapses. Once the natural turgidity is lost, it cannot be restored (Reeve 1970). Therefore, turgor pressure within cells is the determining factor in cell wall collapse at the time of water migration from cells.

4.4.4 Shape and Size of Sample

Besides the composition, the sample dimension and exchange surface area also influence the moisture and temperature distribution (Mulet et al. 2000) because the shape and size of a sample determine the boundary of the temperature profiles. The microstructural images obtained from the study of Joardder et al. (2013) found that porosity varies with a variation in thickness in apple samples. It was found that less fracturing occurred in a sample of less thickness, whereas severe collapse appeared in the thicker sample. One of the possible explanations of this result is that the thicker sample was exposed for a longer time to the hot air to achieve the sample moisture level.

In the case of the cylindrical samples, the final porosity is influenced by the cylinder diameters. As shown in Fig. 4.4, Desmorieux et al. (2010) determined the effect of the size of the *Arthrospira Spirulina* samples on porosity.

It is apparent from the figure that a more porous structure developed in the larger-diameter sample. At a lower moisture content, the highest porosity (0.8) was found for the sample with a 6 mm diameter, while the lowest porosity (0.65) was found for the sample with a 2 mm diameter. In addition, in the case of a cylinder, the lower porosity develops in the direction (across the characteristic length) of heat and mass transfer.

Both external and internal pore formation also depend on the shape of the sample. To investigate this, samples with three different shapes (e.g., cube, slice, sphere) were dried to approximately the same moisture content using hot air drying in the same drying conditions. It is clear from Fig. 4.5 that a less severe collapse of the cell wall occurred in the spherically shaped sample, whereas a severe collapse occurred in the cube sample. The slice sample shows intermediate cell wall fracture during drying. One of the possible explanations of these results is that the comparatively higher porous surface develops with a higher specific exposed surface area.

Even for the same fresh material, when dried as a whole it can show completely opposite trends of porosity evolution compared with the slice sample. For example, Lozano et al. (1983a) found an increasing porosity trend for a whole piece of garlic, whereas diminishing porosity was obtained for sliced garlic with a decreasing moisture content.

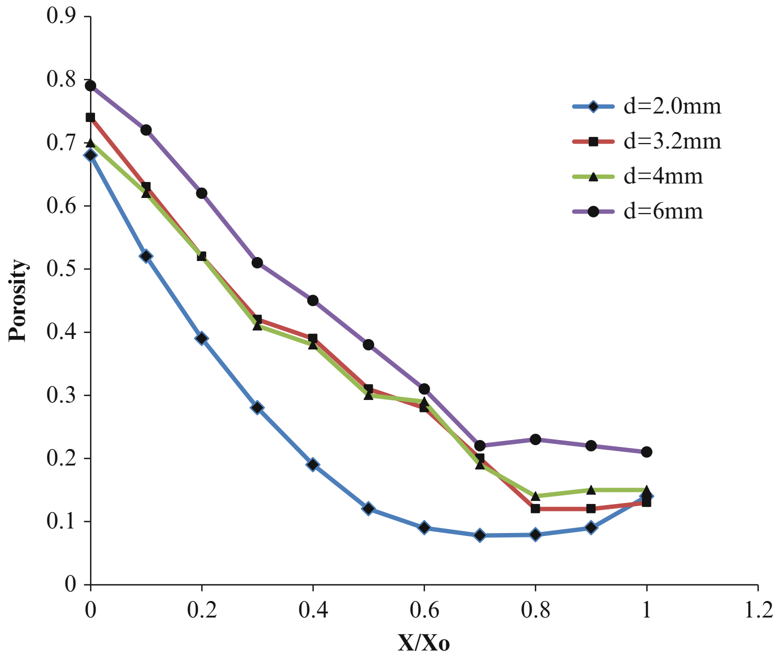


Fig. 4.4 Effect of diameter on pore formation at different levels of moisture content. Adapted from Desmorieux et al. (2010)

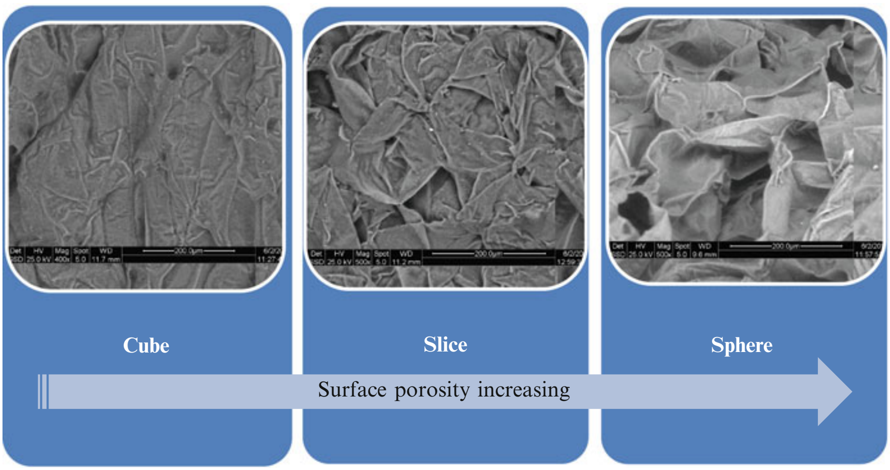


Fig. 4.5 Microstructure (from SEM ×500 magnification) of dried apple slices with different shapes at 70 °C

On the whole, the shape and size of the sample, particularly the characteristic length and exposed surface area, are significant factors that need to be considered to maintain the appropriate pore structure of dried foods.

4.5 Drying Process Conditions

Process parameters are the key determinants of the structural changes of food material over the course of drying. Because of the migration of water at a higher temperature than the glass transition temperature, a plant-based food matrix becomes rubbery, turning the structure softer over the course of drying. In the foregoing sections, the effect of different process parameters was described briefly.

4.5.1 Temperature and Drying Rate

The drying rate in general influences the structure of the outer and inner portions of food samples and determines whether or not the outer and internal structures will be porous. In general, low temperatures lead to low drying rates, as the diffusion moisture transfers from the inner to the outer part of the food material at a rate almost equal to that of surface evaporation, causing an insignificant moisture gradient within the product with low internal stresses. Consequently, the material shrinks down uniformly into a solid core, which leads to pore formation and evolution continuing until the last step of drying (Mayor and Sereno 2004).

In the case of a high drying rate, a transition of rubber-glassy states prevails on the outer surface owing to low moisture content, which gives rise to a porous, rigid crust on the surface, or case hardening (Wang and Brennan 1995). Subsequently, the surface moisture decreases very quickly and internal stresses develop in the tissue, consequently negatively affecting the shrinkage and resulting in a highly porous interior (Aguilera and Stanley 1999; Mercier et al. 2011). This phenomenon is widely known as case hardening (Souraki et al. 2009). Another remarkable phenomenon, crust formation, occurs owing to the precipitation of nonvolatile compounds on the surface (Ramos et al. 2003). These types of nonvolatile compounds generally migrate along with the diffusing water; however, water vapor leaves them on the surface of the food material.

When the temperature of the drying air increases, the capacity of the air to hold vapor also increases. However, there is a limit to how much water vapor the air can hold at any given temperature. Experimental results from various studies show that porosity increases with temperature at different moisture contents. In the case of drying bananas at 30, 40, and 50 °C, a higher porosity was found at a temperature of 50 °C (Katekawa and Silva 2004). For potatoes (Wang and Brennan 1995) and eggplant (Russo et al. 2012) significantly higher porosity was found during air drying at 70 °C compared with 40–60 °C. However, for some agricultural products the maximal porosity can be found at the intermediate drying temperature. For instance, Djendoubi Mrad et al. (2012) investigated the effect of temperature in the range of 30–70 °C on pears and found that the highest porosity was found at 50 °C throughout the drying process, except at the end stage, where the highest porosity was found at 70 °C.

In the case of freeze drying, porosity decreases with temperature (Krokida et al. 1998a). From Fig. 4.6 it is clear that for all selected food materials, porosity decreased with an increase in freeze drying temperature. However, some food materials, such as abalone, potatoes, apples, and dates, were found to have higher apparent porosity at higher temperatures (Sablani and Rahman 2002).

Structural collapse in amorphous materials depends on the difference between the drying temperature and the glass transition temperature, T_g. Food processing at or above the glass transition temperature causes cell collapse and porosity reduction. In some cases, the collapse temperature is higher than T_g. Therefore, the value of $T - T_g$ is an important factor that can influence the structural modification.

Uneven temperature distribution throughout a sample causes irregular pore formation. In particular, drying with uneven heating, such as microwave heating, causes nonuniform temperature distribution. Joardder et al. (2013) investigated the influence of temperature distribution on dried apples during microwave drying. In that study, the higher temperature region showed higher porosity, and lower temperatures achieved higher collapse. Therefore, to produce a uniformly porous dried product, a uniform temperature is essential.

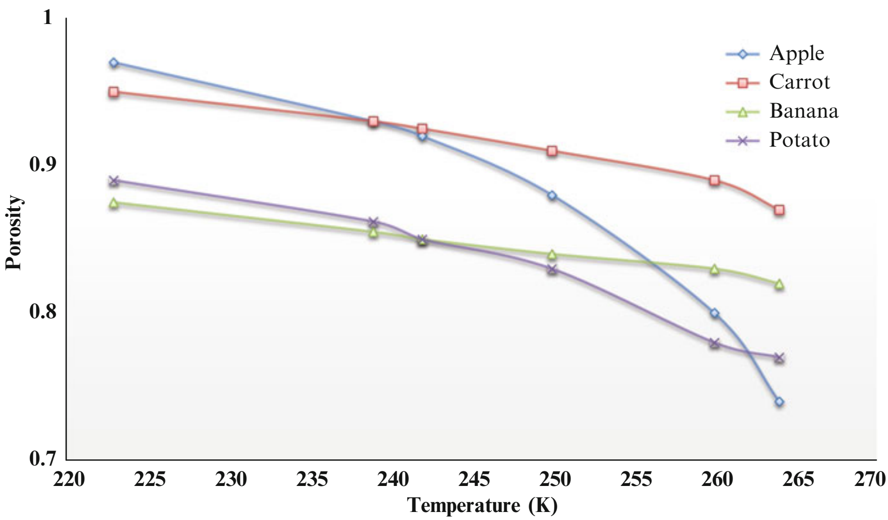


Fig. 4.6 Porosity versus temperature of freeze-dried food materials. Adapted from Krokida et al. (1998a)

4.5.2 Pressure

Vapor phase development positively affects pore formation, whereas water flux causes the collapse of a structure. Most drying processes are performed at atmospheric pressure, with the exception of vacuum drying. The porosity of dehydrated products increases as the vacuum pressure decreases, which means that shrinkage can be prevented by controlling the pressure, allowing high porosity values in the final products. In a study conducted by Krokida et al. (1997), the atmospheric pressure was found to affect the porosity of potatoes, apples, bananas, and carrots significantly.

Variation of pressure in other drying methods, such as electrospraying and osmotic drying, affects pore formation significantly. Nyström et al. (2012) observed more porous particles under reduced pressure than fabricated particles under atmospheric pressure during electrospraying. The pressure gradient in osmotic dehydration influences the rates of solid gain and water loss (Sutar and Sutar 2013). This gradient consequently maintains the expansion and compression of the internal pore gas of the tissue, and the porous structure is also affected by the pressure gradient.

Pressure variation in vacuum–freeze drying also affects the porosity of agricultural products. Similar to vacuum drying, porosity increases with decreasing vacuum pressure. For example, applying a 0.06–0.15 mbar vacuum pressure on selected agricultural products, Oikonomopoulou et al. (2011) found that the porosity of all the selected products decreased with increasing vacuum pressure, as shown in Fig. 4.7.

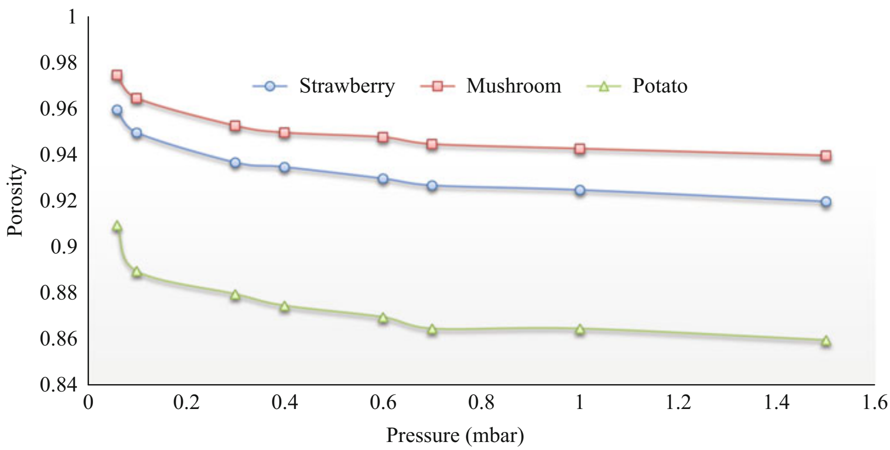


Fig. 4.7 Variation in porosity of freeze-dried product with applied pressure. Adapted from Oikonomopoulou et al. (2011)

Table 4.2 Effect of concentration of coating materials on porosity of food materials

Ethanol concentration (%, w/w)	Bulk density (g/m^3)	Porosity (%)
95	0.024	98.0
85	0.032	97.8
80	0.062	95.5
75	0.077	95.0
60	0.300	79

For these reasons, applying the correct pressure during the drying process is vital for achieving the expected porosity of a food product, in particular where pressure variation is obvious.

4.5.3 Coating Treatment

High-moisture-content tissues, such as those of fruits and vegetables, do not possess enough structural strength to prevent shrinkage during drying. Improving the structural strength can retain the structural rigidity of the product and reduce solid matrix mobility. Therefore, a special process called *edible coating* can be introduced in food materials prior to the drying process. This coating generally retains vapor, which allows sufficient internal pressure to cause solid materials to expand during drying (Askari et al. 2006). In other words, the coating treatment can hinder rapid vapor removal from a sample and puff up the solid matrix to retain a firmer structure that does not collapse. Eventually, the coated solid matrix encounters less shrinkage and encompasses a more porous dried structure (Funebo et al. 2002). Kunzek et al. (1999) reported their observations of the effect of ethanol concentration prior to the drying of apple slices (Table 4.2).

From Table 4.2 it is explicitly observed that porosity markedly increases with an increase in ethanol concentration, which indicates the occurrence of less shrinkage owing to a higher concentration of the coating solution.

Similar to this edible coating, osmotic pretreatment also causes sugar coating on a solid matrix. It has been reported that sugar infusion during osmotic pretreatment at higher solute concentrations prevents more shrinkage than infusion owing to the lower solute concentration (Del Valle et al. 1998). However, different coating materials affect the textural quality of food materials in different ways.

Clearly, the degree to which the structural strength is improved depends on both types of coating material and its concentration.

4.6 Other Process Conditions

Apart from the aforementioned properties of material and process conditions, many other process parameters directly or indirectly influence the porosity evolution in food materials over the course of drying. The effects of such parameters can be found in the literature. However, the results of those studies are unclear and inadequate to generalize the effect of such parameters on pore formation. For example, an increase in air velocity causes higher porosity in potatoes, apples, and carrots (Ratti 1994). In the case of relative humidity, little to no effect has been reported in various studies (Ratti 1994; Lang and Sokhansanj 1993).

4.7 Porosity Changes in Different Drying Processes

Methods of drying are diverse and depend on the purpose of the process. There are more than 200 types of dryers (Mujumdar 1997). For every dryer, the process conditions, such as the drying chamber temperature, pressure, air velocity (if the carrier gas is air), relative humidity, and product retention time, must be determined according to feed, product, purpose, and method.

The various drying processes have different process conditions that are important in terms of how they influence the product structure and lead to different final outcomes that differ in terms of porosity (Krokida and Maroulis 2001a, b). The porosity of freeze-dried materials (80–95 %) is always higher in comparison to all other dehydration processes. Microwave-dried potatoes have higher porosity (75 %), while microwave-dried apples do not show high porosity (25 %). Vacuum-dried apples develop high porosity (70 %), while vacuum-dried potatoes' porosity values are lower (25 %). Table 4.3 provides the varying porosities of some fruits and vegetables under various drying methods.

The foregoing discussion concerns pore structure properties under different types of drying processes.

4.7.1 Air Drying

Porosity during the air drying of foodstuffs can show different behaviors depending on drying conditions and types of food. In some cases, porosity may decrease, as found in the case of sweet potatoes, while in other cases it may increase during the drying process, such as occurs with apples and bananas (Lozano et al. 1983a; Krokida and Maroulis 1997). This different behavior can be associated with the initial structural and compositional characteristics of the raw material, as well as the drying process conditions.

Cell separation at higher temperatures during convective drying also leads to a comparatively more porous product for some food materials such as apples (Lewicki and Pawlak 2003). Owing to the thermal exposure of the cells, there is significant collapse. A significant amount of variation on pore formation can be observed on the surface of food materials and inside food materials (Fig. 4.8). In light of this finding, as shown in Fig. 4.8a, on the surface of a food, most cells collapse and case hardening occurs.

Table 4.3 Comparison of porosity of different foodstuffs under various drying methods

Food material	Porosity in different drying processes					References
	Convective drying	Microwave drying	Osmotic drying	Vacuum drying	Freeze drying	
Apple	0.6	0.75	0.55	0.50–0.73	0.75–0.92	Krokida et al. (1997, 1998b), Giraldo et al. (2003), and Karathanos et al. (1996)
Banana	0.20	0.25	0.20	0.20–0.70	0.80–0.90	Krokida and Maroulis (1997) and Krokida et al. (1997)
Potato	0.20	0.70	–	0.15–0.25	0.78–0.87	Krokida and Maroulis (1997), Krokida et al. (1997), and Karathanos et al. (1996)
Carrot	0.10	0.70	–	0.10–0.50	0.88–0.94	Krokida and Maroulis (1997) and Karathanos et al. (1996)
Blueberry	0.15	0.21	–	0.45	0.70	Yang and Atallah (1985)
Quince	0.17	–	0.08	–	0.72	Koç et al. (2008) and Tsami and Katsioti (2000)
Tuna strips	0.24	–	–	0.46	0.76	Rahman et al. (2002)

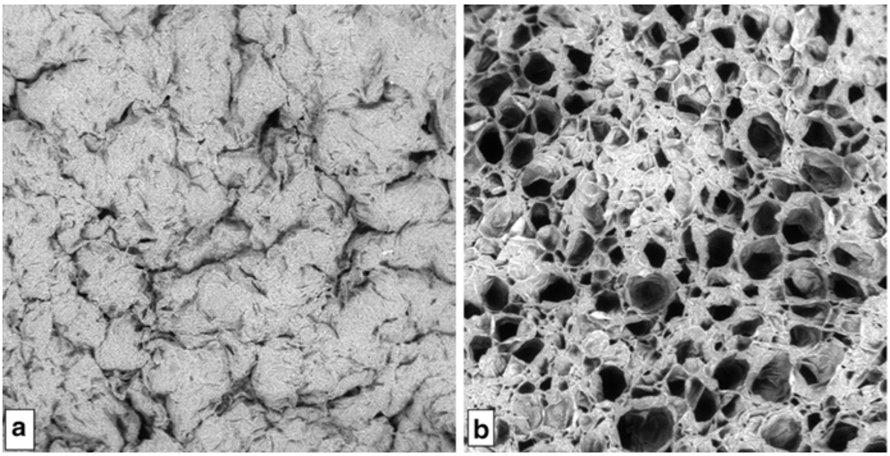


Fig. 4.8 Microstructure of surface (**a**) and inside (**b**) of air-dried apple

In contrast, a noticeable amount of cells inside the food remain intact and possess more pores than the surface structure. However, the pore size of air-dried foodstuffs are much smaller than the dimensions of freeze-dried food owing to the shrinkage and structural collapse that occur in air-dried food samples during drying (Karathanos et al. 1996).

As a final consideration, to obtain highly porous materials, an optimum temperature should be chosen that allows quicker drying and less structural collapse.

4.7.2 Osmotic Drying (OD)

Cell structure modification takes place during the osmotic dehydration of fruits, in particular, changes occur in the cell wall, tissue shrinkage takes place, and the solid matrix arrangement is altered (Sharma et al. 1998). Many studies have found that the porosity of dehydrated samples initially decreases but then increases in the later stages in the osmotic drying of different fruits (Giraldo et al. 2003; Nieto et al. 2004; Lozano et al. 1983a). The initial decrease in sample porosity can be explained by the fast initial impregnation of the tissue with the osmotic solution, which penetrates into the external pores by capillary forces and other mass transfer mechanisms. The accumulation of sucrose in the external surface of the material generates a dense layer that hinders the further penetration of the osmotic solution and simultaneously minimizes the gas flow from the material to the solution. These combined phenomena increase the food porosity, as shown in Fig. 4.9. However, some of the food materials show decreasing porosity in the entire osmotic process (Lewicki 1998). Furthermore, Mavroudis et al. (1998a) observed a decreasing average porosity in osmotic-dehydrated apples over the entire course of the osmotic drying process.

The solution penetration and porosity evolution is not uniform throughout the sample. For example, Mavroudis et al. (1998a) found that apple undergoing osmotic process at 20 °C achieved an increasing trend in porosity at the outer tissue, whereas the inner tissue was found to be less porous. A possible explanation of this phenomenon may be that the concentrated solute penetrates in greater quantities into the inner intercellular spaces of tissues than the outer spaces.

Osmotic pretreatment also affects the size of pores during further drying under other drying processes. To demonstrate, Therdthai and Visalrakkij (2012) reported that dried mangosteen with OD had finer pores, whereas mangosteen without OD had larger pores.

In addition to bulk porosity, the formation of microscopic channels has been found in ultrasound-assisted osmotic dehydration (Fernandes et al. 2009). In other words, these micropores develop as a result of a loss of adhesion that increases the intercellular spaces and ruptures the cell wall during osmotic dehydration.

In summary, the infusion of solutes into the solid matrix of plant-based tissues increases the glass transition temperature and collapse temperature of porous food materials. This increase in structural strength leads to less shrinkage, higher porosity, and better appearance.

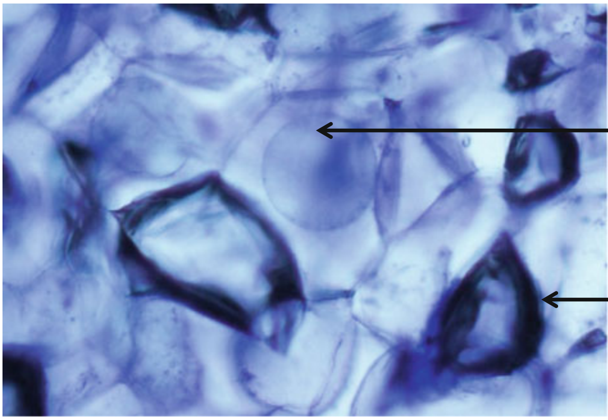


Fig. 4.9 Morphology of apple tissue under light microscopy during osmotic drying (×100)

4.7.3 Freeze Drying

Freeze drying provides almost freshlike properties of food products owing to the minimal overall structural damage (Khalloufi and Ratti 2003). Accordingly, freeze-dried products are usually classified as highly porous materials compared to the products of vacuum and hot-air drying (Krokida et al. 1998a, 2000).

During freezing, ice crystals grow and compress, push, and rupture cell walls, subsequently causing cell damage in the form of expansion and shrinkage. Porosity in freeze-dried products greatly depends on the freeze-drying conditions. The crystal growth strongly depends on freezing rate, water contents of the materials, temperature, and freezing time (Voda et al. 2012). Krokida et al. (1998a) found that the pore characteristics of dried garlic at −25 and −15 °C were similar, but different from those of samples dried at −5 °C. The number of open pores was significantly lower with samples dried at −5 °C when compared to samples dried at −15 and −25 °C. At higher freezing temperatures (−5 to −15 °C), the porosity of all materials was higher (as much as 90 %), while it decreased for drying at lower freezing temperatures (around −45 °C) (Krokida et al. 1998a). The reduction in porosity, as a result of this range of freezing temperatures, varied from 30 % for apples to 10 % for other food materials.

Similar to the degree of porosity, pore size also is significantly affected by freeze-drying conditions. Researchers have found much larger pore sizes in dried foods during freeze drying compared with air drying (Rahman et al. 2005). This is because the size of crystals, which is the main property of frozen materials, depends on the freezing rate (Roos 2012).

The foregoing discussion makes it clear that to maintain a better structure of freeze-dried products, the freeze-drying temperature and rate should be at an intermediate level.

4.7.4 Microwave Heating

The development of dehydration processes on the basis of electromagnetic energy may lead to a major breakthrough with respect to the retention of product quality. The electromagnetic energy–based drying process may produce materials of a desired structure, with less collapse or the formation of a highly porous structure (Nijhuis et al. 1998; Bimbenet and Lebert 1990). Electrotechnology, including radiofrequency, microwave, and infrared, can be applied to obtain a homogeneous moisture distribution within a product, and the avoidance of case hardening can be achieved by balancing energy flow to the surface and volumetric heating. Furthermore, the application of microwaves leads to a higher driving force for moisture flow by increasing the vapor pressure difference between the interior and surface of food materials. Eventually, this increased vapor pressure enhances the porosity of plant-based food materials (Therdthai and Visalrakkij 2012).

Sometimes, this higher driving force causes water to migrate in such a way that it develops numerous tiny pores (Fig. 4.10), which are not observed in air-dried samples. This may be because a higher microwave power means a higher drying

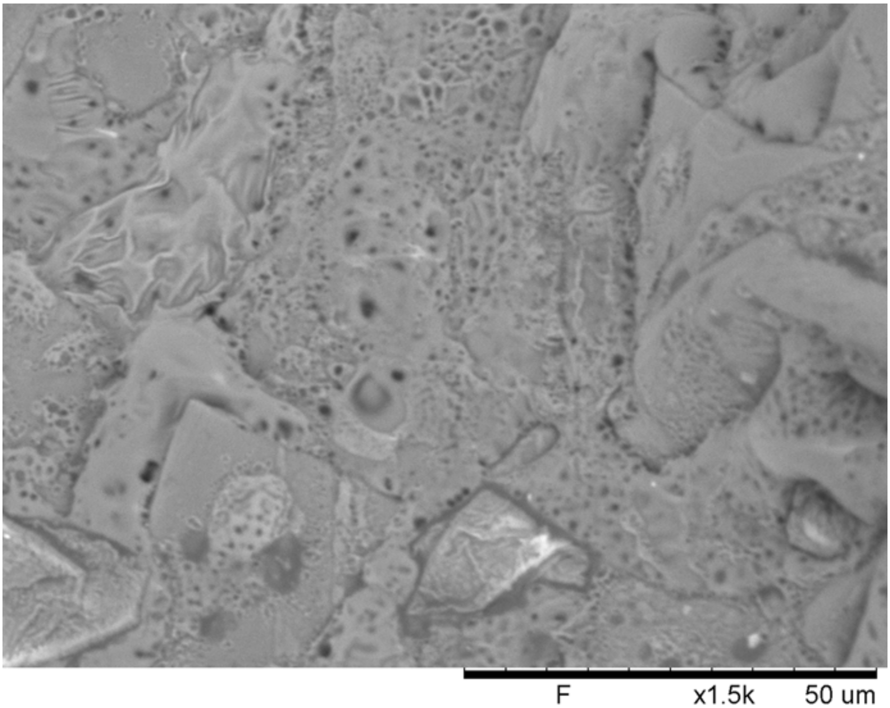


Fig. 4.10 Microstructure of surface of microwave-dried apple

rate, which causes a rupture in cell walls, subsequently leading to the development of tiny pores. In contrast, at a low microwave power, the cell structure remains intact owing to the weak induced force (Khraisheh et al. 2004).

In the case of carrot slices, higher porosity was observed when the slices were dried in a vacuum microwave compared to air drying. This variation indicates that in addition to the electromagnetic energy and moisture transport mechanism, the structure affects pore formation.

It is still not clear when microwaves should be applied to obtain a finished product with a more porous structure. Some studies (Zhang et al. 2006) assert that microwave heating applied in the earlier stages of drying leads to a more porous product, whereas others (Askari et al. 2006; Argyropoulos et al. 2011) indicate that the incorporation of microwave heating in the final stage leads to a more porous structure. The latter argues that the application of microwave heating in the initial stages facilitates cellular collapse and shrinkage of tissue.

Furthermore, intermittency in microwave application, combined with other drying methods, in many cases causes a uniform porosity throughout a sample, owing to a uniform distribution–redistribution of moisture and temperature (Kumar et al. 2014; Gunasekaran 1999; Joardder et al. 2013).

4.7.5 Vacuum Drying

Vacuum drying offers better quality for heat-sensitive food materials. In general, no color change is observed during vacuum drying because the absence of air prevents a color-changing reaction (Amellal and Benamara 2008). Actually, vacuum drying can be considered a so-called moderate drying method in terms of structural deterioration, color retention, cost, drying kinetics, and porosity (Krokida et al. 1997) in comparison with other conventional drying processes. A comparison of the structural properties of vacuum-dried products shows them to be better than air-dried products and closer to freeze-dried products.

Vacuumed-dried product porosity varies with applied pressure values during drying. Most fruits and vegetables show higher porosity at lower pressure. Krokida et al. (1997) found that vacuum pressure affected the porosity of potatoes, apples, bananas, and carrots significantly over the course of drying.

It is clear from Fig. 4.11 that the porosity of dried food products significantly increases with decreased pressure for bananas, carrots, and potatoes. However, apples show exceptional response owing to their initial high porosity.

In addition to this, microwave-vacuum drying also produces a more porous structure than air drying and a unique puffed structure (Giri 2006; Lin et al. 1998; Chauhan and Srivastava 2009). Likewise, vacuum-dried and vacuum-cooled food products show significantly higher porosity than normal cooling-processed foods (McDonald and Sun 2001).

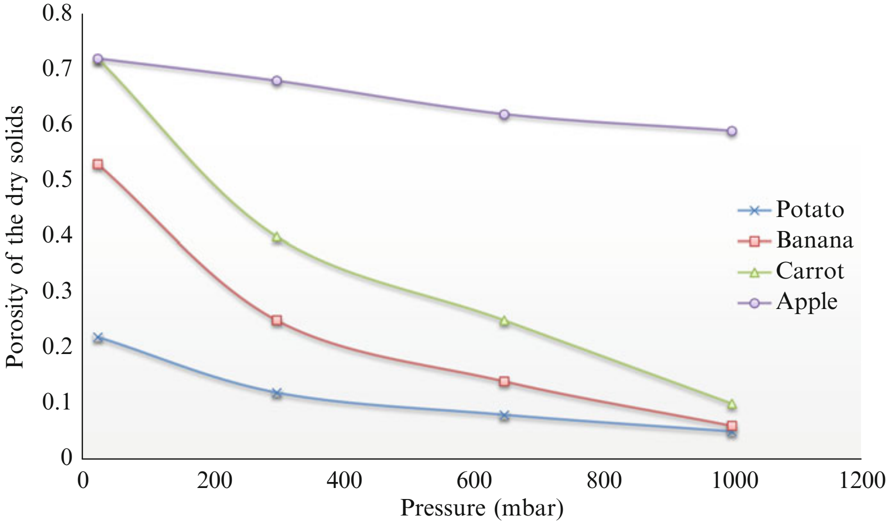


Fig. 4.11 Variation in porosity of dry solids against varying levels of atmospheric pressure. Adapted from Krokida et al. (1997)

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Chapter 5
Effect of Porosity on Drying Kinetics and Food Properties

5.1 Introduction

Quality is the extent to which a product meets the needs of the consumer. It includes sensory properties, psychological factors, and other characteristics such as contributions to health and compatibility with lifestyle conditions (Bruhn 1994; Bonazzi et al. 1996). Several authorities have defined quality in various ways, but the term generally appears to be associated with the degree of fitness for use or the satisfaction derived from it by consumers (Rahman 2005). Quality attributes can be divided into two major categories: sensory and hidden.

1. **The sensory** characteristics of quality include color, gloss, size, shape, texture, consistency, flavor, and aroma, which consumers can evaluate with their senses (Salunkhe et al. 1991; Bruhn 1994; Avila and Silva 1999). One of the most important sensory quality attributes is color because it measures the first impact of the product on consumer perceptions (Avila and Silva 1999; Bonazzi et al. 1996). Other important attributes in the initial acceptance of a food are its appearance, flavor, and texture.
2. **Hidden quality** attributes, which consumers cannot evaluate with their senses, are hidden characteristics, such as nutritive value and the presence of harmful or toxic substances (Salunkhe et al. 1991).

In addition to the foregoing classification, Rahman and McCarthy (1999) proposed a classification containing four major classes: (1) physical and physicochemical properties, (2) kinetic properties, (3) sensory properties, and (4) health properties. Quality attributes are presented in Fig. 5.1.

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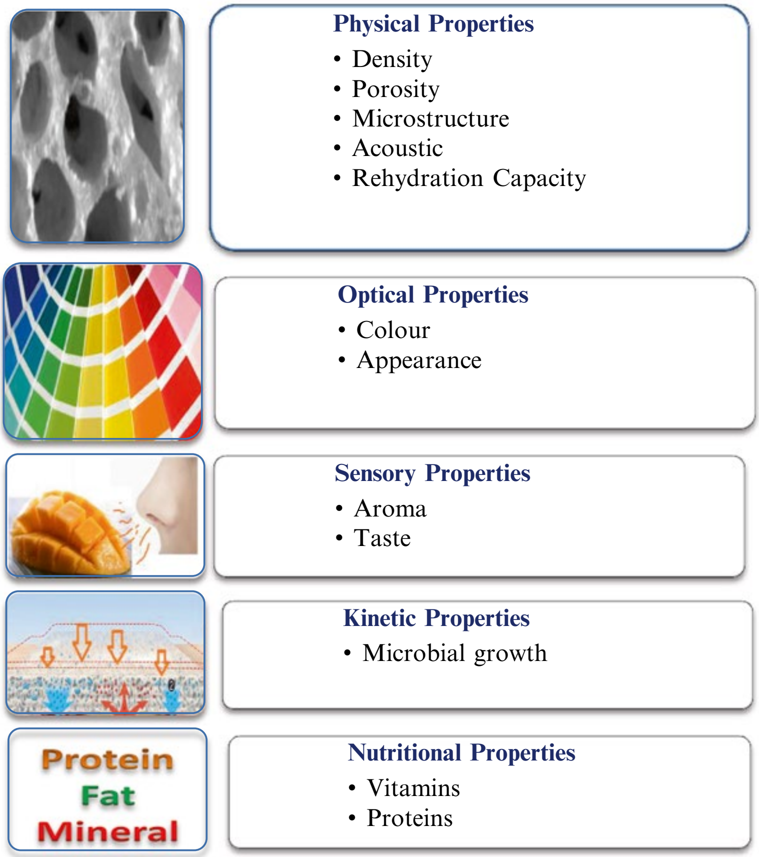

Fig. 5.1 Classification of food quality attributes

Owing to the complex nature of food products and the wide range of temperatures and moisture contents developed within the food sample, the quantitative description of the relations between processing conditions and product quality has proved difficult (Franzen et al. 1990). For example, the severity of processing also results in higher nutritional loss and in general poorer product quality. It is therefore obvious that an optimum combination of processing time must be established to obtain the desired food characteristics. In many cases, the right levels of the various processing parameters are needed to develop the appropriate flavor, texture, and aroma.

However, the porous structure of biomaterials is a key factor that affects heat and mass transport in capillary-porous biomaterials (Luikov 1975; Krokida and Maroulis 1999) and the quality attributes of food products. The influences of porosity on different food properties, such as effective diffusivity, dielectric properties, and thermal properties, and dried food qualities, such as food stability, texture, sensory properties, and rehydration, are described in what follows.

5.2 Transport Properties

The transport properties of biomaterials, for instance, thermal diffusivity, moisture diffusivity, and dielectric properties, significantly depend on the materials' porous structure. Therefore, porosity is a very relevant factor that needs to be taken into consideration for establishing drying models.

5.2.1 Mass Transfer in Porous Food

Mass transfer in porous materials is caused by bulk flow, capillary flow, and diffusion flow. The driving forces of these types of flow, such as the pressure gradient, capillary forces, and concentration, are affected by the porous nature of food materials.

In the case of large pores, fluid flow occurs mostly outside of the solid. Fluid flow in this case is through the empty spaces of these stacked systems and is treated as a Navier–Stokes analog that is a generalization of Darcy flow. On the other hand, in the case of smaller pores, the flow generally occurs inside the solid. Examples of this include moisture transport inside the solid of many food processes such as drying, frying, and microwave heating. Here the fluid transport through the pores of the solid is treated in terms of the simplest version of Darcy flow as opposed to its generalization into a Navier–Stokes analog.

Diffusion mechanisms are present at different stages of drying, and their relative importance depends on drying conditions, pore geometry, pore topology, and the wall composition of the porous medium (Rassis et al. 1997). Effective moisture diffusivity can be expressed as a function of porosity (Kasapis et al. 2007; Guillard et al. 2013; Prakotmak et al. 2010):

$$\frac{D_{A}\varepsilon}{\tau} = D_{eff} \tag{5.1}$$

where D_A is the binary molecular diffusivity and τ is the tortuosity (tortuosity is known as the ratio of the flow line between two points on the flow channel to the straight distance of those two points). From the foregoing equation it can be assumed that the moisture diffusivity is proportional to the pore area.

From Eq. (5.1) it is clear that a fresh portion of the same material with higher initial porosity shows higher effective diffusivity. This is why different studies dealing with the same material under the same drying conditions reported different values of effective moisture diffusivity.

In the case of highly porous material, the effective diffusivity encompasses both liquid diffusion of water (10^{-10} m^2/s) and vapor diffusion of water (10^{-5} m^2/s), D_{eff} increases with increases in the porosity of the food materials over the course of drying (Guillard et al. 2013). In other words, when there is less water content in pores, the vapor saturation is higher; consequently, vapor diffusivity is the dominant mechanism of water migration from food material. In addition, some drying processes produce higher amounts of vapor within the food material, ensuring a higher effective diffusivity of water. Taken together, effective diffusivity for liquid water and vapor is caused by the porosity gradient, moisture concentration gradient, and temperature gradient (Dhall and Datta 2011).

Not only the porosity value but also the pore size distribution affects the transport of moisture (Rahman et al. 2002). Prachayawarakorn et al. (2008) studied the effect of pore size distribution width on transport properties, as shown in Fig. 5.2.

It is clear from Fig. 5.2 that the effective diffusivity decreases with increases in the value of σ/μ, where σ is the standard deviation and μ denotes a normal size distribution. The effective diffusivity value varies within a range of 9.4×10^{-11} to 8.3×10^{-11} m^2/s for a pore size distribution width range (σ/μ) of 0 to 0.3.

Similarly, the permeability of air through porous materials is considerably affected by the value of porosity. Goedeken and Tong (1993) investigated permeability through porous dough and found that it followed Darcy's law. In addition to this, porosity directly influences permeability, which ranges from 0.02 darcies at a porosity of 0.1 to 0.23 at a 0.6 porosity. As shown in Fig. 5.2 that permeability sharply increases with increases in porosity, and when porosity exceeds 0.4, it may be due to a greater number of interconnections between pores.

In summary, the effective moisture diffusivity is greatly influenced by the microstructure and porosity of food material (Prakotmak et al. 2010; Prachayawarakorn et al. 2008; Fernandes et al. 2008). In particular, increases in porosity, along with more open pore structure, have been found to increase the effective moisture diffusivity (Baik and Marcotte 2003). On the other hand, a reduction in porosity on a

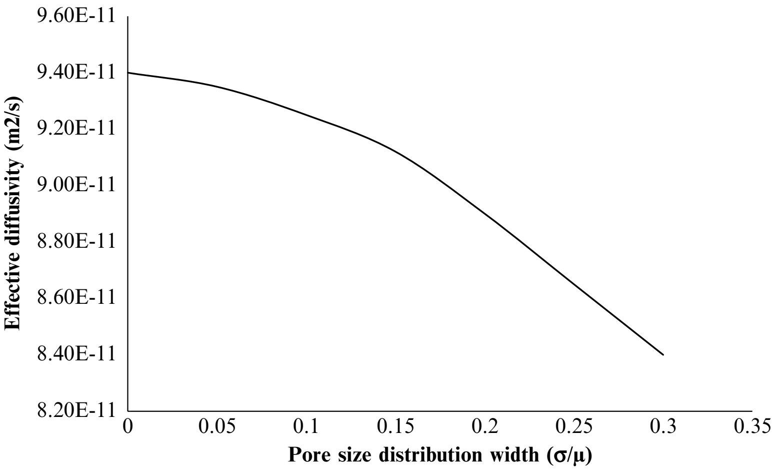

Fig. 5.2 Effect of pore size distribution width on effective diffusivity ($\mu = 40$ μm). Adapted from Prachayawarakorn et al. (2008)

food surface leads to the formation of crust; consequently, the effective diffusivity of water decreases significantly. Insight into pore structure may help to determine the dominant mechanisms of mass transfer and their contribution in realistic transfer modeling. However, as far as we know, no models exist that deal with the relationship between effective moisture diffusivity and changes in porosity during the drying of food materials. One of the main hurdles in connection with the establishment of this relationship is the in situ determination of porosity.

5.2.2 *Permeability*

Permeability is an important factor in describing water transport due to the pressure gradient in unsaturated porous media. The value of permeability determines how much pressure will be inside the material. The smaller the permeability, the lower the moisture transport and the higher the internal pressure, and vice versa.

The permeability of a material to a fluid, k_{i}, is a product of the intrinsic permeability, $k_{\mathrm{i,i}}$, of the material and the relative permeability, $k_{\mathrm{i,r}}$, of the fluid to that material (Bear 1972):

$$k_{\mathrm{i}} = k_{\mathrm{i,i}} k_{\mathrm{i,r}} \tag{5.2}$$

The intrinsic permeability depends on the internal structure of the material and represents the permeability of a liquid or gas in fully saturated states. This is constant for nonhygroscopic material since the solid structure remains fixed. But for hygroscopic materials, the porosity and volume of the material change and thus modify the permeability. The relative permeability can serve as a proxy for those changes (Ni et al. 1999).

Measuring the permeability value of deformable hygroscopic materials such as food is difficult (Ni 1997). Therefore, some reasonable approximation is made to calculate permeability.

The intrinsic permeability depends on the pore structure of the material. Feng et al. (2004) experimentally determined the value of intrinsic and relative permeability for the flow of humid air in porous apple tissues. The intrinsic permeability for apple tissues varied from 8.89e−13 to 4.57e−11 for porosity ranging from 0.33 to 0.77. The intrinsic permeability of apples can be expressed as a function of porosity using the Kozeny–Carman model, where intrinsic permeabilty increases with porosity, as shown by the following equation:

$$k_{\mathrm{i,i}} = 5.578 \times 10^{-12} \frac{\varepsilon^3}{(1-\varepsilon)^2} \quad (0.39 < \varepsilon < 0.77), \tag{5.3}$$

where $k_{\mathrm{i,i}}$ is the intrinsic permeability of air in a porous medium.

5.2.3 Rehydration

It is essential that porous dried biomaterials be rehydrated quickly to obtain the desired sensorial and textural properties. Rehydration is the process of moistening a dry material. In most cases, dried foods are soaked in water before cooking or consumption, and so rehydration is an important factor. In practice, most of the changes that occur during drying are irreversible, and rehydration cannot be considered simply as the reverse of dehydration (Lewicki et al. 1998).

In general, the absorption of water is rapid at the beginning of the process. A rapid moisture uptake is due to surface and capillary suction. Porosity, capillaries and cavities near the surface, temperature, trapped air bubbles, the amorphous-crystalline state, soluble solids, and the pH of the soaking water are the factors that affect rehydration kinetics (Weerts et al. 2003; Rahman and Perera 1999; Lewicki et al. 1998). However, porosity is the dominant factor affecting rehydration mechanisms (e.g., diffusion, capillary imbibition) of dried food materials (Karathanos et al. 1993; Farkas and Singh 1991; Marabi and Saguy 2004).

Furthermore, rehydration may be taken as a measure of the damage to the food material caused during drying. Therefore, the rehydration capacity depends highly on the nature of the porosity; a low porosity leads to products with poor rehydration capabilities (Mcminn and Magee 1976; Mayor and Sereno 2004). For example, Marabi and Saguy (2004) investigated the effects of porosity in a range of 0.13–0.90 on the rehydration of dried carrots and found faster rehydration kinetics for samples with higher porosity. This is due to the irreversible collapse phenomenon following the loss of turgidity during drying.

Rehydration starts from the surface and moves to the inside of the food material, and so much so that the surface moisture reaches saturation at the very beginning of wetting. In contrast to this, rehydration of inner portion of the sample substantially depends on trapped air contained in the pores. In other words, the major hindrance to the invasion of the pores by the rehydrating fluid is the existence of air bubbles. However, water can insert infiltrate a sample without any hurdles through some of the larger pores. Therefore, pore structure and the presence of air bubbles in pores prevent the absorption of rehydrating water.

In addition to this, the ability to reconstitute varies with drying conditions, and the same fresh materials might end up as an entirely different product. For example, freeze-dried materials seem to have a greater capacity to rehydrate (and to do so quickly) than air- and microwave-dried products (Oikonomopoulou and Krokida 2013; Pei et al. 2014; Laurienzo et al. 2013).

Volume changes over the course of rehydration largely depend on the porosity and relaxation of the shrinkage stress of dried plant tissues (Witrowa-Rajchert and Lewicki 2006). For this reason, dried food with a higher porosity gain little to no volume as rehydrated water fills the food material's pores. On the other hand, in the case of dried products with low porosity, rehydrated water penetrates into the solid matrix, which leads to swelling; consequently, the volume of the rehydrated sample increases considerably.

Apart from the porous structure, pretreatment also influences rehydration. As much as threefold more rehydration capacity has been reported in pretreated samples in the literature (Funebo et al. 2002).

Therefore, to ensure better quality dried food, which can be reconstituted properly after rehydration, there should be an intact structure with intact cell walls, minimum collapsed cells, and intact intercellular spaces.

5.2.4 Thermal Diffusivity

Thermal conductivity is defined as the ability of a material to conduct heat. The structure of a foodstuff, its composition, heterogeneity of food, and processing conditions affect the thermal conductivity of foods (Sablani and Rahman 2003; Hamdami et al. 2003). Dry porous solids are very poor heat conductors because the pores are occupied by air. For porous materials, the measured thermal conductivity is an apparent one, called the *effective thermal conductivity*. It is an overall thermal transport property, and there is an underlying assumption that heat is transferred by conduction through the solid and porous phases of the material.

Structural factors, including pore characteristics and the distribution of the different phases, such as air, water, ice, and solids, affect the overall thermal diffusivity of food materials. Furthermore, processing factors, including temperature, pressure, and the mode of heat or energy transfer effect the thermal diffusivity. Rahman et al. (1997) and Rahman (1995) developed the following equation to correlate thermal conductivity and porosity:

$$\frac{\dfrac{k_{\mathrm{th,eff}} - \varepsilon k_{\mathrm{th,air}}}{(1-\varepsilon-X)k_{\mathrm{th,s}} + Xk_{\mathrm{th,w}}}}{1-\varepsilon+\left[\dfrac{k_{\mathrm{th,air}}}{\left(k_{\mathrm{th,w}}\right)_{\mathrm{ref}}}\right]} = 0.996\left(\frac{T}{T_{\mathrm{ref}}}\right)^{0.713} X^{0.285}, \quad (5.4)$$

where $k_{\mathrm{th,\,eff}}$, $k_{\mathrm{th,\,s}}$, $k_{\mathrm{th,\,air}}$, and $k_{\mathrm{th,\,w}}$ are the effective, air, solid, and water thermal conductivities; X is the mass fraction of instantaneous water of the food materials; and T_{ref} and $(k_{\mathrm{th,\,w}})_{\mathrm{ref}}$ are respectively the reference temperature and conductivity at 0°C. This model has been successfully applied to selected food materials.

In porous solids, such as foodstuff, thermal conductivity depends mostly on composition, but also on many factors that affect the heat flow pathways through the material, such as void fraction, shape, size and arrangement of void spaces, fluid contained in the pores, and homogeneity (Sweat 1995).

5.3 Glass Transition

It has been reported in the literature that, in general, porosity significantly affects the glass transition temperature (Ross et al. 2002; Kasapis 2012). However, Kasapis (2012) found an explicit effect of porosity on the glass transition temperature that ranges from −26 to −45 °C for apples with a porosity of 0.35–0.85. He found that the glass transition temperature decreased with increases in porosity. In addition, extruded samples with the highest porosity showed a T_g higher than the samples containing the lowest porosity (Ross et al. 2002). Moreover, sample pore size affects the nature of the glass transition; T_g was found to decrease with decreasing sample pore size (Jackson and McKenna 1991).

5.4 Dielectric Properties

The dielectric properties of food materials determine the degree of interaction between an applied microwave field and food products. These properties also determine the heating rate of food products by microwave power and are significantly affected by the moisture content, composition of the food, and, to some extent, the structure of the foodstuff (Martín-Esparza et al. 2006). The effect of porosity on dielectric properties is related to the low dielectric strength of air. Air has a relative dielectric constant of 1 and a loss factor of zero. Therefore, air is considered to be transparent to microwaves. It has been established that the more porous a material becomes during drying, the greater the volume of entrapped air in it. Consequently, the material shows low dielectric strength (Feng et al. 2012). In addition, a more specific surface area also affects the dielectric strength of porous materials (Jones and Or 2002).

5.5 Chemical Reaction and Stability

The interaction area of a solid sample is a vital parameter of chemical reaction kinetics. On the other hand, porosity characteristics are the determining factors of the interaction area, and eventually determine the amount of specific surface area. Because of this concerns, several researchers have tried to correlate the effect of porosity on the kinetics of some chemical reactions in foods undergoing drying and storage (White and Bell 1999; Labrousse et al. 1992; Shimada et al. 1991). White and Bell (1999) reported that in a model food system composed of glucose and glycine included in an inner matrix, the elimination of porosity owing to structural collapse decreased the glucose loss rate constant. In model food materials with encapsulated lipids, structural collapse can lead to the release of oil from the matrix, followed by its oxidation in contact with the oxygen of the gas phase of the food system (Labrousse et al. 1992). Remaining encapsulated lipids are more stable to oxidation (Shimada et al. 1991). In addition, certain dried foods, such as freeze-dried food, contains higher porosity. This high porosity allows for a larger interaction area with oxygen, so that freeze-dried food shows a low oxidative stability (Sablani et al. 2007).

The effect of porosity may be discernible in diffusion-controlled reactions, such as Maillard browning reaction. The movement of reactants could happen more easily in pores than in the rest of the solid matrix. Bell et al. (1998) hypothesized that physical collapse during the rubbery state of an amorphous food system reduces the reactant

Table 5.1 Glucose loss and browning rate constants in solid PVP-LMW at pH 7.5 and 25 °C as affected by porosity and collapse (White and Bell 1999)

System description	Porosity	Initial moisture content	T_g (°C)	Glucose loss rate constant × 10^3 (M^{-1} d^{-1})	Browning rate constant (OD g^{-1} d^{-1})
High porosity	0.79	10.7	30	21 ± 3	13 ± 2
Medium porosity	0.72	10.5	31	23 ± 2	13 ± 2
Low porosity	0.53	10.8	30	23 ± 3	14 ± 2
Partially collapsed	0.18	10.5	31	21 ± 4	12 ± 2
Collapsed	–	8.9	37	6 ± 0.7	10 ± 1

loss through the Maillard reaction because of reduced porosity compared to the glassy state. In contrast, a reduction in porosity owing to a collapse in the glassy state with a low moisture content has a minimal effect on a Maillard reaction and, consequently, less effect on brown pigment development. White and Bell (1999) investigated the effect of porosity and collapse on glucose loss and Maillard browning in polyvinyl-pyrrolidone (PVP-LMW) with different levels of porosity. From their findings, as shown in Table 5.1, it implicitly appears that the absence or presence of porosity is a critical factor in both glucose loss and the Maillard browning reaction.

Therefore, the effect of porosity and collapse on chemical stability should be taken into consideration during the development and processing of food materials.

5.6 Mechanical Properties

The mechanical properties of food materials, in particular cellular food materials, are determined by the cell wall composition and solid matrix architecture. Among the mechanical properties; stiffness and share strength of food can be correlated to the porosity, degree of porosity, and other characteristics of pores (Gogoi et al. 2000; Bhatnagar and Hanna 1997; Ross et al. 2002). Variations in porosity, average pore size, pore size distribution, and specific surface area also have significant effects on the mechanical, textural, and other quality characteristics of dried foods. In general, porosity allows fluid to flow from food under compression during consumption, thereby influencing the mechanical properties of dried food (Ralfs 2002).

Vincent (1989) pointed out that torsional stiffness (0.5–7 MPa) changes with variations in porosity (0.84–0.54) in the case of fresh apples. It has also been found that stiffness maintains a linear relation when plotted as a dependent variable of $\varepsilon_0^{2/3}$. However, the prediction of mechanical properties by considering the torsional stiffness is complicated and uncertain owing to the morphological anisotropy of food materials.

In addition to these factors, the hardness of a sample is strongly affected by its pore characteristics. The results of several studies indicated that increased pore size reduces the hardness of dried samples (Therdthai and Visalrakkij 2012; Liu and

Scanlon 2003). Furthermore, the softness of dried tissue occurs in those locations where larger pores exist. It seems possible that tissue with larger and more numerous pores have a solid matrix of reduced strength; consequently, it can be easily broken.

5.7 Sensory Properties

The sensory properties of a product vary depending on the drying conditions. The food matrix largely controls flavor release at all stages of food processing and consumption (Druaux and Voilley 1997; Lafarge et al. 2008). Bubbles or pores also affect the sensory properties of foods. The perception of food factorability involves receptors sensitive to vibration. Vibrations are likely to be produced when the cellular structure of food is fractured. Stiff-walled cells are filled with air in low-moisture foods and with liquid in high-moisture foods. When sufficient force is applied during crushing by biting, there is a serial bursting of the cell walls. Thus, vibratory sensations of sound are involved when cellular or porous foods are crushed. A broad frequency band of sounds of irregularly varying amplitude was produced by crushing low- and high-moisture foods identified as being crisp (Vickers and Bourne 1976; Christensen 1984).

Texture is one of the vital sensory attributes (Moyano et al. 2007) and one of the important factors that control the consumer's perception (Wilkinson et al. 2000). This property of texture largely depends on physical properties (Wang and Brennan 1995). Porosity is one of the vital physical properties characterizing the texture of dried food materials (Schubert 1987).

To produce the desired quality of food, an understanding of the relationship between sensory qualities and structure is essential (Langton et al. 1997). A modified food structure and viscosity changes the association of flavor release and the breakdown of foods in the mouth (Baines and Morris 1987).

5.8 Collapse and Shrinkage

Microstructural changes during drying lead to macroscopic deformation and shrinkage.

Both collapse and shrinkage occur in food materials during most of the drying process. There exists a subtle distinction between shrinkage and collapse; shrinkage refers to a reduction in the volume of a food sample, whereas collapse represents an irreversible breakdown of the structure at either the cellular or tissue level. Structural changes at the cellular level occur over the period of drying owing to a loss of water, and as a consequence, damage to or collapse of cellular walls may occur (Ramos et al. 2003; Devahastin and Niamnuy 2010). Continuing with this idea, negative pressure resulting from moisture migration is the main reason for volumetric shrinkage over the course of drying. Furthermore, negative pressure arises owing to an inadequate collapse of cell walls to compensate for moisture flux and for a pore opening that is insufficient to allow air inside the food sample (Pakowski and Adamski 2012).

Pore formation is averted by both shrinkage and collapse of the food material during drying (Witrowa-Rajchert and Rzaca 2009). On the other hand, uniform pore formation reduces shrinkage, and consequently rehydration properties increase significantly. However, the collapse of cells and intercellular spaces occurs following the loss of water (Wang and Brennan 1995). Porous foods tend to shrink less than nonporous foods during drying because porous foods normally have less initial moisture content than nonporous foods (Srikiatden and Roberts 2007). In the early stages of drying, the volumetric shrinkage is generally much closer to the amount of removed water. Under this circumstance, it becomes very difficult to predict the exact degree of porosity because the sample may undergo shrinkage and pore formation simultaneously. However, this linear correlation between volume reduction and moisture migration has not always been found in the literature. Many mathematical models of shrinkage are available in which porosity is taken into consideration (Lozano et al. 1983a; Katekawa and Silva 2006).

Moreover, the nature of collapse and shrinkage to a remarkable degree depends on the strength of cell walls, intercellular adhesion, and the porosity of the tissue. Tissue with high porosity shrinks in response to moisture migration, whereas tissue with low porosity and strong intercellular adhesion would fail by collapse (Ormerod et al. 2004).

Apart from shrinkage, cell collapse is an important phenomenon that significantly alters porosity. Different types of shrinkage and cell collapse are shown in Fig. 5.3.

Initially, food material undergoes shrinkage without collapse. Following the removal of most of the water, collapse occurs during the latter stages of drying. In short, ideal shrinkage occurs when the volume reduction of the solid matrix is equal to the volume of the mass removed from the food material. It may happen when there

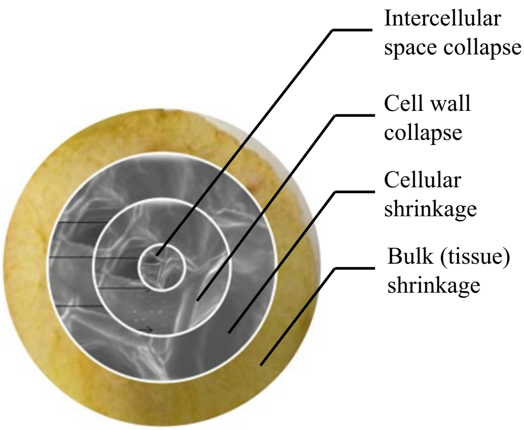

Fig. 5.3 Collapse and shrinkage phenomena during drying process

Table 5.2 Shrinkage models including porosity of agricultural products

References	Empirical equation	Food item	Nomenclature
Perez and Calvelo (1984)	$\frac{V}{V_0}=\frac{1}{(1-\varepsilon)}\left[1+\frac{\rho_0(X-X_0)}{\rho_w(1+X_0)}\right]$	Beef meat	$\frac{V}{V_0}$ = Shrinkage ? V = Instantaneous volume
Lozano et al. (1983b)	$\frac{V}{V_0}=\frac{1}{(1-\varepsilon)}\left[\frac{\left(\frac{\chi_{cw}}{\rho_{cw}}+\frac{\chi_{sg}}{\rho_{sg}}+\frac{\chi_{st}}{\rho_{st}}+\frac{X}{\rho_{sn}}\right)\rho_0}{(1+X_0)}\right]$	Carrot, garlic, pear, potato, sweet potato	V_0 = Initial shrinkage ε = Porosity X = Moisture content (dry basis) M = Mass fraction (kg/kg, total mass)
Modified Perez and Calvelo (Mayor and Sereno 2004)	$\frac{V}{V_0}=\frac{1}{(1-\varepsilon)}\left[1+\frac{\rho_0(X-X_0)}{\rho_w(1+X_0)}-\varepsilon_0\right]$	Apples, potatoes, carrots, squid	χ = Volume fraction of water (volume of water/total volume) ρ = Density *Subscript* cw = Cell wall material
Rahman et al. (1996)	$\frac{V}{V_0}=\frac{\rho_0}{\left(\frac{1-\varepsilon_{ex}-\varepsilon}{\sum_{i=1}^{n}\frac{M_i}{(\rho_T)_i}}\right)}\left[\frac{\rho_0}{(1+X_0)}\right]$	Calamari	sg = Sugar st = Starch w = Water ex = Excess volume i = Component n = Number of components
Madiouli et al. (2011)	$\frac{V}{V_0}=\frac{1-\varepsilon_0}{1-\varepsilon}\frac{1}{\left(\frac{\rho_S}{\rho_W}\right)X+1}\left[1+X\left(\frac{X}{X_0}\frac{\rho_S}{\rho_W}\right)\right]$	Banana	s = Solid 0 = Initial

are no mechanical restrictions on the shrinkage of the solid matrix. In the literature, this type of shrinkage is also called *free shrinkage* (Katekawa and Silva 2006).

Because of the close interrelationship between shrinkage and porosity, many shrinkage models take into consideration porosity, as shown in Table 5.2.

On the whole, porosity and shrinkage are very closely related. One of them can be predicted and calculated after obtaining the information about the other. In other words, controlling the shrinkage can reveal the expected porosity of the dried product.

5.9 Nutritional Quality

The rate of nutrient delivery evidently depends on food structure because structure controls the diffusion of nutrient molecules (Sharma 2012; Palzer 2009). Several factors, including food structure, processing conditions, and environmental conditions, affect the bioaccessibility of food nutrients (Parada and Aguilera 2007; Sensoy 2014).

The structural properties of food materials play a significant role in the absorption and release of nutrient components (Norton et al. 2007). For example, ascorbic acid loss is higher for larger exposed surface areas owing to higher O_2 interaction (Santos and Silva 2008). In addition, the complex structure of foods may prevent the bioaccessibility of nutrients because most nutrients remain either inside cells or connected to the cellular matrix (Sensoy 2014).

The intact cell walls of particular plant foods sometimes hinder the release of nutrients for digestion (Waldron et al. 2006). There is increasing evidence that during any type of processing, cell wall collapse significantly increases bioaccessibility. Because nutrients are generally located within cells and cell walls (Parada and Aguilera 2007), the porous characteristics of any food material, whether fresh or processed, allow the nutrients to move with less resistance. In other words, the specific surface area increases with increases in the porosity of the food material. For this reason, the area of release of nutrients increases considerably; consequently, more migration of nutrients is possible during passage through the gut. Mesh carrot juice, for example, penetrates through cells to an astonishing degree, making the nutrients more easier to absorb (Aguilera 2005). However, it cannot be ensured that complete collapse of a cell structure would allow for full absorption or release of a specific nutrient (Parada and Aguilera 2007). Clearly, then, drying can moderate (either decrease or increase) bioaccessibility and the rate of digestion.

Similar to drying process, nutrient degradation can also occur owing to factors such as storage temperature, exposure to oxygen and light, and porosity (Sablani 2006). Furthermore, Parada and Aguilera (2007) postulated that the disruption of a natural matrix or microstructure modified during processing may affect the release, alteration, and subsequent absorption of some nutrients in the digestive tract.

The corollary of the aforementioned finding is that more research needs to be done to investigate how structural changes alter the accessibility of nutrients. Successful study of this issue could pave the way to determining the optimal processing conditions that would make it possible to achieve maximum retention of nutrients.

5.10 Consumer Appeal

The more dried food looks like fresh food, the more consumers will like it (Oikonomopoulou and Krokida 2013). Appearance is defined by a food's color, shape, and texture.

It is obvious that the color of food material changes over the course of drying (Hansmann and Joubert 1998; Grabowski et al. 2002; Reyes et al. 2002). The prime cause of color change during drying is the browning reaction due to simultaneous heat and mass transfer (Fu et al. 2007). The kinetics of color change is notably affected by the structure of food tissue. Loss of cellular turgor pressure leads to a change in porosity. Subsequently, it may increase the effective release of different chemical reacting agents, accelerating the Maillard reaction and resulting in higher browning rates (Acevedo et al. 2008).

In addition, the appearance of food materials depends directly on several factors, including the ability of food material to scatter, absorb, transmit, and reflect visible light (Wyszecki and Stiles 2000). Therefore, modifications to a food surface's light reflectance ability owing to the evolution of porosity and changes in the surface texture must also be taken into consideration (Lewicki and Pawlak 2003; Lewicki and Duszczyk 1998; Fornal 1998). Moreover, a structure that is altered in the course of drying may also affect the dispersion of photons on the surface, resulting in changes in the degree of scattering (Romano et al. 2012).

Shrinkage and a change in shape, in most cases, make a negative impression on the customer (Mayor and Sereno 2004). Because greater porosity ensures less shrinkage and uniform shape change, porous foods enjoy higher customer acceptance. In addition, for many dried and processed food materials, crispiness is an important factor that appeals to consumers. It is reported in the literature that crispiness is strongly related to a food's microstructure and porosity (Aguilera and Lillford 2008).

Overall, with respect to customer satisfaction, color, shape, and texture are the most important factors to take into consideration. Maintaining the proper degree of porosity can ensure the appeal of dried food materials.

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Chapter 6
Relationship Between Drying Conditions, Pore Characteristics, and Food Quality

6.1 Process Parameter and Quality Correlations

Food preservation focuses on the stability of food materials in terms of physical, chemical, microbial, and nutritional aspects. Among preservation techniques, drying provides a high level of stability. However, the consequence of simultaneous heat and mass transfer is damage to the food material tissue. Sometimes these consequences result in consumer dissatisfaction. Porosity denotes the level of physical modification with respect to the initial structure of food materials. Knowledge of pore formation and evolution in food materials during drying is fundamental for the design and development of effective drying processes (Oikonomopoulou and Krokida 2013). However, there still exists much uncertainty about the relation between drying process conditions and product quality. An understanding of the interrelationship between the process conditions and dried product quality will yield the following benefits with respect to the drying of food materials:

(a) Generic drying models: Most prediction models available in the literature deal with a specific type of drying method. Even slight changes to process parameters and material can significantly alter the predicted result of a model. Therefore, any theoretical model based on the interrelationship between process parameters and product quality may lead to the development of a generic model.
(b) Maintaining optimal drying conditions: Various changes, such as shrinkage, porosity, and color modification, occur over the course of drying; however, the rate of such changes is not uniform throughout the drying process. On the other hand, moisture content and the kinetics of heat and mass transfer directly influence the rate of quality changes. Therefore, success in establishing a relationship between the process parameters and quality may pave the way toward optimizing drying conditions. Real-time analysis of food material qualities over the course of drying, and controlling the process parameters accordingly would

M.U.H. Joardder et al., *Porosity*, SpringerBriefs in Food, Health, and Nutrition, DOI 10.1007/978-3-319-23045-0_6

yield an effective drying system with an excellent quality of dried foods. This would also improve energy efficiency and lead to a sustainable drying system.

6.2 Relation Between Process Parameters, Pore Characteristics, and Food Quality

As discussed in previous chapters, several factors involved in the drying process affect pore formation and evolution throughout the drying process. The intensity of these factors significantly affects the porosity, and controlling these to appropriate levels can result in the optimum degree of porosity.

Some factors cause an increase in porosity with an increase in their intensity, as shown in Fig. 6.1, including sample shape, temperature, mobility of the solid, and the coating treatment. On the other hand, porosity decreases with increases in certain factors, such as pressure in the drying system and the drying rate.

However, in both cases, exceptions sometimes arise, which are reported in the literature. If these factors are regulated through the choice of the appropriate drying process, then the porosity of the dried food can be controlled.

Just as different factors affect porosity, porosity exerts a considerable influence on dried food quality. Based on findings reported in the literature, it can be hypothesized, as demonstrated in Fig. 6.2, that porosity can be the bridging factor between drying parameters and dried food quality.

In other words, by controlling the process parameters, an expected degree of porosity can be achieved, while confirming the level of porosity will determine the

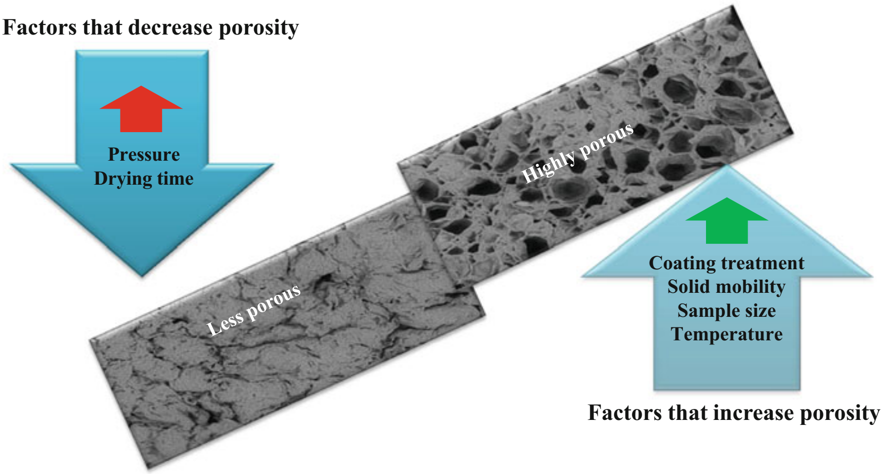

Fig. 6.1 Factors affecting porosity during drying of food materials

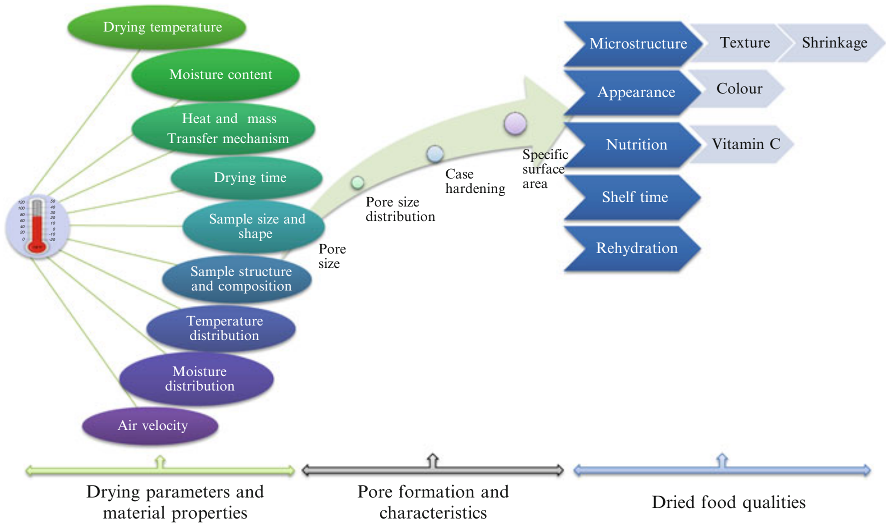

Fig. 6.2 Hypothesized relationships among drying parameters, pore formation and evolution, and dried food qualities

anticipated quality of dried food. In the previous section, both the positive and negative influences of porosity were discussed for different quality attributes of dried food materials. Accordingly, predicted quality attributes can be managed by maintaining porosity within the dried food by controlling the process parameters.

Since porosity influences water transport to a considerable degree, food quality is significantly affected by the level of porosity. Therefore, successful establishment of such interrelationships could confer the following benefits:

(a) Real-time control of quality: The quality of dried food material strongly depends on the various processing parameters. In addition to this, the quality of food materials varies with variations in the different parameters of the drying process. Numerous interrelationships exist between process parameters and quality attributes. Therefore, it becomes almost impossible to monitor the process parameters so as to control all of the quality attributes. Measurement of instantaneous porosity can be one route of controlling process parameters to manipulate the quality of dried food materials.
(b) Drying kinetics optimization: Since porosity significantly affects moisture transport, its real-time evaluation is essential for the optimization of drying and quality control.
(c) Energy optimization: Quality optimization demands moderate processing conditions, which leads to higher processing times. On the other hand, increasing the efficiency of the process generally results in lower product quality (Mahn et al. 2011). These conflicting and opposing influences of the productivity of industrial operations and the final product quality can be balanced to produce the optimum energy application (Holdsworth 1985). Controlling the expected

porosity can serve as the means for achieving the optimum energy supply because porosity significantly influences the rate of moisture transport and volume reduction.

(d) Effective preservation system: Knowledge of the interrelationship between structure and quality can be application to the design of better storage and packaging systems.

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Concluding Remarks

Drying parameters and food properties show different responses in terms of physical modification during drying. The information presented here regarding pore characteristics could be useful in modeling transport properties and rehydration and studying the oxidative stability of porous products. Because food materials are structurally complex, it is almost impossible to establish a generic relationship for all types of food. However, approximate relationships between process parameters and product quality can be achieved by consideration of pore characteristics. There remains huge scope for further research into those types of relationships, and the authors of this book are currently engaged in such research, paying particular attention to porosity. A better quality of dried food and the optimum drying conditions will be attained if the aforementioned relationships are definitely established in the future.

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