FLAVOR DELIVERY SYSTEMS

1. Introduction

For several decades, many flavors have been encapsulated, generally in solid matrices and often by spray drying, although other delivery systems and encapsulation techniques are also commercially being used (1). The primary and classical purposes of encapsulation are to protect volatile flavor compounds from evaporation and those susceptible to oxidation from degradation by atmospheric oxygen during storage in low moisture states. Besides providing a degree of protection, which can be very high especially for dense, glassy systems (2,3), encapsulation converts the liquid flavor into a solid, ideally free-flowing powder that is easier to handle.

During the last one and a half decades, the motivations to encapsulate flavors have become more varied as attention has shifted from protecting the flavor

in dry powder form to optimizing the performance of the flavor in complex food matrices. These food matrices are often moist or liquid and the performance of the flavor in such matrices is often unsatisfactory because of a limited chemical stability, or because of a premature, unbalanced, or incomplete release from the food matrix. To counter these negative effects, and to optimize the rate and extent of release of the flavor during food manufacturing, storage, preparation immediately prior to consumption and during consumption of the food product, extensive ranges of so-called controlled release or controlled delivery systems were developed (4,5).

Flavor compounds, which comprise both the volatiles that are sensed by the olfactory epithelium in nasal cavities and the nonvolatiles that impact the taste buds in the mouth, differ widely in chemical and physical nature. The volatile compounds, which are known as aroma compounds, are usually of low molecular weight ($M_w < 250$ Da), are liquid at STP (STP = standard pressure and temperature) and most of them are fairly-to-highly hydrophobic. A limited number of important impact compounds are hydrophilic. Encapsulation of flavors is primarily directed toward the volatile compounds, as the major stability and handling issues are experienced with these compounds. This article is also largely focused on volatile aroma compounds, but the terminology "flavor" is retained throughout the article. In fact, although often developed for the volatile flavor compounds, many encapsulation technologies can also be applied to nonvolatile taste compounds.

In this article, overviews are given of the various techniques developed to encapsulate flavors, and of the principal ways of applying flavor delivery systems in food applications and verifying their performance. The principal conceptual distinction we retain throughout this article is between flavor encapsulation systems whose primary function is to protect the flavor during storage and those whose aim is to control the release of the flavor during food processing, in the food matrix, and during consumption of the food product. As this first class of delivery systems is invariably based on amorphous carbohydrates in the glassy state, we coin the term "glass encapsulation" (6).

The discussion of glass encapsulation systems is divided into two main parts: a section on the various technologies used to produce the capsules and a section in which the general physical principles underlying the protective effect of such systems are presented. Strong emphasize is placed on the physical factors controlling capsule manufacturing and performance during storage. In particular, the water content and water activity of the encapsulation matrix are key parameters in understanding the physical behavior and barrier properties of amorphous carbohydrates as water is a highly efficient plasticizer of amorphous carbohydrates (7).

In our discussion of controlled delivery systems for flavors, we restrict ourselves, for reasons of brevity, to a discussion of the principal technologies, without elaborating too much the underlying material science and physical chemistry, although selected key references on these topics are provided.

Flavor encapsulation systems aimed at controlling release of the flavor are necessarily more diverse in working principle (the retention and release of flavor compounds), in composition and in the technologies used to prepare them than

glass encapsulation systems. The general objective of controlled release systems is to enhance the impact of the flavor in the food product during consumption by controlling the rate and extent of release of the encapsulated flavor. This enhanced flavor impact can be achieved during food processing, during storage of the food product, during preparation of the food product directly prior to consumption or during consumption of the food product. The common feature of all controlled release systems is that, in the food matrix, they retain a core structure whose role is to control both the rate and the extent of release of the encapsulated flavor. Such a core structure usually forms a kinetic barrier toward the transfer of the flavor compounds into the food matrix or the headspace. Generally, the flavor compounds also have a high affinity for this core structure that both retards the release of the flavor and limits the maximum extent of release. Examples of kinetic barriers are films, coatings, or interfacial surfactant layers with a selective permeability for flavor compounds, polymer gels, and solids (lipids, fats, and amorphous carbohydrates in the glassy state). Flavors compounds generally have a high affinity for lipid phases and can form reversible complexes with specific carbohydrates like cyclodextrins and starches.

For glass encapsulation systems, the release of the encapsulated flavor is generally fast and virtually complete as soon as the capsules are brought into contact with water or a moist food matrix. In the case of controlled release systems, the situation is more complicated as both the start of the release and the kinetics of release vary from system to system and from application to application. Often, the release is activated by water or moisture, but also other triggers are commonly employed, like temperature and mechanical or osmotic stress. In addition, when the release is activated, the rate and extent of flavor release is highly variable depending on the controlled release system, the physico-chemical nature of the flavor compounds and the conditions in the food matrix.

Because of the comparatively well-defined release aimed for, the selection and method of application of a controlled release system for flavors is critical and must be tailored for a specific application. A section is devoted to the application of flavor delivery systems and ways to assess the performance of these systems in food matrices, as these aspects are critical to the functionality of the encapsulated favor and the ultimate success of the both flavor and the delivery system. Such a discussion is essential, because a structured approach toward the application of controlled release systems has proved to be very difficult to integrate into mainstream food research and development. It often leads to a misappraisal of innovative and basically very useful flavor delivery technologies. We therefore attempt to synthesize recent scientific and technological developments. In recent years, the range of potential applications for flavor delivery systems has rapidly extended, but the necessity to tune the delivery system to the application and the substantial effort usually required to establish the performance of the delivery system has limited the number of commercial applications. An integrated approach toward flavor delivery includes advances in the materials science of food matrices, flavor physico-chemistry, and chemistry combined with technological developments and focused product development. We refer to some pertinent literature and speculate on some future developments in these fields.

2. Encapsulation Technologies: Glass Encapsulation

2.1. General Principles of Glass Encapsulation and Material Science of Amorphous Carbohydrates. Although the size, shape, and structure of glass encapsulation systems varies widely (Figs. 1**a**,**b**,**e**,**f**; Fig. 2; Table 1), the working principle of all these systems is the same and is based on the material science of amorphous carbohydrate glasses. Almost invariably, water-soluble carbohydrates in the amorphous, glassy state are used as encapsulation matrix, since, under controlled conditions, they combine high physical and chemical stability with very high barrier properties with respect to oxygen and organic molecules. In addition, they are chemically inert with respect to most classes of small organic compounds, which is important because of the wide chemical variety of flavor compounds. They are also fairly cheap and available in highly pure form.

As for all amorphous materials, amorphous carbohydrates exhibit at least two important phases, a rubbery, viscoelastic state, and a glassy, brittle state (7–10). Identical from a structural point of view, the distinction between these two states is in the rate and extent of molecular motion. In the rubbery state, translational and rotational motion of the matrix molecules is still possible, but in the glassy state large-scale molecular motion is effectively inhibited (11,12). These two phases are separated by a second-order phase transition, the glass-rubber transition, which is characterized by the glass transition temperature (T_g). The T_g of an amorphous matrix is dependent on its composition, with low molecular weight compounds generally having a lower glass transition temperature than high molecular weight compounds (13–16) (Fig. 3**a**). Of particular importance for amorphous carbohydrates is that the glass transition temperature strongly decreases with increasing water content or water activity (14,15,17), as illustrated in Figure 3**a**.

Although large-scale motion of the matrix carbohydrates are effectively blocked, small molecules like gases (18,19) and small organic molecules (20,21)

Table 1. **Characteristics of the Most Important Glass Encapulation Systems**

	Capsule type				
Characteristic	Spray-dried	Spray dried and agglomerated	Extruded	Vacuum-dried	Fluidized-bed dried[a]
size	20–150 μm	100–250 μm	0.4–2 mm	50–400 μm	0.3–2 mm
density	low	medium	high	variable	medium
flavor load	<25%	<25%	10–15%	<10%	<10%
flowability	poor	good	good	variable	good
surface oil	medium	medium	high [b]	high	low
processing	simple	standard	standard	simple	complex[c]
shelf life[d]	1 year	1–2 years	~4 years	1–2 years	1–2 years

[a] Limited controlled-release properties when coated.
[b] Low when washed.
[c] Depending on the number of coatings.
[d] Oxidation sensitive flavor.

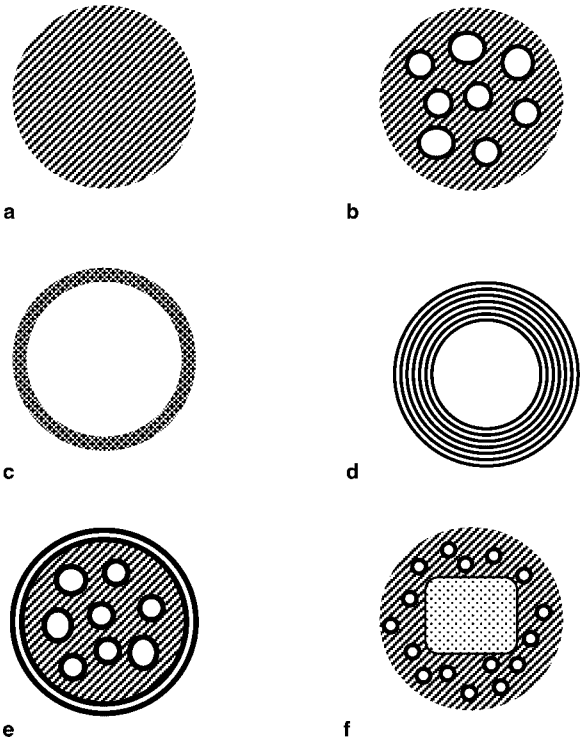

Fig. 1. Commonly occurring structures of flavor delivery systems. (**a**) Matrix morphology, flavor dissolved in matrix; (**b**) matrix morphology, discrete flavor inclusions; (**c**) core-shell morphology; (**d**) onion morphology; (**e**) and (**f**) composite morphologies; (**e**) coated matrix system; (**f**) fluidized-bed encapsulated flavor with inert core.

are also able to migrate through an amorphous material below the glass transition because of thermally induced density fluctuations (22,23). The rate of migration is very strongly dependent on the size of the permeating molecule (21,23) and effective mobilities need only to be considered for oxygen and the smallest flavor compounds.

The glass-rubber transition is an important concept in glass encapsulation. It demarcates the regime in which the encapsulation matrix is physically stable, ie, not undergoing any significant structural changes or molecular rearrangements on the time frame of the experiment (eg, the shelf life of the encapsulated flavor), from the state in which the matrix is soft, sticky, and moldable. Therefore, to ensure that the capsules retain their structure and properties during shelf life, one requires that the encapsulation matrix is in the glassy state under normal and often accelerated storage conditions. From Figure 3**a**, it is obvious that at any given water activity, this condition is more easily met by an encapsulation matrix of higher (average) molecular weight.

The intrinsically positive effect of increasing molecular weight on the T_g of the encapsulation matrix is counteracted by the free volume and residual porosity of the matrix, which is generally higher for high molecular weight compounds. The reason is that it is usually more difficult to efficiently pack large

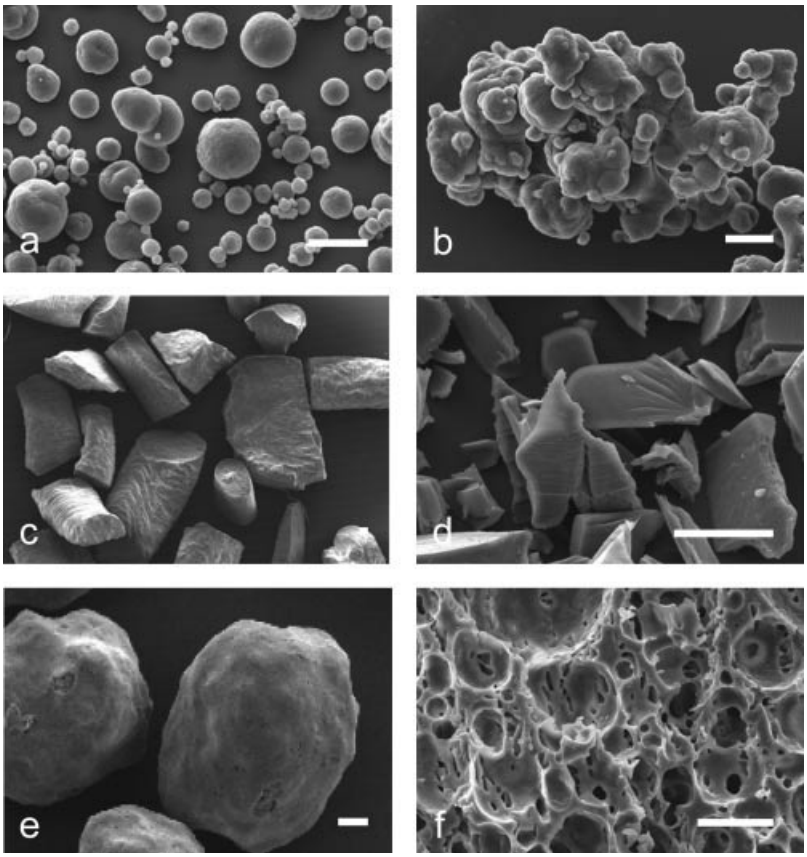

Fig. 2. Morphologies of the most important glass encapsulation systems used in flavor encapsulation. (**a**) Spray dried capsules; (**b**) spray dried and agglomerated capsule; (**c**) extruded capsule; clearly visible on the fracture interface are the flavor inclusions (average size ~20 μm); (**d**) vacuum-dried capsules; (**e**) fluidized-bed dried capsules; (**f**) freeze-dried capsules. Although freeze drying is not widely used as flavor encapsulation technique, the image is shown because of the continued importance of freeze drying in food manufacturing. The size bar in each image represents 100 μm, but should be taken as an approximate indication only as capsule size may vary depending on processing conditions and composition of the encapsulation matrix.

molecules into a dense matrix than small molecules. Also, during processing in the rubbery state, the time until the matrix settles is often longer for a matrix composed of larger molecules because of the higher viscosity. The higher free volume and porosity under the same conditions, will enable, a higher rate of oxygen uptake and will thereby decrease the shelf life of the encapsulated flavor, as determined, eg, by the concentration of flavor oxidation products as depicted in Figure. 3**b**. The effect of a higher matrix porosity with increasing molecular weight of the encapsulation matrix is particularly apparent for porous delivery systems like spray-dried capsules, but is probably of lesser importance for the high density matrices produced by melt extrusion.

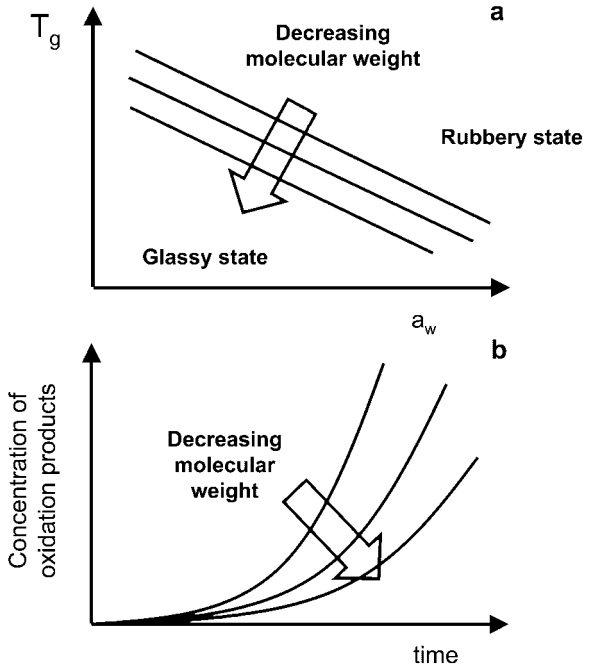

Fig. 3. Schematic depiction of the molecular weight dependence of the physical and structural properties of glass-encapsulation systems. (**a**) A decrease in the average molecular weight of the carbohydrate matrix leads to a reduction of the glass transition temperature at given water activity. The maximum permissible water activity, which is determined from the requirement that the encapsulation matrix should be in the glassy state at the storage temperature of the capsules, is lower for the low molecular weight matrices. (**b**) It is generally found that the concentration of oxidation products of encapsulated flavors during storage is lower for low molecular weight matrices, in particular when they are produced by spray drying. This is explained by the lower residual open and closed porosity (including matrix free volume) of the capsules prepared with low molecular weight carbohydrates.

Generally, a compromise is made between the physical stability of the encapsulation matrix, which is favored by increasing the molecular weight of the encapsulation matrix, and the oxygen permeability, which is usually minimized by reducing the molecular weight of the encapsulation matrix. In most commercial products, as prepared by, eg, melt extrusion and spray drying, the encapsulation matrix is composed of a mixture of intermediate or high molecular weight carbohydrates (eg, starches and maltodextrins of low DE) and low molecular weight carbohydrates (usually disaccharides, eg, sucrose) (24–26).

The T_g is not only important during storage or use of the capsules, but also during production, and should in this case be considered in relation to the matrix viscosity. During production, the capsules obtain their final shape and size in the rubbery state. Then, by drying, cooling, or both at the same time, the encapsulation matrix is quenched into the glassy state. During processing, the viscosity of the encapsulation matrix is one of the main controlling factors, because of its impact on the ease by which the viscoelastic encapsulation matrix is conveyed, pumped, homogenized, sprayed, and extruded.

Many carbohydrates not only occur in the amorphous state, but also in one or various crystalline forms (27,28). For encapsulation, the crystalline state is generally unsuitable, since no continuous barrier can be formed from crystals and since crystals generally have the tendency to exclude foreign compounds like flavor molecules. Usually, small carbohydrates like mono- and disaccharides are able to form crystals, although the ease and rate of crystallization depends strongly on the type of sugar [mannitol, eg, crystallizes very rapidly (29,30)]. In addition, the crystallization of a sugar can often be effectively inhibited by the addition of another compound, often a sugar itself (31,32). Oligo- and polysaccharides can also form crystals, although the overall degree of order in the crystal is often lower than in case of the mono- and disaccharides (eg, the crystalline form of a polysaccharide can have a well-defined orientational order, but its positional order can be absent or be less well defined). Complex mixtures of carbohydrates often do not easily crystallize, unless phase separation between two carbohydrate phases occurs, and crystallization is often also effectively inhibited if the molecules are branched. Maltodextrins, which are probably the most important materials used in glass encapsulation, are both highly heterodisperse and contain branched molecules. Therefore, they do not show any appreciable tendency to crystallize, which is one important reason for them being so useful as encapsulation matrices.

Most of the important flavors are hydrophobic, including all citrus oils and many of the savory top notes, are dissolved in a solvent, which is often an oil like MCT (MCT = medium-chain triglyceride), and their dosage in the capsules is high, often >10% (see Table 1). Therefore, the flavor will not completely dissolve in the essentially hydrophilic carbohydrate matrix but will remain phase separated. In effect, during encapsulation, a solid matrix is usually formed around liquid droplets of flavor and flavor oil (Fig. 4). To ensure a proper embedding of the flavor in the capsules [ie, to minimize surface oil (Fig. 5)], and to minimize

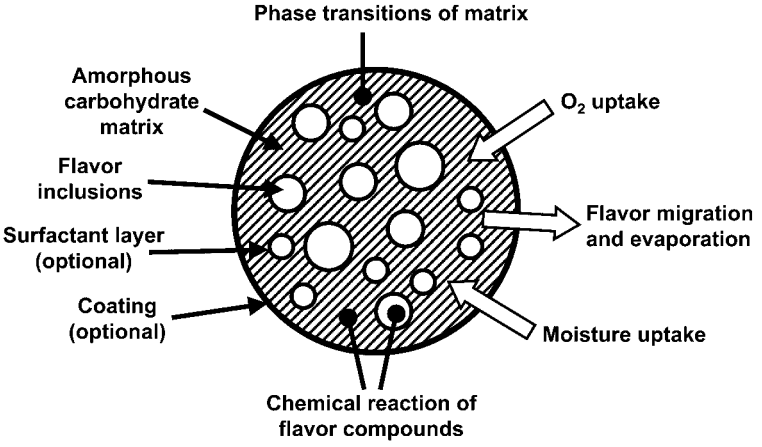

Fig. 4. General characteristics of glass encapsulated flavors. Indicated are the main structural features and the principal physical and chemical effects influencing the stability of the encapsulated flavor.

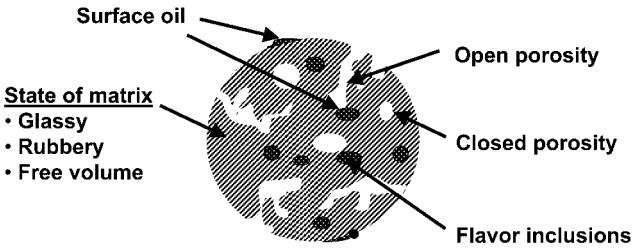

Fig. 5. Structural defects of glass-encapsulated flavors. These structural defects reduce the shelf life of the flavor by enabling the rapid uptake of atmospheric oxygen and, to a lesser extent, the evaporation of encapsulated flavor. Generally, the negative effects of open porosity and surface oil are more pronounced than those associated with closed porosity.

the leakage of flavor upon rupture of the capsules, the flavor droplets should be as small as possible, preferably <1 μm in diameter (5,33). The exception to this rule in glass encapsulation is encapsulation by melt extrusion (Fig. 6), where larger droplets (up to $\sim$20 μm) can be tolerated as the capsules are large (typically $\sim$1 mm; Fig. 2**c**) and the matrix is very dense (ie, no pores). In addition, in case of extruded products, the surface oil is often washed off during production (see Fig. 6**a**).

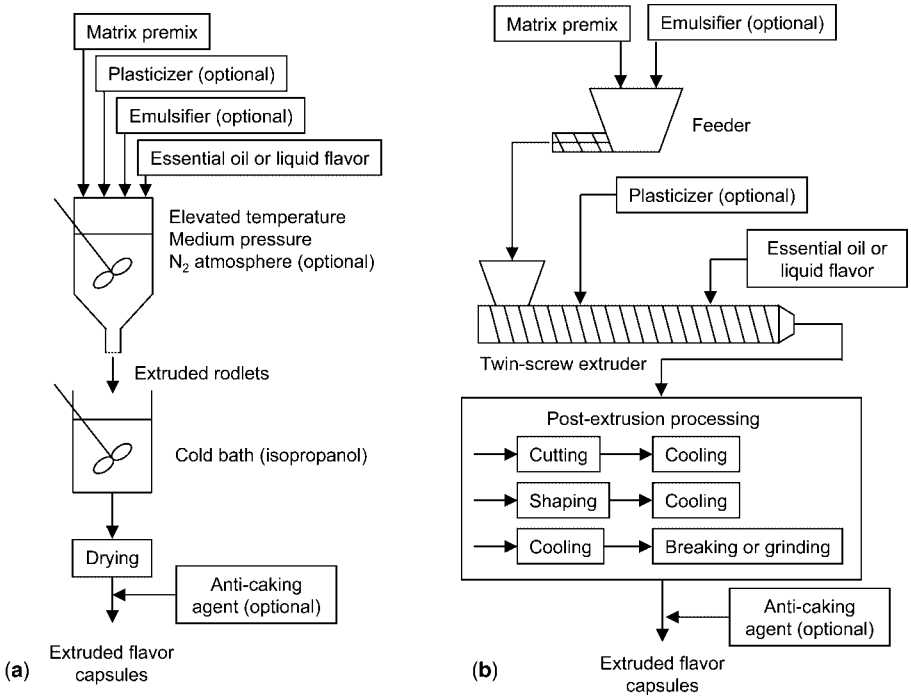

Fig. 6. Scheme of flavor encapsulation by extrusion. (**a**) Setup using a vertical, screwless extruder. (**b**) Setup using a twin-screw extruder. A variety of postextrusion steps to reduce particle size are shown.

In order to achieve such small oil droplets, emulsifiers are needed. These emulsifiers can either be the encapsulation matrix [eg, gum acacia (34), which is an arabinogalactan with surface active properties (35)] or can be added to the encapsulation matrix in the relatively small amounts needed to cover only the surface of the oil droplets [eg, starch esterified by 1-octenyl succinic anhydride (OSA starches) (36)], sucrose esters and the like]. Important criteria for successful flavor emulsifiers are that they are food-grade, form stable oil-in-water emulsions with a wide variety of hydrophobic compounds, have a relatively simple phase behavior (eg, do not show multiple dispersed phases in mutual equilibrium) and do not interact with the flavor compounds. This effectively excludes proteins as flavor emulsifiers as they chemically react with important classes of flavor compounds like aldehydes (in analogy with the protein crosslinkers formaldehyde and glutaraldehyde) and thiols (37).

Glass encapsulation systems show various structural imperfections, which negatively influence the performance of the capsules, in particular the shelf life. The most important of imperfection are the open and closed porosity and the surface oil (Fig. 5). The open porosity comprises the volume fraction of voids within the particle open to the environment whereas the closed porosity is the void space fully enclosed within the matrix of the particle. Surface oil is undesirable because a certain fraction of the flavor is not encapsulated, but is instead directly exposed to the outside atmosphere. Surface oil includes oil on the outer surface of the capsules but also in the open pores. Open pores are undesirable because they can penetrate into the oil inclusions and because they enhance the rate of oxygen uptake up by matrix as the effective diffusion paths are reduced. The negative effects of closed pores are less easy to point out, but generally they reduce the mechanical properties of the capsules. In addition, the internal rates of diffusion (in particular of gases like oxygen) increase considerably when the closed porosity is $>20-30\%$ (19).

2.2. Extrusion Encapsulation. The encapsulation of flavors by extrusion was initiated in the 1950s after initial trials on the encapsulation of citrus oils in hard-candy matrices demonstrated the suitability of carbohydrate matrices for the encapsulation of oxygen-sensitive essential oils (38,39). The primary objective of the development of an extrusion technology for flavors was then to retain the dense structure of the hard-candy matrix while reducing the particle size to within acceptable limits.

The encapsulation technology employing a vertical extrusion setup (Fig. 6**a**) developed at the time for flavor encapsulation differs quite substantially from modern conventional extrusion technology. Because of the low melt viscosity of the carbohydrate mixture commonly used for such encapsulation, the mixing of the matrix melt and the essential oil can be carried out by conventional dispersion units (Fig. 6**a**) and gravity supplemented with moderate levels of overpressure (1–7 bar) suffices as driving force to extrude the homogenized melt.

Many variations of the vertical extrusion encapsulation process are known (38–45,146), but the central steps are all essentially the same. A carbohydrate melt is prepared by heating the carbohydrate encapsulation matrix in a closed vessel, optionally in the presence of a plasticizer like water or glycerol. Although the temperature of the melt is variable, to avoid excessive thermal degradation of the flavor, maximum temperatures in the range of 110–140 °C are usually

employed. After preparation of the melt, the flavor is added under vigorous stirring in order to disperse it. A distinction should be made here between flavors that completely dissolve in the carbohydrate melt (ie, most hydrophilic flavors) and those that do not dissolve but remain in the form of a dispersed phase (ie, hydrophobic flavors, essential oils, flavors containing a hydrophobic solvent like MCT). As a finely dispersed phase is desirable to minimize surface oil, emulsifiers are frequently added. In cases where the flavor is sensitive toward oxidation, the process is carried out under a protective atmosphere (usually nitrogen) and occasionally antioxidants are added.

The melt containing the flavor is forced through a die plate containing a large number of openings. The thin, viscoelastic strands that are formed are immersed in a cold organic fluid (usually isopropanol) where they are quenched into the glassy state. The cold bath has two other functions: because of the vigorous stirring, the thin, glassy rodlets break up into small pieces (average length $\sim$2 mm at a strand diameter of typically 1 mm) and the substantial amount of surface oil (largely created during strand breakage) is washed off. The final product is obtained by separating the solids from the solvent, evaporating the remaining solvent and, optionally, adding an anti-caking agent.

The twin-screw process is more recent, but is rapidly becoming the standard melt-extrusion process in the flavor industry. Encapsulation by twin-screw extrusion is carried out following the next essential steps (Fig. 6**b**) (24,46–51). A carbohydrate melt is prepared by feeding a powder premix into the extruder, heating the extruder barrel and, optionally, by injecting a plasticizer into the barrel. The flavor is also injected in the extruder barrel and dispersed by mixing elements. Again, to improve the dispersion of the flavor in the carbohydrate melt, an emulsifier is often employed. The emulsifier is usually added to the extrusion premix. The carbohydrate melt is extruded through a die plate containing a large number of small openings and is quenched into the glassy state either by air cooling or by cooling in a cold bath. In one variation, the extruded material is cooled under pressure in a pressure vessel in order to maximize the density (49).

The extrusion field has been very active in developing matrices for flavor encapsulation as witnessed by the large number of patents. It is not our purpose to review them all here, but with reference to the section on the material science of carbohydrate matrices, some of the developments deserve attention. An early improvement was the use of noncrystallizing carbohydrates (40) which improves the facility of processing as no attention needs to be paid to avoid undesired matrix crystallization. High molecular weight polymers, hydrocolloids and proteins, in some cases with hydrophobic properties, like methylcellulose (51), pectin (51), agar (54) and whey protein (55), may be added to slightly tune the rate of flavor release and thus form a bridge toward controlled release systems that are discussed in more detail below. One patent is of some curiosity value. Whereas it is almost invariably assumed that, in order to obtain a carbohydrate matrix with high protective properties, the matrix must be in the glassy state, in (56) such protective properties are claimed also for matrices that have a T_g below room temperature. We do not have any experience with such systems, and its eventual usefulness can only be demonstrated in practice.

2.3. Encapsulation by Spray Drying. Spray drying is the most widely used technique to produce dried foods. It is also used as an encapsulation

technique for food and pharmaceutical ingredients because of its relatively simple, continuous operating conditions, and easily accessible machinery (57–61). In spray drying of an oil-based flavor, the flavor is emulsified into an aqueous solution, or dispersion, of an edible carrier material, usually a carbohydrate, and the emulsified material is pumped through a spraying nozzle or atomizer into a high temperature chamber (Fig. 7**a**). As water rapidly evaporates, particles of carrier material are formed and the flavor is partly entrapped in the interstitial spaces, dissolved in the matrix or sticks on the surface of the powder particle.

The ideal carrier should have good emulsifying properties, be a good film former, have low viscosity at high solids levels (the typical viscosity of a modern spray-drying emulsion is <500 cps at solids levels of 45% or higher), exhibit low hygroscopicity, and release the encapsulated ingredients when reconstituted in a finished food product (48). Furthermore, the infeed solid content is important. A high infeed solids level means that a semipermeable membrane can quickly be formed and thus flavor retention is favored (62,63). It has been found that each carrier has a unique optimum infeed solids level (64).

The retention of flavor compounds during spray drying is best understood according to the selective diffusion mechanism (62,63,65,66). Flavor compounds are preferentially retained in the drying droplet because the diffusion coefficient of organic compounds decreases much faster with decreasing water content than the diffusion coefficient of water. This is partly because the mobility of molecules in dense matrices is strongly size dependent (65,66). An additional effect slowing down the diffusion of organic compounds is microentrapment of hydrophobic

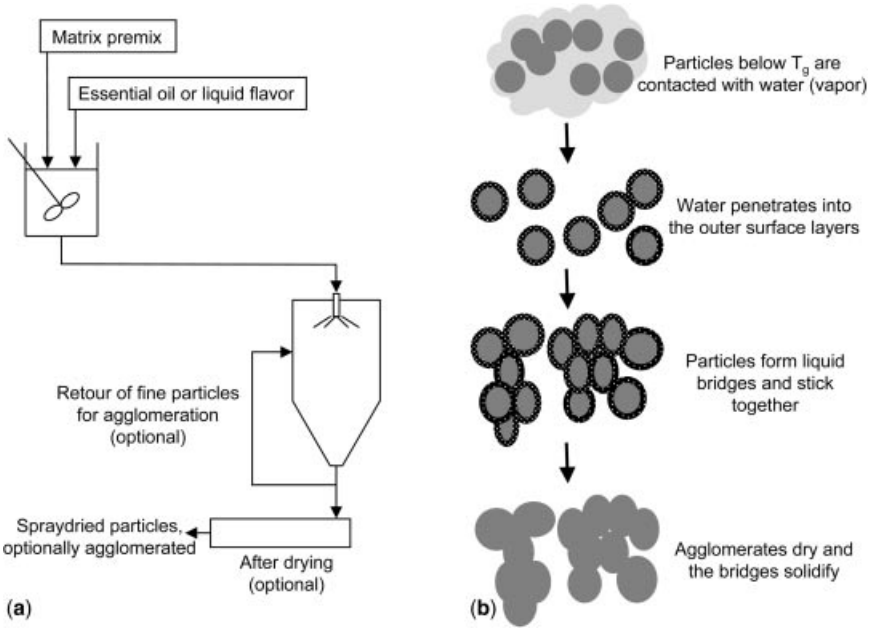

Fig. 7. Scheme of (**a**) flavor encapsulation by spray drying and (**b**) flavor encapsulation by spray drying and subsequent agglomeration.

compounds in small inclusions (67,68) leading to an effective slowing down of the rates of release of organic volatiles because of the partitioning of the aroma compounds into the hydrophobic inclusions (21,69).

Two types of atomizers are widely used in the industry: single-fluid, high pressure spray nozzles and centrifugal wheels (59). Atomization parameters have a significant effect upon the particle size distribution of the resultant powders. Particle size may have a minimal influence on flavor retention during drying (70–72), although it is often desirable to produce large particles to improve flowability and to aid in dispersion upon reconstitution. A convenient way to do so is by agglomeration (Fig. 7**b**), which, when properly carried out, does not significantly influence flavor retention (73). A recent development is the use of novel spray dryers enabling in-line agglomeration of the spray-dried particles (Fig. 7**a**,**b**).

2.4. Encapsulation by Freeze Drying and Vacuum Drying. In this section, two drying technologies are discussed that are occasionally used to encapsulate flavors. Although of little direct commercial relevance for the flavor industry, they are nevertheless of importance in the food industry, in particular for a number of specific products.

Freeze drying is a multiple-step operation in which the dispersion containing the matrix material (usually largely consisting of carbohydrates) and the flavor is first frozen, then dried by direct sublimation of the frozen solvent, and by desorption of the sorbed or bound solvent under reduced pressure. The time and freezing temperature are a function of the solutes in solution. During freezing, the solutes become concentrated in the unfrozen portion of the mix and the freezing point continually decreases until all the solution is frozen (74–76).

Freeze drying consists of two steps. First, because of the low pressure applied, the water vapor generated in the sublimation interface is rapidly removed through the outer porous layers of the product. Then, when no more ice is present in the product, the moisture from partially bound water within the product is removed. The latter step typically takes up to one-third of the total drying time. The result is a porous, nonshrunken structure.

Freeze drying is practical only for encapsulating heat-sensitive flavors. Major disadvantages of freeze drying are the high energy cost and the long drying time (76,77). In addition, the powders are fragile and protection of oxidation-sensitive flavors is non-optimal because of the extensive open porous structure.

Vacuum drying is widely used to preserve the aromatic qualities of herbs and spices but can also be applied to entrap flavors in glassy carbohydrate-based matrices, eg, maltodextrin and starches. In this case, it is of particular relevance for dehydrated culinary products, where, because of cost issues, flavors encapsulated by advanced technologies like spray drying or extrusion can not always be used.

In the encapsulation of flavors by vacuum drying, one usually starts with a dispersion of high solids content. The dispersion is then spread in a thin layer in a tray and dried under reduced pressure and elevated temperature. In order to speed up the drying process, the dispersion is occasionally foamed before drying. After drying, the brittle cake is milled to the desired particle size.

2.5. Fluidized-Bed Encapsulation Technologies. Fluidized-bed technologies are used to coat solid powders with a polymer film and usually produce a

core-shell morphology or particles with an onion-like structure (Fig. 1). The process involves spraying a polymer solution or dispersion onto a fluidized powder and evaporating the solvent to leave a polymer film covering the powder particles. During fluidized-bed encapsulation, one starts with the core particles, which are to be coated (the so-called support material). The support material is fluidized with air in a fluidized-bed chamber (78–81) (Fig. 8**a**). The material to be deposited is either dissolved or dispersed in an appropriate medium or solvent (for operations in the food industry usually water) or melted and sprayed onto the fluidized core particles by one of a variety of spraying techniques (79). The most important spraying techniques are shown in Figure 8**a** and are briefly discussed below. After spraying, the powder is either kept in a fluidized state to reduce the solvent concentration to the desired level, or the powder is cooled down to (further) harden the coating if a hot-melt coating was applied. Using fluidized-bed encapsulation, a large number of layers can be applied onto the same core, leading to capsules with various functionalities.

In the case of flavors, the first motivation to use fluidized-bed encapsulation techniques is to create relatively large particles with regular (usually spherical) shapes and a narrow particle size distribution. A second motivation is to create capsules with controlled release properties by applying one or more coatings with

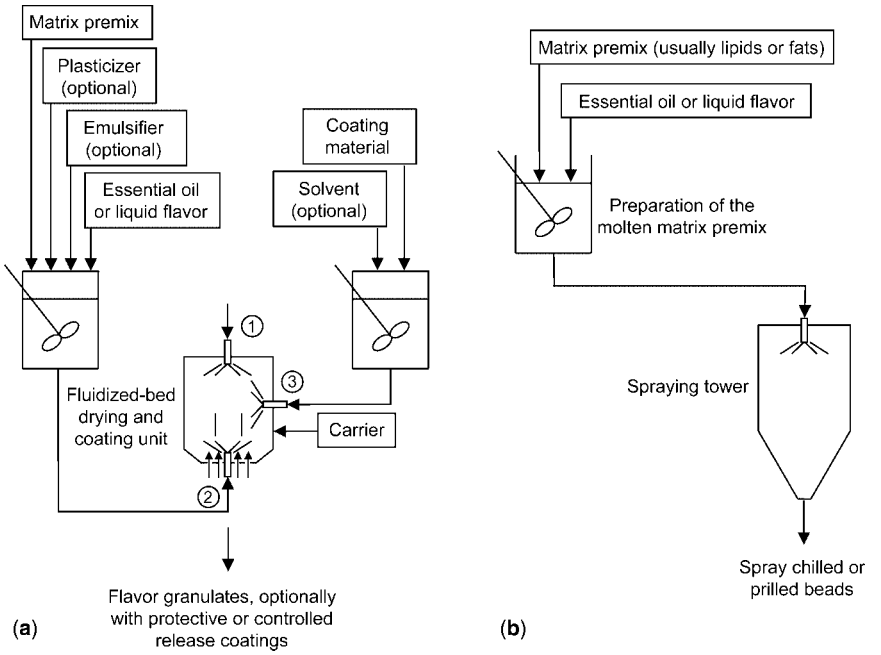

Fig. 8. Scheme of (**a**) flavor encapsulation by fluidized-bed drying and coating and (**b**) flavor encapsulation by spray chilling. In (**a**), the three principal methods of fluidized-bed drying and coating are depicted: (1) top spray; (2) bottom spray or Wurster system; (3) side or tangential spray. In the figure, the flavor emulsion is applied by bottom spraying and, in a subsequent step, an exterior coating is applied by side spraying. The various spraying configurations usually have a varying reactor geometry. Schematically shown is the insert commonly used for bottom spraying; for tangential spraying the reactor is normally equipped with a rotor at the bottom end (not shown).

specific functionalities to the core particles. In most applications of fluidized-bed encapsulation techniques apart from flavors, the support material on which the coatings are applied essentially consists of the active ingredient [which can be, eg, drugs, agrochemical compounds or food ingredients (82)], which are then coated to provide a certain protection to the active ingredient or create a controlled release functionality. On the contrary, in flavor encapsulation by fluidized-bed techniques a suitable support material containing sufficient amounts of the flavor generally does not exist as such core particles are too small and too irregular in shape to allow the proper application of a continuous coating. Therefore, in flavor encapsulation by fluidized-bed techniques, the process generally comprises at least one step in which a flavor emulsion is sprayed onto a suitable core (see Fig. 8**a**). The support material can either be an inert solid like for example sugar crystals (83) or starch granules (84) or it can be a flavor encapsulate prepared by, eg, spray drying (85).

In order to ensure a proper embedding of the flavor, the flavor emulsion generally contains a significant fraction of water-soluble carbohydrates like maltodextrins and other starch hydrolysis products (83,84) and/or low-molecular weight carbohydrates. Often-used emulsifiers are gum acacia and OSA starches (83–85). The solids content of the emulsion is generally ~40% or even somewhat higher.

As the primary structure of the capsules is a core covered by a layer of dried flavor emulsion in the amorphous, glassy state, the fluidized-bed encapsulated flavors are regarded as glass encapsulation systems. Nevertheless, limited controlled release properties can be obtained by coating the particles with one or more layers that provide some protection against, eg, moisture uptake, or that lead to a certain delay of the release of the flavor during the use of the capsules. Full controlled release properties using fluidized-bed techniques are difficult to obtain in the case of flavors, as the flavors are embedded in a water-soluble, amorphous matrix, that rapidly softens and dissolves upon increasing water content. Even when coated with a hydrophobic coating, the resulting osmotic forces usually lead to a rapid and complete loss of the functionality and performance of the outer, controlled release coatings because of extensive cracking. Note that in other applications, eg, for solid drugs or for solid food ingredients, this osmotic cracking is usually not a dominant factor and high level controlled release properties are commonly obtained.

Coating materials often employed to provide a certain degree of protection against moisture uptake or to impart controlled release properties either are solvent based or are applied in the form of a hot-melt coating. Such coating materials comprise, eg, lipids, modified cellulose, and the like (86). Increasingly popular is the use of polymer lattices, as it allows the use of water as a dispersion medium instead of organic solvents (87) and thereby extends the range of materials that can be handled in conventional food manufacturing equipment.

This section would not be complete without a brief discussion of the various spraying techniques that are commonly employed in fluidized-bed encapsulation. A detailed treatment is beyond the scope of this article and can be found elsewhere (79). In essence, three different spraying techniques for fluidized-bed encapsulation are employed (Fig. 8**a**). The first spraying technique is top spraying (*1*), in which the atomizer is placed at the top of the fluidized-bed chamber

and is directed downward. Advantages of this technique are that it is easy, cheap, and large batches can be easily handled. Significant disadvantages are that the distance between the atomizer and the fluidized powder particles is large and variable, leading to a premature evaporation of solvent or hardening of the coating droplets and a high variability in the quality and amount of the deposited coating. With bottom spraying or Wurster coating (*2*), the atomizer is placed close to the air inlet at the bottom of the fluidized-bed chamber, pointing upward. The distance between the fluidized particles and the atomizer is much smaller than in the case of top spraying, and, moreover, the fluidization of the particles is better controlled by the use of an insert as depicted in Figure 8**a**. These factors lead to a much better defined coating deposition, and, consequently to a better coating quality. The third method of spraying is side or tangential spraying. (*3*) This method is usually combined with a rotor configuration of the fluidized-bed chamber (not shown in Fig. 8**a**), which imparts a strongly agitated, supposedly helical trajectory to the fluidized particles. In this case, particle mixing is very intense and high quality coatings may be obtained with generally a reduced variability in coating quality between the particles in one batch in comparison to the bottom-spray process.

Applied to flavor encapsulation, all three processes would in principle suffice to spray the flavor emulsion onto the support material. When, however, very smooth, spherical particles are desired (eg, to facilitate further application of controlled release and protective coatings), bottom and side spray are usually the better choice. This finding is even more the case when applying protective or controlled release coatings, as any crack or hole in such coatings would severely impair the functionality and performance of the coatings. It should be emphasized, however, that the coating quality of the fluidized-bed coated capsules is not only dependent on the spraying technology, but also on the viscosity and wetting behavior of the coating liquid, and the size, geometry, and fluidization performance of the fluidized-bed chamber.

2.6. Comparison of Glass Encapsulation Systems. Although the working principle of all glass encapsulation systems discussed in this section is the same, (ie, protecting sensitive flavor and essential oils in amorphous, glassy carbohydrates during storage in low moisture states), the wide variety in structure, size, and shape (Fig. 2 and Table 1), and the varying conditions during capsule production often lead to clear advantages of one type of capsule over another.

If the shelf life of an oxidation-sensitive flavor is of prime importance, eg, for citrus oils in instant beverages and pharmaceutical products, an extrusion-encapsulated product would often be preferred because of its excellent barrier properties with respect to oxygen. Extruded capsules also have some disadvantages, notably large particle size, high temperatures during processing, and also are relatively expensive.

If the price is of key concern, and if the flavor to be used is not too sensitive toward environmental factors such as atmospheric oxygen, spray drying is the method of choice. By far, spray drying covers the largest segment of the market for encapsulated flavors. Spray-dried capsules are available with variations in matrix composition, particle size and structure, emulsifier type and content and flavor load. Classical spray-dried products, which are cheap, have as

major disadvantages a small particle size, which causes the products to dust and that leads to powder settling in powder mixes, a poor flowability and a fairly limited shelf life (which, however, in many applications is not so crucial). In addition, the dissolution characteristics of the fine powder are often not very good. Spray-drying technology has much progressed and high quality spray-dried and agglomerated flavors with improved shelf life and flowability characteristics are now commonly available. Also, significant improvements were achieved in minimizing flavor losses during spray drying.

Fluidized-bed encapsulation is an emerging technology for flavor encapsulation, albeit for niche applications. The principal reason to apply fluidized-bed encapsulation is that the particles are very regular in shape and usually also rather large. If colored, they can also be used to give a visual aspect to the product in which they are applied. In addition, fluidized-bed capsules can be coated with a variety of materials to provide for (limited) controlled release properties. Disadvantages of fluidized-bed encapsulation are their relatively low flavor load, the complexity of the process, and concomitantly the high cost of the final product.

Freeze drying has found only limited application as a flavor encapsulation technology due to its higher operating cost and longer process time. In addition, freeze-dried powders are mechanically delicate because of their extensive open porosity and thin lamellae, which also leads to increased rates of oxygen uptake from the environment. In addition, the effective flavor load is low. An advantage is that dissolution properties are usually excellent. Although not widely applied for flavor encapsulation as such, in cases where powder appearance is of importance, freeze drying is still a useful technique to entrap flavors. A typical example is soluble coffee (76,88).

3. Encapsulation Technologies: Controlled Release Systems

3.1. Overview. In contrast to glass encapsulation systems, controlled release systems have a variety of objectives (see Table 2). The principal aim is control the release of the flavor in the food application, but this is a general statement, which in reality covers a large number of situations. Retarded flavor release can be desirable during food processing or food preparation, usually to minimize flavor losses due to excessive volatilization or temperature- or moisture-induced chemical instability. Conversely, in situations where the flavor would strongly, sometimes irreversibly bind to food matrix constituents, and so never be released from the food matrix, a controlled release system can be helpful to speed up the rate of flavor release. In still another situation, a controlled release system might be used to modulate the release of individual flavor compounds from the food product during food consumption, thereby providing a more interesting flavor profile to the consumer. Another important factor in applying controlled release systems is the desired trigger of the flavor release. This trigger is usually temperature, moisture or mechanical forces, but other triggers like pH can also be applied.

As the desired mode of release of controlled release systems varies widely, large numbers of conceptually different systems have emerged from industrial

Table 2. **Characteristics of a Number of Controlled Release Systems**

	Capsule type							
	Coacervate	Polymeric extrudate	Alginate	Fluidized-bed[b]	Spray-chilled	Emulsion [a]	Microemulsion, complex fluid [a]	Cyclodextrin complex [a]
size	5–200 μm	0.1–4 mm	50–700 μm	0.3–2 mm	20–200 μm	1–20 μm	<1 μm	~1 nm
physical state	solid, slurry	solid	solid	solid	solid	liquid, dispersion	liquid	solid, liquid
flavor load	<40%	10–15%	10–15%	<10%	<10%	<25%	<15%	<10%
type of flavor [c]	hydrophobic	general	hydrophobic	general	general	hydrophobic	hydrophobic	compex-building
release mechanism[d]	diffusion and partitioning; capsule rupture	diffusion	diffusion and partitioning	capsule erosion	diffusion, dispersion	partitioning	partitioning	partitioning
trigger [d]	moisture, temperature	moisture, temperature	moisture, temperature	moisture, temperature	temperature	contact with food matrix	contact with food matrix	contact with food matrix
shelf life[e]	6 months	2 years	6 months	1–2 years	6 months	1–6 months[f]	1–6 months [f]	6 months–2 years [f]

[a] These systems are often themselves encapsulated in another matrix, for instance by extrusion or spray drying, to reduce their fragility, to improve flavor stability and retention, to facilitate handling and to reduce flavor release rates.
[b] Controlled release functionality when coated. For flavors, the system is principally listed as a glass encapsulation system.
[c] Systems indicated as 'general' either work for both hydrophobic and hydrophilic flavors or specialized systems exist for both hydrophobic and hydrophilic flavors.
[d] Principal mechanism. Several mechanisms are illustrated in Figure 12.
[e] Prior to application in the food matrix; oxidation-sensitive flavor.
[f] Further encapsulation of these systems may increase the shelf life to 1–2 years.

and academic research. Many products are commercially available and find successful application. However, many controlled release systems are still in a research or development phase and will probably never appear in actual food products, often because the technology is too expensive or because of unwanted side effects like a very limited shelf life or negative sensory or textural aspects.

In this section, a selection is made of the many controlled release systems for flavors, which are around. Priority has been given to those systems that have proven merits in actual food applications (coacervate capsules, spray-chilled capsules, and inclusion complexes). In addition, a number of promising or otherwise interesting technologies are discussed, eg, extrusion encapsulation, gel encapsulation, and complex fluids. Fluidized-bed encapsulation is not specifically discussed in this section, as, for flavors, it is primarily a glass-encapsulation technology with optionally limited controlled release properties. Some representative samples of controlled release capsules are shown in Figure 9.

3.2. Coacervation Encapsulation and Gel Encapsulation. Hydrophobic materials, including hydrophobic flavors and essential oils, can be encapsulated in polymeric shells and matrices by making use of the thermodynamic properties of dilute, aqueous solutions and mixtures of (bio)polymers. Aqueous polymer solutions display a great variety of phase behavior including gelation,

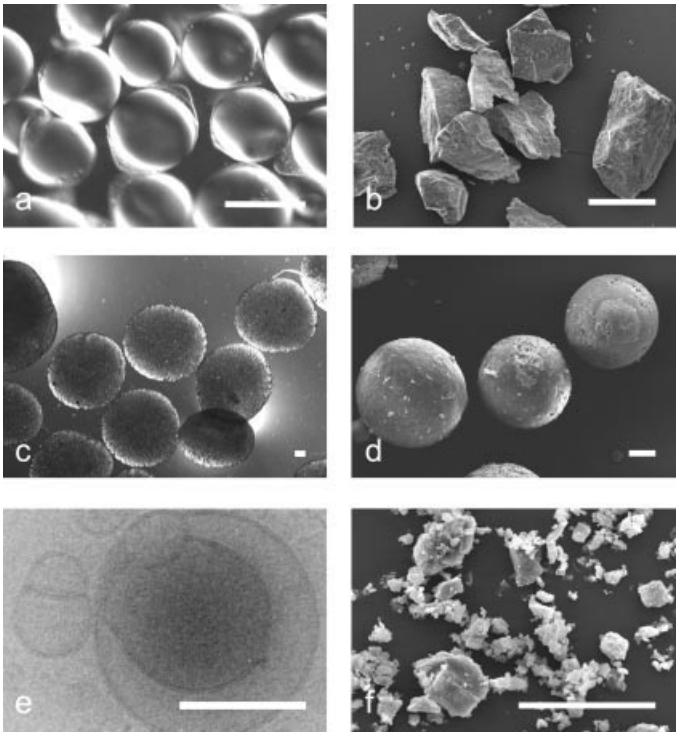

Fig. 9. Morphologies of the most important controlled release systems used in flavor encapsulation. (**a**) Coacervate; (**b**) polymeric extrudate; (**c**) alginate capsule; (**d**) spray-chilled capsules; (**e**) emulsion; (**f**) cyclodextrin-flavor complex. The size bar in **a**–**d**, **f** represents 100 μm, but should be taken as an approximate indication only as capsule size may vary depending on processing conditions and capsule composition. The size bar in **e** is 100 nm.

complexation, precipitation, phase incompatibility and cosolubility (see, eg, (89) for a general reference). The type and properties of the various polymer phases and the transitions between them are sensitively dependent on a considerable number of parameters, eg, temperature, polymer concentration, stoichiometry of the polymers in a mixture, ionic strength and pH. In all these phenomena, inter and intramolecular interactions and excluded volume effects between the polymers play a dominant role.

For encapsulation purposes, two phenomena involving polymer phase behavior are of significant importance: gelation and coacervation.

Coacervation is the formation of phase-separated, fluid polymer phases in an aqueous medium (90–93). Two types of coacervation are generally distinguished: simple and complex coacervation. Although the definitions of simple and complex coacervation do not always agree (91–96) we adopt here the convention originally used by Bungenberg de Jong (91) and that is retained in most of the recent literature (93–95). Whereas in simple coacervation, a polymer phase, usually but not necessarily composed of a single polymer, phase separates by hydrophobic interactions, in complex coacervation the separated phase is constituted of two polymers which are oppositely charged (91,93). The two oppositely charged polymers form a electrostatic complex which is overall close to electric neutrality and separates out of solution in the form of small globules leaving a depleted aqueous phase (91,93).

Complex coacervation is used for the encapsulation of hydrophobic substances (active ingredients, excipients or solvents) in either the solid or the liquid state. Developed originally for the encapsulation of staining ingredients for carbonless copy paper (97–100), encapsulation by complex coacervation has found widespread use for a wide range of active ingredients including flavors and essential oils (101–103).

In order to form a shell around the hydrophobic substance to be encapsulated, either of the polymers or the polymer–polymer complex should possess hydrophobic properties, so it associates with the surface of the dispersed hydrophobic substance forming a thin, continuous shell. As coacervation is an essentially reversible phenomenon, the formed capsules are usually cross-linked to preserve their integrity under an extended range of conditions.

Encapsulation by complex coacervation proceeds via the following steps (illustrated in Fig. 10**a**). For flavors, one starts with either a flavor solvent (like vegetable oil, MCT oil) or a flavor oil that is dispersed in an aqueous medium by agitation. Then, an emulsifying hydrocolloid is added, which partially adsorbs on the surface of the oil droplets. Usually, an arabinogalactan like gum acacia is used as it is both anionic and as it possesses surface active properties owing to proteins associated with the carbohydrate (35). The capsule size is largely determined at this stage as it will be close to the droplet size of the dispersed hydrophobic phase. In the next step, a solution containing the second polymer is added under conditions where this polymer stays in solution. If the first polymer is anionic, the second polymer should be cationic, at least under certain solution conditions like temperature, pH, or ionic conditions. Conventionally, proteins are used, as their overall charge can be easily adjusted from negative to positive by lowering the pH. Gelatin is a preferred choice because of its gelation properties, ability to form a smooth film and interactions with

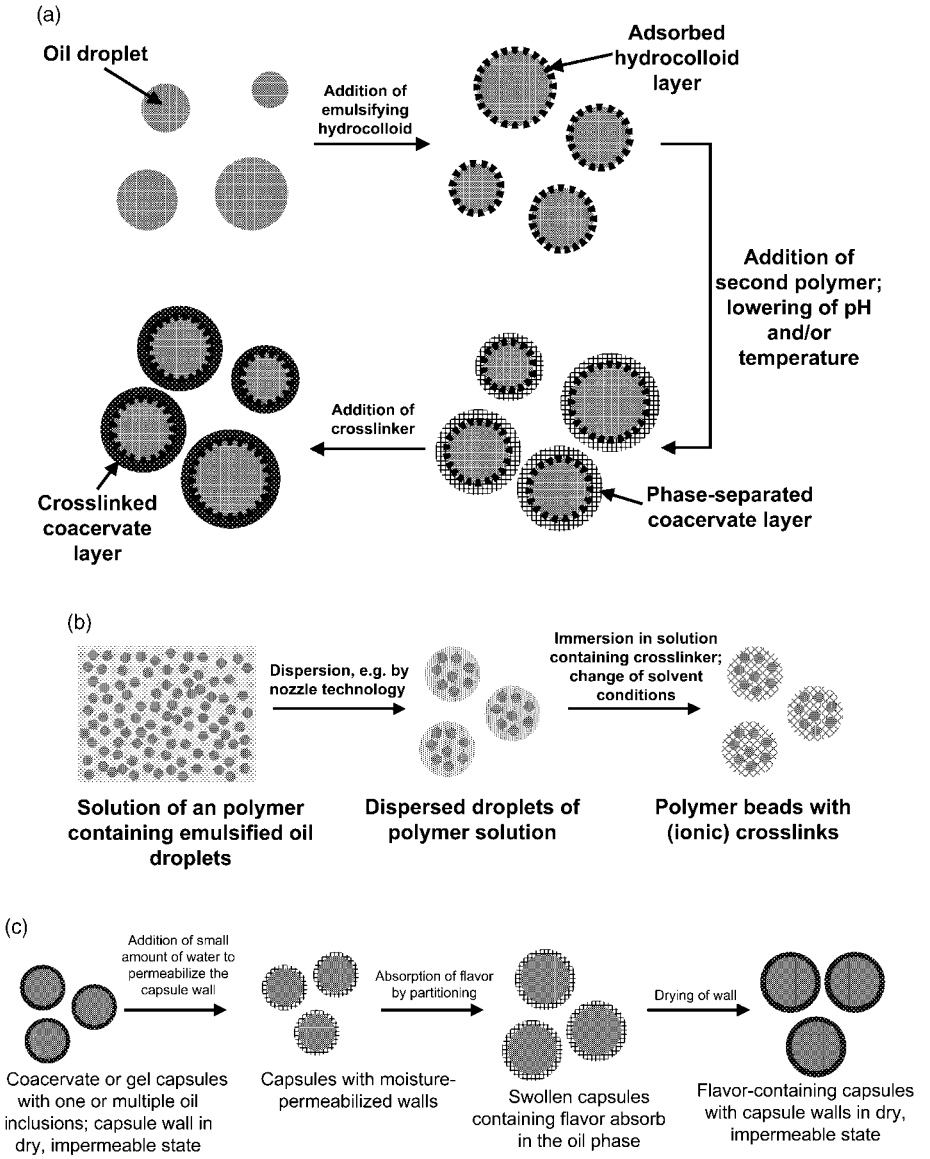

Fig. 10. Flavor encapsulation in hydrocolloids. (**a**) Coacervate formation; (**b**) formation of polysaccharide beads by dripping and ionic cross-linking. Hydrocolloid-based delivery systems are used in either slurry form or in dry form. In case the final product is a slurry, the flavor is usually directly encapsulated in the hydrocolloid. When the final product is a dry powder, the flavor is encapsulated by absorption after preparation of the hydrocolloid beads as illustrated in (**c**) and described in the text.

anionic polysaccharides (104). By lowering the temperature, the pH, or both, the second polymer is made to precipitate on the hydrocolloid adsorbed on the oil droplets forming a coacervate complex fully covering the oil droplets.

The capsules are then normally cross-linked to enhance their mechanical strength and to preserve their integrity when the solution conditions change.

In the formation of crosslinks, often functional groups of the protein are used which may be cross-linked either chemically [eg, by formaldehyde (98) or glutaraldehyde (101)] or enzymatically (by transglutaminase (105,106)). After crosslinking, the capsules are collected by centrifugation or filtration and may be kept either as a concentrated slurry or they may be dried to obtain a powder. As the capsules tend to remain slightly sticky in the dry state, an anticaking agent must be added to obtain a free flowing powder.

The size of coacervates is dependent on a number of process variables and may extend from a few micrometers in diameter to several hundreds of micrometers. For flavor encapsulation, usually the slightly larger coacervates are preferred as they have a higher maximum flavor load (because of the higher oil content) and because the flavor release from the larger capsules is generally somewhat slower. Although the inner oil droplet in the coacervate capsules is often close to spherical, the coacervate capsules usually are not, as the agitation that is continuously applied during the process leads to a preferential adsorption of the coacervating polymers on two opposite sides of the oil droplet leading to somewhat elliptical capsules. For flavor release, the thinnest part of the capsule wall, which is usually between 5 and 25 μm thick, are determinant as it limits the mechanical strength of the capsules (in case of flavor release by capsule rupture). It also determines diffusional release when the capsules stay intact during use (107).

Various polymers may be used for complex coacervation. Often-used anionic polymers are gum acacia, pectin, carboxymethyl cellulose and alginate but also other anionic polymers like xanthan and gellan can, in principle, be used. The most widely used cationic polymer is gelatin, but other proteins like zein, albumin, casein and cationic polysaccharides like chitosan can be used. Extensive lists of suitable polymer combinations are given in (102,108).

Gel encapsulation is a process that is considerably simpler than encapsulation by complex coacervation. In gelation, the gelating polymer generates a permanent three-dimensional network in solution by the formation of physical bonds (hydrogen bonds, ionic bonds) between polymer segments, often but not always involving a conformational change of the polymer in solution. Gelation is distinct from simple coacervation in that the gel often does not phase separate from the solution.

In gel encapsulation of flavors or flavor oils, one generally proceeds as follows (see Fig. 10**b**). As a first step, the flavor oil or solvent is dispersed in an aqueous medium using an emulsifier. Next, the gelating polymer is added but the solution is kept under conditions where the polymer does not gel. As gelating polymer, gelatin is an obvious choice, but gel-forming polysaccharides like alginate, gellan, and pectin are also be used. Gelation is induced by changing the solvent conditions (lowering the temperature in the case of gelatin; addition of a divalent cation like calcium in the case of alginate, gellan and pectin). During the gelation, the droplets of flavor oil are entrapped in the polymer gel and are effectively encapsulated.

An essential distinction between encapsulation by gelation and by coacervation is that in the latter case, individual capsules each containing one oil droplet are formed because of the phase separation of the polymers and their affinity for the hydrophobic oil surface. In case of gelation, individual capsules containing a

single oil droplet are not formed as the gelating polymer tends to occupy the whole solution volume or at least a large part of it, and often also lacks significant hydrophobicity. One option to obtain small particles is to cut the gel directly after formation or to grind the gel after drying (109), but more often nozzle techniques are used to obtain spherical particles (110,111). Spherical capsules of polysaccharides that can be ionically cross-linked may be obtained by dripping a solution of the polysaccharide into a hardening bath containing calcium ions (Fig. 10**b**) (112). Nozzle techniques were also developed to form spherical core-shell capsules with gelatin via coextrusion (so-called gelatin capsules). With all nozzle techniques, one is severely restricted with respect to the smallest particle size, which can be obtained. When dispersing a solution of ionically cross-linked polysaccharides using a dripping technique, the smallest attainable particle size is $\sim$50 μm, with the largest sizes up to a few millimeters. Coextrusion techniques for the preparation of core-shell gelatin capsules usually lead to considerably larger particle sizes, with the smallest particles being $\sim$1 mm in diameter and the largest in the order of a few centimeters. It is clear that these large particle sizes strongly limit the range of application of such capsules as they are very clearly perceived in most food matrices because of their texture and because of the very local and heterogeneous flavor release.

Some specific difficulties are encountered with both coacervation encapsulation and gel encapsulation of flavors. As the capsules are prepared from a dilute aqueous solution, they contain very significant amounts of water directly after production. When the final product is an aqueous slurry of capsules, this strongly limits the shelf life of the encapsulated flavor. In addition, when dry capsules are desired, flavor losses during drying are usually excessive, except for the least volatile and most hydrophobic flavors because of the generally thin polymer shells and the high permeability of the polymer shell especially at high water content. A convenient way to avoid such flavor losses is to first prepare the dry capsules with only an encapsulated flavor solvent (vegetable oils, MCT oil), and then load the capsules with the flavor by partitioning between an hydrophilic polymer phase and the hydrophobic solvent phase (112). Because of the higher molecular weight and high hydrophobicity, solvent molecules will not have a strong tendency to diffuse out of the capsules. The capsules can be loaded with the flavor by permeabilizing the capsule wall using trace amounts of water and letting the flavor partition into the encapsulated oil phase (Fig. 10**c**). The capsules can be sealed after loading by redrying the capsule wall (Fig. 10**c**). Because of the low amount of water employed, loading of the flavor into the capsules is rather efficient even for flavor compounds, which are only moderately hydrophobic.

3.3. Extrusion Encapsulation. One of the most suitable and flexible ways to prepare polymeric matrices for controlled release of active ingredients, including flavors, is extrusion. For controlled release applications in the food domain, the polymers that can be used are almost all largely hydrophilic. To avoid premature dissolution of the polymer matrix in the final application, one is forced to use high molecular weight polymers. These high molecular weight materials cannot easily be processed by other techniques, eg, spray drying, because the viscosity of the melt is too high. In addition, in order to reduce the rate of water ingression into the capsules and thereby slow down the release of

the flavor, the matrix should be as dense as possible and this is also most easily realized by extrusion technology.

Extrusion encapsulation to prepare controlled release systems is in many respects very similar to glass encapsulation by twin-screw extrusion. A general outline of a typical extrusion process is shown in Figure 6**b**. However, because of the higher molecular weight of the encapsulation matrix, either temperature or plasticizer content or both are generally higher than with extrusion of low molecular weight carbohydrates. Because of these factors, significant degradation of the encapsulated flavor is often induced, either during extrusion (if the processing temperatures are too high) or during postextrusion treatments like drying when high levels of water were added prior or during the process. Plasticizers other than water, eg glycerol, are also commonly used (33,113–115). As they are much less volatile than water, they are retained in the matrix. This may result in a final product that is in the rubbery state at ambient temperatures and therefore exhibits reduced barrier properties.

One of the most popular food polymers used for preparation of controlled systems by extrusion is starch (33,113–116). Starches are available with highly diverse molecular weights, compositions and structures. A number of starches may be processed in such a way that a thermoplastic, essentially water insoluble matrix is obtained. This thermoplastic matrix retains the capacity to slowly swell in moist environments and thereby triggers the release of the encapsulated flavor. Also other hydrocolloids like agar (54) and proteins like whey (55) can be used to obtain matrices exhibiting controlled release properties.

In order to modify the release behavior, either low molecular weight compounds can be added (54) that results in enhanced release rates, or water absorbing compounds (114), which results in a slower release. Also, the release rates are reduced by adding hydrophobic materials to the extrusion matrix or by coating the final product (114).

As with glass-encapsulation by extrusion, a major problem is the amount of surface oil liberated upon breaking or grinding of the extruded capsules. This problem can be largely overcome by reducing the size of the flavor inclusions in the matrix, or by using a matrix material in which the flavor completely dissolves. Current ways of reducing the size of the flavor inclusions are either by adding an emulsifier to the matrix premix (113), or by injecting the flavor in a pre-emulsified form into the extruder barrel (33).

There are numerous options to treat the extruded materials after extrusion. Because of the high melt viscosity, it is often not possible to extrude the mass trough a die plate with openings that are sufficiently small to obtain the desired particle diameter (typically $\sim$1–2 mm), as with glass encapsulation using low molecular weight matrices. Therefore, other methods common to extrusion technology are employed like cutting using a rotating knife (33,114), particle shaping using indented corotating drums and quenching and grinding or impact breaking.

3.4. Spray Chilling. In spray chilling, the carrier material is heated to above the point of fusion, mixed with the active ingredient, and atomized into a cooled chamber (117,118). The layout of the process (Fig. 8**b**) is very similar to spray drying, but in spray chilling no solvent needs to be evaporated. Instead, a solid matrix is obtained by rapidly cooling the matrix with the dispersed active

ingredient to below its melting point. As encapsulation matrix, usually lipids are used. The technique is variously known as spray chilling if the melting point of the encapsulation matrix is low (~30–45 °C) and as spray cooling if a high melting point matrix is selected (>45°C). Suitable encapsulation matrices are fats and waxes like hardened vegetable oils, stearine, hard mono and diglycerides (119). An important factor to control during spray chilling is the crystallization of the fat, as fat polymorphism significantly influences the properties of the matrix (eg, melting point and barrier properties (117)).

Spray chilling finds limited application in the flavor field for both hydrophobic and hydrophilic flavors. In the case of hydrophobic flavors, the flavor compounds will essentially dissolve in the fluid fat matrix, and will influence the state of the matrix after cooling (120). Hydrophilic flavors compounds do not mix well with the fat matrix and are supposed to form liquid flavor inclusions in the solidified fat matrix. The technique finds a more widespread application for the encapsulation of spices, but this field falls outside the scope of this article.

The mechanism of flavor release from spray-chilled beads is in principle by melting of the encapsulation material and therefore the principal application of spray-chilled flavors is in products that undergo a heat treatment. Flavor molecules are small, however, and diffusional release may already take place at temperatures significantly below the melting point of the matrix. The protective effect of the fat matrix is generally rather limited, and, in particular oxidation reactions still proceed at appreciable rates in fat matrices (121).

3.5. Encapsulation in Complex Fluids. Under the heading "complex fluids", we denote here all materials and structures that combine hydrophobic and hydrophilic properties in one structure and that form, at ambient temperatures, fluid, fluctuating systems. This finding implies that the intermolecular interactions holding the structure together are of the same order of magnitude as thermal energy. The classical example of a complex fluid in food technology is an water-in-oil (W/O) or an oil-in-water (O/W) emulsion (122). In the field of flavor encapsulation O/W emulsions are traditionally used to aid in the dispersion of water-insoluble flavor compounds in aqueous systems like beverages (123). In encapsulation, emulsions are widely used to disperse flavors and flavor solvents in the encapsulation matrix (see the discussion on glass encapsulation systems and on coacervation and gel encapsulation). Emulsions, however, also influence the release of flavors from a food matrix (124–126) and thereby in part determine the flavor perception. Although these effects are relatively limited for most flavor compounds, the retardation can be substantial, in particular for very hydrophobic compounds. Emulsions may thus be seen as examples of controlled release systems for flavors.

In recent years, the interest in various other complex fluids, like microemulsions (127), micelles (128), liposomes (129–131) and liquid-crystal phases (132,133) as devices to modify the release of aroma compounds from food matrices has increased. The general idea is to use the locally varying hydrophobicity and hydrophilicity with the usually tortuous and/or layered structure of such complex fluids to first either absorb hydrophobic flavors by partitioning in the hydrophobic phase (which can be an oil phase or the surfactant interface) or to entrap hydrophilic flavors in a surfactant-covered shell, and then, in the application, have a slow release of the flavor compounds.

Although they have interesting capabilities to subtly influence flavor release from food matrices, complex fluids do not yet find widespread use in flavor delivery applications, with the exception of classical W/O and, less frequently, O/W emulsions. This is due to a number of causes. In the first place, because of the "soft" nature of complex fluids, their structure is often difficult to preserve during food processing, not only because of mechanical stress but also because such systems are very sensitive to changes in environmental conditions and may undergo sudden phase transitions disrupting their structure. Also, because of the (very) small size of the individual structures and the strong perturbation by thermal fluctuations, the release of the flavors from the delivery system will be very fast, unless the flavor compounds have a very high affinity for the complex fluid or the structure of the device is very tortuous. In effect, the release rates of individual compounds from complex fluids in many cases do not differ much from lipid-containing food products like milk. An additional limitation in applying complex fluids for flavor delivery is that such systems are difficult to prepare using only food-grade materials. For example, for microemulsions, usually considerable amounts of nonfood-grade cosurfactants are needed (134). The last factor hampering large-scale utilization of complex fluids as delivery devices for flavors is the cost of application, which is often high as the raw materials are usually expensive and the flavor load is generally low.

3.6. Inclusion Complexation. Inclusion complexation, also known as molecular encapsulation, primarily uses cyclodextrins to complex and entrap molecules. Other materials that form (inclusion) complexes with flavors and which are of potential interest for flavor delivery are starch (135,136) and various proteins like albumin (137). However, for reasons of brevity, we restrict ourselves here to a discussion of inclusion complexation using cyclodextrins.

Cyclodextrins are formed by enzymatic degradation of cornstarch with alpha amylase, followed by treatment with the enzyme cyclodextrin transglycosylase (138). The products of reactions are α-, β-, and γ-cyclodextrins containing 6,7, and 8 glucose units, respectively, linked by α-(1→4) bonds. The diameter of the hollow cavity of a cyclodextrin is 0.5–0.8 nm. The β-form is the most extensively used cyclodextrin and can complex a wide range of flavor molecules, usually in a 1:1 stoichiometry. The functional properties of cyclodextrins are conferred by the difference in the hydrophobicity between the center and outside of the molecule (139). The degree of complexation between cyclodextrin and flavor compounds is dependent on a number of parameters, like the physico-chemical nature of the flavor compound, the shape of the flavor compound (linear molecules usually bind much stronger than branched ones), the presence of other flavor compounds (competitive binding) and the solution conditions (primarily temperature and pH) (140). In the center of the cyclodextrin, water molecules are replaced by less polar molecules.

Encapsulation of flavor compounds in cyclodextrins is carried out by dissolving the cyclodextrin in water and adding the flavor under vigorous stirring (139). Often, temperatures of ∼60–80°C are used to improve the aquous solubility of cyclodextrin and to accelerate complex formation. On an industrial scale, the amount of water is usually minimized and complex formation is carried out using a cyclodextrin dispersion. The complex is recovered and dried by conven-

tional means. To improve protection of the flavor a second encapsulation step (eg, spray drying or extrusion) can be applied to prolong the shelf life in a dry state (141).

The principal functionalities of cyclodextrins in flavor encapsulation are to protect the flavor from volatilization and chemical reaction (142), and to modify the release of the flavor in the food product (139). The release of the flavor is modified because the complex of cyclodextrin and flavor molecule is not volatile and flavor is only released when the complexation equilibrium shifts towards the dissociated state.

4. Application of Flavor Delivery Systems and Outlook

The flavor and fragrance industry has annual U.S. sales of over U.S.$ 10 billion (worldwide U.S.$ 14 billion) and is growing at an appreciable rate (143). It is estimated that the field is almost evenly split between flavors and fragrances. Although there are many players in the field, the flavor and fragrance industry is dominated by a limited number of large companies (144). Flavors are used in highly diverse fields but the principal applications are in beverages, confectionery, dairy and culinary products (Table 3). Precise information on the turnover of encapsulated flavors is not available in the public domain, but estimates are that ~20–25% of all flavors are sold in an encapsulated form, of which 80–90% are encapsulated by spray-drying. The flavor field is currently exceptionally active in both industrial and academic research, as is witnessed for instance by the number of annual citations recorded in *Chemical Abstracts* (Fig. 11**b**). Figure 11**a** shows that, although it is only a fraction of the size of the whole flavor field, flavor encapsulation activities are also rapidly increasing.

Given that major applications for flavors, (instant) beverages and culinary products, are generally dry, powdered products in the form in which they are sold to the consumers, or during a certain stage of production or storage, it is clear that glass encapsulation systems still play a dominant role in the whole of the flavor encapsulation field. This is particularly the case for beverage applications, as citrus aromas need to be glass encapsulated to ensure a sufficiently long shelf life. Apart from spray drying, melt extrusion finds a wide application, mainly again for citrus flavors in beverage and pharmaceutical applications, because of the extended shelf life offered by this technology. However, extruded flavors are available covering the full range of flavors, eg, savory top notes.

Table 3. **Main Application Areas of Flavors**[a, b]

Product category	Flavor usage of total (%)
beverages	31.5
confectionary	20.0
dairy, fats, oils	15.0
culinary products	14.5
oral hygiene	8.0

[a] Industry size is in excess of $10 billion.
[b] Chemical Manufacturing Reporter, 2001.

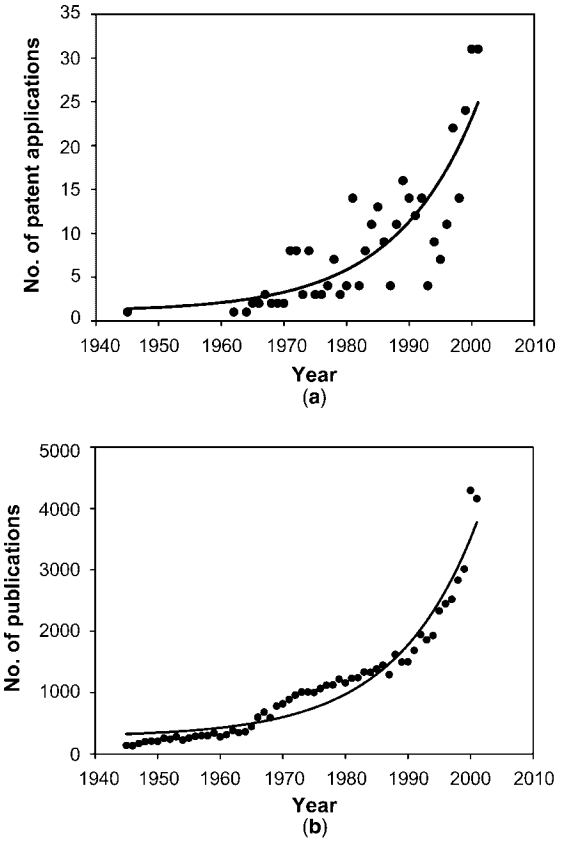

Fig. 11. Activities in the flavor encapsulation field and in the flavor field as witnessed by the number of publications per year. (**a**) Number of patent filings under "flavor and encapsulation" (**b**) Total number of publications under "flavor". Source: *Chemical Abstracts*.

Given the tremendous commercial success of glass encapsulated flavors and the very high protective properties that are currently attainable using modern technology (twin-screw extrusion, combined spray-drying and agglomeration towers), and that are combined with superior powder properties like good flowability, physical stability and narrow particle size distribution, glass encapsulation will probably dominate the industry for a long time to come. This in particular as some new glass-encapsulation technologies, like fluidized-bed encapsulation, are experiencing a rapid growth in niche applications where some additional benefits (particle size, shape, color) related to these technologies are paying off.

Controlled release systems for flavors still occupy a rather small part of the total field for flavor encapsulates, which is partially because such devices have not been on the market place for very long. In addition, although prototypes are offered to customers by the flavor industry on a large scale, few controlled release systems are actually commercially available at an acceptable price and

in sufficiently large quantities to have a serious impact on the market. Currently, the main controlled release technologies on the market are coacervate capsules and spray chilling. Spray chilling is essentially a low-cost operation by which large quantities of flavors can be easily encapsulated. Coacervation encapsulation, conversely, is a complex technology, but because of simplified procedures like the loading of flavors into empty capsules containing vegetable oil, costs can be kept within acceptable limits. A third controlled release technology which finds commercial application is fluidized-bed encapsulation and coating technology. The principal areas of application of controlled release flavors is in frozen and chilled foods, pasta, culinary products like instant soups and sauces and chewing gum. Chewing gum is in some senses an exception in this list as the principal objectives in controlled release in chewing gum applications are to speed up flavor release and to avoid irreversible binding of the flavor to the gum base, so glass-encapsulation systems can be used.

As emphasized earlier, controlled release systems need to be carefully tuned for both the flavor they are supposed to deliver and for the food matrix in which they are applied. This necessarily means that: (*1*) a specific controlled release system is not as widely useable as any of the glass encapsulation systems, limiting the commercial prospects, and (*2*) any effort to tune the delivery system is bound to be costly, because of the extensive testing and evaluations that are needed even if process modifications to the actual encapsulation process are not required. Thus, for controlled delivery systems, R&D expenditure is not only associated with the development of the actual delivery system, but continues throughout the life cycle of the system as for many of the new applications, elaborate performance assessment trials need to be carried out. A comparison of controlled release technology for flavors with those in other domains is also illustrative for the specific issues encountered in the flavor field (Table 4).

We still expect, however, that demand for controlled release systems will rapidly grow in the future, as in the food industry, the trend is toward high quality foods that combine excellent flavor and texture with an image of freshness and healthiness. Also, consumers increasingly demand a flavor impact in processed foods, which is as close as possible to traditionally prepared foods but that can be very rapidly and easily prepared using simplified cooking procedures. This means that food development efforts need to be strongly focused on innovative ways to introduce flavor compounds in a wide variety of food matrices, to retain them in these products and to release them at the required moment. This task is truly challenging as many of the targeted food products are moist, which means that it is very difficult to control flavor migration, even before consumption of the food product. In addition, many of the most interesting flavor impact compounds are chemically very unstable, particularly in the complex chemical environment of a moist food matrix.

Although much of the needed science and technology still needs to be explored, in our opinion a structured approach to successful application of controlled delivery systems for flavors should encompass the following elements:

1. Proper knowledge of the physico-chemical properties of the individual compounds making up the flavor composition. This will enable a rough

Table 4. **Key Aspects of Controlled Release of Flavors and Comparison with Other Controlled-Release Fields**

Characteristic	Flavors	Other food ingredients / additives	Drugs	Agrochemicals
active ingredients	large number of compounds	single compound	single compound	single compound
properties	low molecular weight, volatile	diverse, nonvolatile	often hydrophobic, nonvolatile	diverse
storage conditions	determined by foodstuff	determined by foodstuff	determined by active ingredient	determined by active ingredient or by agricultural product
release	in food matrix, occasionally in mouth	in food matrix, in gastrointestinal tract	in gastrointestinal tract, through skin, intraveneous	in environment
protection	against oxygen, evaporation, occasionally against interactions with food matrix	against oxygen, reactions in foodstuff	occasionally against oxygen	against environmental impact (oxygen, moisture, ultravoilet (uv) light)
other functionalities of capsules	conversion of a liquid into a solid	taste masking	taste masking; minimization of exposure prior to application	minimization of exposure prior to and during application
primary constraint in development	food-grade status, price	food-grade status, price	safety	price

prediction of the relative mobility of the flavor compounds and of their affinity for the various phases making up both the food matrix and the delivery device.

2. An understanding of the potential chemical instabilities of the most important impact compounds in the flavor composition, in particular in relation to the composition of the food matrix. This anticipates the hurdles which one is likely to encounter when applying the flavor in the food product.
3. Quantitative knowledge of the release properties of the various available controlled release devices under varying environmental conditions (temperature, water activity) (Fig. 12). In addition, the barrier properties with respect to the uptake of oxygen should be known under these conditions if the encapsulated flavor is sensitive to oxygen.
4. Quantitative relations between the structure, composition and phase transitions of the complex food matrix, under the conditions encountered during production, storage and consumption.

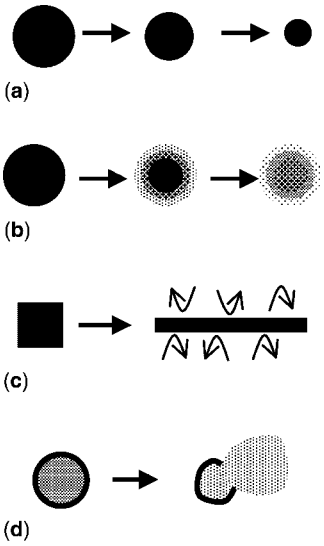

Fig. 12. Principal mechanisms of flavor release from delivery systems. (**a**) Erosion. The product gradually dissolves, the rate of flavor release is proportional to rate of matrix dissolution. (**b**) Diffusion. The flavor diffuses out of delivery system or food product in rubbery or gel-like state; the rate of release of the individual flavor compounds is strongly dependent on their physico-chemical characteristics. (**c**) Extraction. Mechanical forces during chewing or processing renew and/or enlarge surface area of food product in direct contact with saliva or the (fluid) food matrix; the rate of flavor release is controlled by the transfer from the capsule to the food matrix. (**d**) Burst. A reservoir system ruptures under influence of mechanical or osmotic forces.

5. Flexible encapsulation technology enabling the rapid and cost-efficient encapsulation of a variety of flavors. The release properties of the delivery device should preferably be tunable, in order to widen the range of potential applications and so to increase the economies of scale. Moreover, the eventual protective effects of the delivery device should be known.
6. A clear and unambiguous methodology to demonstrate, by chemical analysis and by sensory evaluations, the performance of the delivery device in the food application. Controlled release systems are usually expensive and clear benefits need to be demonstrated.

Although desirable, it will rarely happen that in practice, all these requirements are fulfilled when looking into a potential new application for a controlled delivery device. In many actual situations, systematic testing of flavor-delivery device combinations combined with elementary understanding of chemical and physical processes taking place in the food matrix will lead to successful or at least acceptable solutions. In fact, the chemical and physical processes occurring in a real food product are so complex and, in addition, so interrelated, that the necessary scientific background is not yet completely developed, as is shown by the recent progress reported in two related fields: flavor release (145) and materials science of the amorphous state (146).

5. Concluding Remarks

The flavor industry is one of the oldest and most established fields where encapsulation technology is successfully applied on a commercial scale. In the first decades of development of the field, which started about one-half a century ago, the purpose of flavor encapsulation was essentially limited to protecting the flavor in the encapsulation system during storage in low-moisture conditions. In particular, a traditional key objective of flavor encapsulation has been to protect citrus flavors and essential oils from oxidation by preventing the uptake of environmental oxygen. Using dense matrices of amorphous, glassy carbohydrates, these objectives have been admirably fulfilled as the shelf life of commercial products is currently on average 2 years, with melt-extrusion products having a shelf life of up to 4 years.

In recent years, with the advent of low fat food products, the introduction of novel food preparation processes like microwaving, increasing consumer demand for a better flavor impact and quality, and the trend toward even easier food preparation procedures, emphasis in flavor encapsulation has shifted towards protecting and releasing complex and often sensitive flavors in complex and often moist food matrices. This has inspired a whole range of developments in controlled release systems for flavors. Successful commercial applications of such controlled release systems include chewing gum, pasta, frozen foods, and instant products. However, some serious limitations are currently experienced in the application of controlled release systems for flavors, which impede a truly widespread adoption in the food industry. One major obstacle is that, in order to obtain the desired beneficial effects of the controlled release system, it should be carefully tuned to both the food matrix in which it is applied and the flavor that is to be delivered. This warrants a concerted approach including encapsulation technology, flavor physico-chemistry and chemistry, food materials science and focused product development efforts, which is nowadays not yet common practice in the food industry.

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