Open access • Journal Article • DOI:10.1080/15583724.2015.1091776

Melt Extrusion Encapsulation of Flavors: A Review — Source link

Natalia Castro, Vanessa Durrieu, Christine Raynaud, Antoine Rouilly ...+2 more authors

Institutions: University of Toulouse

Published on: 08 Jan 2016 - Polymer Reviews (Taylor & Francis)

Topics: Spray drying

DOI: 10.1080/15583724.2015.1091776

Melt Extrusion Encapsulation of Flavors: A Review

NATALIA CASTRO[1,2], VANESSA DURRIEU[1,2], CHRISTINE RAYNAUD[1,2], ANTOINE ROUILLY[1,2], LUC RIGAL[1,2] AND CHRISTIAN QUELLET[3]

[1]Université de Toulouse, INP-ENSIACET, LCA (Laboratoire de Chimie Agro-industrielle), Toulouse, France
[2]INRA, UMR-1010-CAI, Toulouse, France
[3]Givaudan Schweiz AG, Dubendorf, Switzerland

Encapsulation of flavor and aroma compounds has been largely explored in order to meet appraisal demands from consumers by improving the impact of flavor during the consumption of food products. Even though several techniques have been used for encapsulating volatile compounds, i.e., spray drying, fluidized bed coating, coacervation, and melt extrusion, those most frequently used in the food industry are spray drying and melt extrusion. In this article, the different techniques of encapsulation of flavors and fragrances in polymer-based matrices by extrusion are reviewed and partly re-defined, emphasizing the differences between the various techniques reported so far and the role of matrix types, additives, and operative conditions. Also, the role of water as a key parameter for controlled release and shelf stability of the delivery system will be discussed.

Keywords microencapsulation, melt extrusion, ram extrusion, melt injection, fragrances, flavors

1. Introduction

Flavors, fragrances, and bioactive food compounds (employed in the nutraceutical and the pharmaceutical domains) are often supplied in powder or granulated form for better handling and more accurate dosing in final product. Over the last decades, encapsulation technologies have added new functionalities to these forms, such as protection against evaporation, oxidation, moisture, and other aggressive environmental agents to provide extended shelf life, or controlled release under pre-determined conditions. [1–6]

The most common encapsulation technologies used in the flavor industry comprise of spray drying, spray coating, and extrusion,[6–12] and earlier variants of extrusion also known as melt injection, have been known since the late 1950s. A common feature to all these technologies is the dispersion of the active substance (or encapsulated material) in a matrix that is impervious to both active substance and external deleterious agents.

Extrusion cooking is widely used in the food industry since the seventies. This highly versatile processing technology allows the combination of many unit operations (i.e.,

Address correspondence to Vanessa Durrieu, Université de Toulouse, INP-ENSIACET, LCA (Laboratoire de Chimie Agro-industrielle), 4 allée Emile Monso, F-31030 Toulouse, France. E-mail: vanessa.durrieu@ensiacet.fr

mixing, grinding, cooking, extraction, etc.), among which encapsulation has recently been investigated. As encapsulation technique, melt extrusion is promising from the economic and environmental points of view, as it is a one pot process (formation of the wall material, dispersion of the active principle, and forming of the encapsulated material), without any use of organic solvent and a reduced energy and water consumption (especially when compared to spray-drying).

This review focuses on the state of the art on melt extrusion encapsulation of flavors and fragrances. This technology was first reported in industrial patents, and is now becoming an academic research topic.

Section 2 covers the basics of flavor encapsulation, emphasizing the influence of matrix materials, compatibilizers, and morphology on encapsulation efficiency and release behavior. Section 3 focuses on the matrix itself, emphasizing the influence of humidity on its encapsulating properties. Usually, this matrix is built up of carbohydrates and is in the glassy state, although other matrices have also been used. The way this matrix is formulated and processed and how the core material is incorporated into this matrix during extrusion are key parameters that are discussed in detail.

Finally, Section 4 deals with extrusion itself, emphasizing the importance of process parameters on the overall quality of the product.

2. Microencapsulation of Fragrances and Odor Active Compounds in Solid Forms

Flavors and fragrances are highly complex chemical compositions of sensitive volatile organic compounds with different physicochemical properties (i.e., volatility, water solubility) and an average molecular weight from about 50 to 300 Da. The capture, the retention, and the rendition of such complex compositions in their integrity, combining with low losses during encapsulation, are the key objectives of encapsulation.[5,6,13–15] In the last two decades, the volume of encapsulated oils has grown significantly. In 2001 it was estimated that 20% to 25% of all flavors commercialized in the world were in an encapsulated form, and between 10% and 20% of these could not be encapsulated by spray-drying.[16] In order to satisfy this important demand, melt extrusion appeared as a suitable and flexible technology to produce such encapsulates in large volumes. Furthermore, extrusion had a number of advantages over spray drying, such as lower energy consumption during operation and minimal emission of odor-contaminated exhaust air. Finally, the conditions of extrusion allow a better control of the state of the matrix, especially if carbohydrates glasses are considered.[17] Benczedi and Bouquerand[18] have demonstrated that lemon, lime, and tangerine flavors had better stability (no oxidation was observed) and longer shelf life when encapsulated by melt extrusion compared to spray-drying (4 years at 20°C compared to 2 years at 20°C). The drawbacks of extrusion are the limited loading, usually not exceeding 15% to 20% and the coalescence of the droplets of active compounds.[19,20]

The two first studies of flavor encapsulation by "extrusion" used a carbohydrate matrix comprising sucrose and corn syrup to entrap the essential oil.[21,22] Following these pioneering works, the development and research of new materials and procedures for the encapsulation of flavors increased significantly in the food industry. Encapsulation of aroma compounds in a carbohydrate polymer in a glassy state, also known as "glass encapsulation"[16] became very popular, and numerous patents were submitted by companies like Griffith Laboratories, Sunkist Growers, Nabisco Brands, and McCormick & Company.[23–27] All processes described herein involve the entrapment of the flavor in a

carbohydrate matrix (starch, modified starch, corn syrup, sucrose, gums, maltodextrins, etc.). Patents disclosing the use of biopolymers-based matrix by melt-extrusion instead of low molecular weight sugars, dextrins, and maltodextrins were mainly published in the 1990s (Fig. 1),[28–30] by industrial companies. Details about the encapsulation process and the key process parameters are usually scarce in such documents.

All of these methods are, however, based on the same process steps:

(i) incorporating a volatile compound (flavor, fragrance, or other sensitive molecules) in a thermoplastic matrix and
(ii) forcing this mass through an orifice or die to shape the encapsulated material.

The release mechanism involved in these technologies is essentially dissolution in water, which may be immediate or delayed in time. Temperature may also be used as a trigger, but more occasionally. Alternative mechanisms, such as diffusion or mechanical breakage of core-shell capsules[6] are not discussed in this review.

The efficiency and quality of the overall encapsulation process is the result of the combination of system morphology, i.e., the way the encapsulated material is dispersed in the matrix, and the physical state of this matrix.

Classically, the system is viewed as a dispersion of the oil phase in the form of small inclusions in the matrix. Different morphologies have been postulated for different release profiles (Fig. 2):

(i) coarse dispersion in the matrix;[23,30–33]
(ii) fine dispersion using emulsifying and/or compatibilizing agents; [34,35]
(iii) film coating of the core material;[36–43]
(iv) fine dispersion and external film coating;
(v) fine dispersion and coating of the core and the matrix.[32]

The most appropriate matrix physical state for encapsulation is the glassy state, where both free volume and molecular mobility are minimized.[30,44–47] Hence, the glass transition temperature of the matrix is a key parameter for encapsulation in solid matrices.

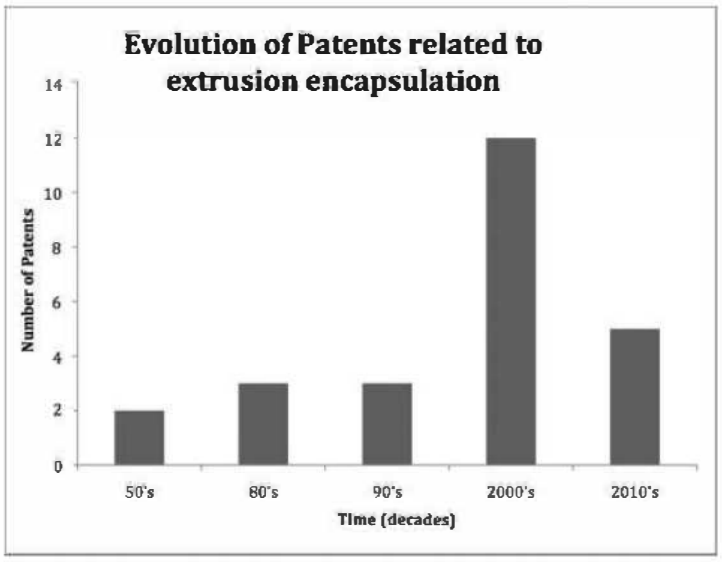

Figure 1. Trends in extrusion encapsulation technologies in the last decades.

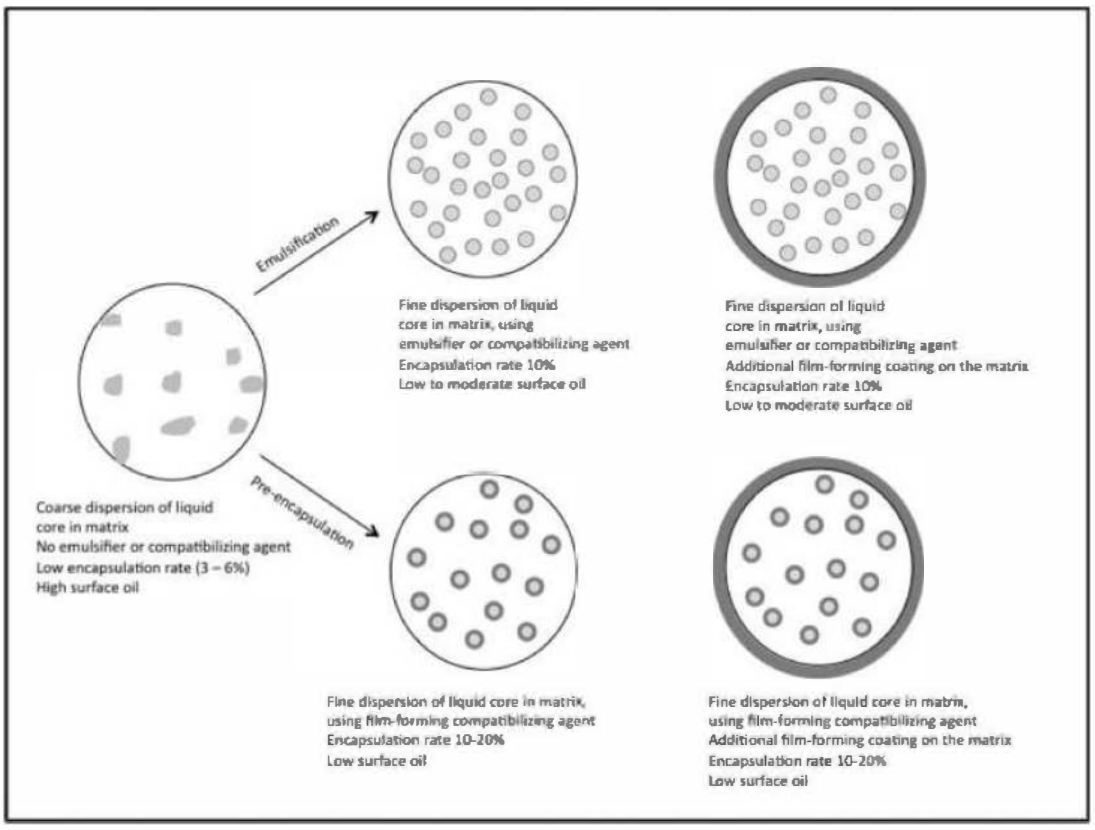

Figure 2. Schematic view of possible encapsulation morphologies obtained using extrusion microencapsulation.

This will be discussed more thoroughly in the next sections. The polarity of the matrix is another key factor that controls both encapsulation and retention of the volatiles. Hence, for hydrophobic ingredients, such as flavor and especially fragrances, the highest retention is obtained in hydrophilic matrices, which can be easily explained in terms of solubility. Besides, hydrophilic matrices have low permeability with respect to oxygen (Section 3.2). Hence, carbohydrates in the glassy state show better retention of volatile compounds and extended shelf life stability.[13,16,46,48–50] The encapsulation in glassy carbohydrates is also referred to glassy microencapsulation.

However, the situation is rendered more complex by the fact that individual molecules may interact with the matrix itself, which in turn affects the properties of this matrix and the release profile of the flavor. The chemical diversity of encapsulated ingredients is therefore another key feature, which must retain attention. The most recurrent flavors used in the food industry and reported in the literature are diacetyl, terpenes, such as d-limonene, terpene alcohols, such as geraniol, menthol, and thymol, terpene ketones, such as camphor and menthone, short chain esters, such as ethyl propionate and isoamyl butyrate, aldehydes, such as acetaldehyde and hexanal, lactones, such as heptalactone and nonalactone, sulfur-containing ingredients, such as 3-methylthiohexanol, thiolactones and the like, and nitrogene- and nitrogene-sulfur heterocycles, such as pyrazines and thiazoles. Flavor (and perfume) ingredients are, therefore, characterized for a broad range of physico-chemical properties, whereas the most relevant of these properties as far as encapsulation is concerned is the presence of chemical functions, molecular weight, and steric hindrance, vapor pressure, and relative solubility in both oil and matrix phase. All

of these parameters control the interactions between the ingredients and the matrix, their diffusion through this matrix, the encapsulation yield, the storage stability of the dry product, and the release profile.[7,10]

The interactions of flavor ingredients and the matrix and their effects on flavor encapsulation and release have been extensively investigated in the literature. In particular, the formation of flavor complex with starch has attracted much interest.[51–54] Most of these studies have, however, been performed in solution, i.e., under conditions where starch is fully plasticized and amylose has a sufficient conformational flexibility to accommodate guest molecules and form the inclusion complexes. It has been proven by DCS and X-ray diffraction measurements, that complexation proceeds through amylose helix formation to form reversible inclusion complexes. Such conditions are not met in extrusion, due to the low water content of the extrudate, unless higher processing temperatures are applied. The formation of flavor-cyclodextrin complex is also well documented.[7,38,42,55] In all cases, the inclusion complexation constant has been found to depend strongly on the molecular shape and polarity of the guest molecule. The encapsulation and release of flavors in and from low molecular weight carbohydrates and carbohydrate oligomers, such as corn syrup solids and maltodextrins, has been extensively reviewed in the case of spray drying Goubet et al.[7] as well as in the case extrusion-mediated glass encapsulation.[17,48,56] It appears from the above studies, that the entrapment of flavor ingredients at the molecular level in the matrix can occur, providing suitable interactions that can lead to flavor-carbohydrate complex with reduced diffusion. Such interactions have been investigated by inverse gas chromatography, providing a better understanding on how retention and release work in these systems. Owing to the complexity and diversity of these oils, the study and quantification of retention or release of volatile compounds remain difficult, and few standardized methods are known. In some studies, polymer-flavor complexes in solution have been analyzed in order to determine the type of interactions involved and how flavors are released.[7,57–59] Other studies focused their attention on determining the type of interactions existing between the solid matrix and two or three specific flavor compounds, thanks to inverse gas chromatography.[60–62] Hence contradictory results are frequent. For example, Gunning et al.[63] observed that the percentage of flavor release from a low water content sucrose/maltodextrin matrix into the headspace increased when temperature raised above 60°C, while the contrary was found in other maltodextrin matrix.[64] In the latter case, thermally enhanced retention was attributed to a change in the polarity of the matrix with increasing temperature.[64] As documented later in this review, such discrepancies are certainly linked to different level of moisture in the matrix.

Direct entrapment or solubilization of the flavor ingredients in the matrix has been considered as a convenient way to encapsulate volatile substances. The quality of such encapsulation process depends, however, on the flavor-matrix interactions mentioned above. For example, lactones are better retained in starch-based matrices, while alcohols are better encapsulated by carbohydrates, whereas flavors ingredients having similar chemical functions but different molecular weights or topologies may show different entrapment behavior.[7] This selectivity may lead to strong distortion of the flavor release profile. Furthermore, the flavor loading that can be reached by this method is limited to 3 to 6 (%w/w) of the extrudate. Above this limit, a flavor exudation occurs during the extrusion process, leading to the formation of separated liquid phase, which may flow out of the extrudate or disperse in the matrix in the form of irregularly shaped liquid inclusion (Fig. 2, case (i)). Such a coarse dispersion leads to the formation of large amounts of surface oil, which is deleterious to the quality of the product. The presence of surface oil is indeed highly undesirable, because

(i) surface oil is not encapsulated and therefore its release is not controlled, and
(ii) such oil is readily oxidized, which leads to loss of product organoleptic quality, and contributes to powder caking. High quality encapsulates must have low surface oil levels.

An intensive development work has been done in the last decades to increase the flavor load in encapsulates, while keeping the surface oil at the lowest possible level and extending the storage stability of the product. This is usually achieved by providing a fine dispersion of the encapsulated oil in the matrix by using suitable combinations of mixing powder and solubilizing or compatibilizing agents[18] (Section 3). The resulting product morphology after drying is that of a "dry emulsion" (Fig 2, case (ii)). Figure 3 shows such morphology in the case of a spray-dried powder with oil inclusions having a diameter of less than one micron. The matrix was obtained by spray drying a high internal phase fragrance emulsion comprising maltodextrins and modified starch. This method allows increasing the payload more than 40%.[8] Another way to reduce surface oil of the extrudate involves preparing an emulsion of the active compound, comprising a film-forming agent, and injecting this emulsion directly into the extruder (Fig. 2, case (iii)). This pretreatment effectively decreases flavor losses during the process and allows co-encapsulation of different flavors in the same encapsulate.[40]

The release of the encapsulated actives from systems based on carbohydrates is triggered by exposure to moisture. Critical water-induced plasticization of the matrix, which is marked by a decrease of the carbohydrate glass transition to sub-ambient temperatures, starts at 50% to 70% relative humidity.[56] Ultimately, the matrix dissolves and the full flavor is released. Figure 4 schematizes the expected influence of the product morphology on the release rate of the active compound over time if the encapsulate is exposed to moisture. *Note that, in the present case, increasing time (at constant moisture) is equivalent to increasing the moisture content or the water activity in the system.* This is, however, an idealized view, which

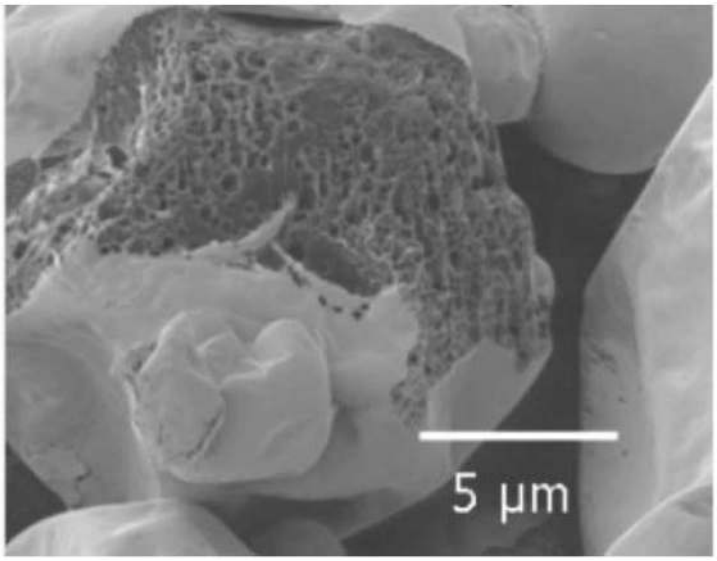

Figure 3. Spray dried particles with "dry emulsion" morphology. © Givaudan Schweiz AG. Reproduced by permission of Christian Quellet. Permission to reuse must be obtained from the rightsholder.

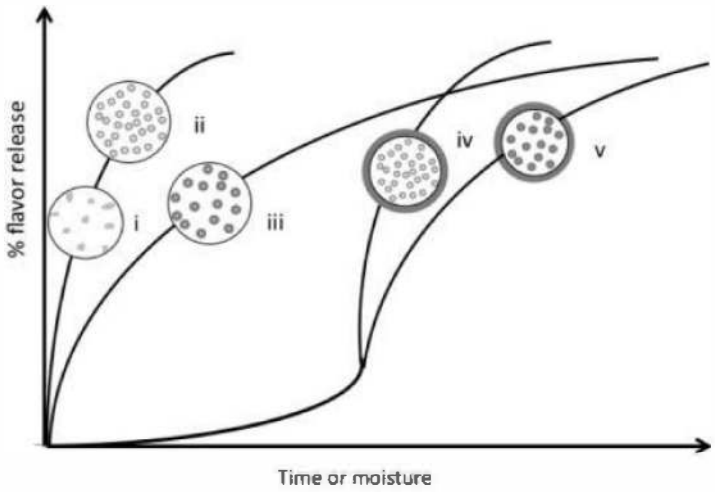

Figure 4. Scheme of release profile depending on the morphology of the delivery system obtained by extrusion.

is shown here for guiding the reader through this review. The fast and early release corresponds to encapsulation of the active compound without any pre-encapsulation or coating treatment prior to extrusion (curves (i) and (ii)). Release of these kinds of structure is more known as a burst-like release, all the compounds are liberated at the same time. Incorporating a film-forming agent at the oil/matrix interface increases the resistance to moisture and may result in a more gradual flavor release (curve (iii)). Finally, combining the above morphologies with an external coating leads to similar release profiles, but delayed in time (or occurring at a higher moisture level)(curves (iv) and (v)). For example, Menzi et al.[65] have proposed to apply a vegetable fat coating on granulated materials obtained by spray coating of a flavor/water emulsion on a sugar carrier material, which was shown to improve the storage stability of encapsulated flavors and to delay their release in chewing gums. Alternatively, Leusner et al.,[66] Bouquerand,[36] and Chang et al.[35] have employed Miglyol as an additive to their formulation, in order to provide extra protection to their active principle, as well as to reduce the release rate. Others techniques and other wall materials have also been explored in order to lower the production cost and to target other application areas.[28,67,68]

It must be stressed, however, that the loss of volatiles from encapsulates during handling and storage starts at water levels much below than the plasticization limit. This leakage involves at least three mechanisms:

(i) evaporation of the surface
(ii) diffusion of the subsurface flavor oil droplets to the surface of the matrix, and
(iii) exudation of the flavor compounds through the matrix fractures or cracking.[63]

Controlling the hygroscopicity and the physical integrity (absence of capillary cracks and other defects) of the matrix is therefore a crucial aspect of flavor and fragrance encapsulation. For example, high molecular weight carbohydrates offer longer shelf live and high stability to active compounds compared to short molecular weight sugars and maltodextrins.[14,69] On the other hand, starch, modified starches, proteins, or gums give delivery systems with thermoplastic behaviors,

which gradually swell in the presence of moist environments and slow down the release of the active principle.[16]

If the aim of the final product is to enhance the release rate, low molecular weight polymers such as maltodextrins having a high dextrose equivalent (DE) must be used. For example, Swisher[22] and Schultz and Calif[21] have used in their formulations low molecular weight carbohydrates (e.g., sucrose, corn syrup). The same effect can be obtained by using plasticizer, such as glycerin and other polyols (Section 3.4.4), which are less volatile than water, and therefore are better retained in the matrix.

The next section provides an overview of the carriers and additives used in extrusion encapsulation.

3. Matrix Materials

3.1. Introduction

Matrix materials used in extrusion encapsulation must combine good processability and good barrier properties. This is achieved by using certain biopolymers or mixtures of biopolymers and low molecular weight molecules, such as sugars and sugar alcohols (Table 1). The most frequently used matrix materials, or carriers, are carbohydrates. The choice of encapsulating materials is based on five criteria: natural origin, barrier properties with respect to gas and small volatile molecules, large scale, and low cost availability.[12,70,71] The advantage of using such biomaterials for microencapsulation is on one hand the simplicity of the release mechanism, mainly triggered by moisture or heat, and on the other hand, their biodegradability. Flavor encapsulation additionally requires food industry authorized materials. However, the major drawback of these natural carriers, when used without additives, is the low flavor load of about 5 to 6% (w/w).[72] The use of lipids and proteins has also been reported (Table 1).

Many researchers have focused their attention on two aspects of biomaterial-mediated encapsulation:

(i) the physicochemical properties of the matrix, such as molecular weight, viscosity, solubility, film forming properties, degree of polymerization, and chemical functional groups, which can significantly affect the retention and release of aroma compounds,[7] and
(ii) the physical state of the carrier, which, as mentioned above, is a key parameter to successful encapsulation.

Carbohydrate oligomers, starch and proteins, like most non cross-linked, thermoplastic polymers, can be found in two physical states: a viscoelastic or "plastic"-state, where the polymers are characterized by a high chain mobility, and where the active materials can be dispersed in the matrix; and a glassy, brittle state, where active materials have a very low mobility and are therefore entrapped in the carrier (or matrix).[7,12,29,69]

A major prerequisite for stable encapsulation of volatile materials is that the matrix is below its glass transition temperature T_g. Indeed, below T_g, diffusion processes slow down dramatically, due to the abrupt decrease of the mobility of the polymer chains and the concomitant decrease of the matrix free volume in the matrix.[56,63] However, it has been demonstrated that diffusion is more important in the vicinity of the polymer matrix glass transition temperature, than above this temperature, because the free volume below

Table 1
Review of all the different wall materials and additives used in extrusion microencapsulation (melt injection and melt extrusion) in chronological order.

Reference	Wall material
(Swisher, 1957)	Corn syrup
(Schultz and Calif, 1958)	Corn syrup, sucrose, dextrose, maltose, mannose, galactose
(Sair and Sair, 1980)	Casein, sodium hydroxide
(Miller and Mutka, 1987)	Carbohydrates, i.e starch, modified starch, sucrose, maltose, corn syrup, fructose, dextrose, glycerol, maltodextrins (DE2-DE20)
(Saleeb and Pickup, 1989)	Maltose monohydrate, maltodextrins, mannose,
(Carr et al., 1991)	Native corn starch
(Kollengode and Hanna, 1997a)	Corn starch+ β-cyclodextrins
(Kollengode and Hanna, 1997b)	Corn starch
(Black et al., 1998)	Whey protein, lipids, modified starch, maltodextrins, dextrose, sucrose, lactose,
(Hau et al., 1998)	Wheat starch
(Porzio and Popplewell, 1999)	Maltodextrins (DE5-DE15), corn syrup (DE24-DE42), starch, modified starch, gum, gelatine
(Saleeb and Arora, 1999)	Maltose, glucose, maltotriose, mannose, sucrose, dextrose, xylitol, arabinol, sorbitol, mannitol, corn syrup,
(Reifsteck and Jeon, 2000)	Corn syrup, flour, starch
(Ubbink et al., 2001)	Potato, corn starch, modified starch, proteins, glycerol

(*Continued on next page*)

Table 1

Review of all the different wall materials and additives used in extrusion microencapsulation (melt injection and melt extrusion) in chronological order. *(Continued)*

Reference	Wall material
(Benczedi and Bouquerand, 2001)	Sucrose, glucose, lactose, maltose, fructose, ribose, dextrose, sorbitol, mannitol, xylitol, lactitol, pentatol, arabinose, pentose, xylose, galactose, maize syrup, maltodextrins (DE8-DE10), gums
(Porzio and Popplewell, 2001)	Maltodextrins (DE10-DE15), corn syrup (DE24-DE42), gums, starch, modified starch, methoxypectin, ribose, glucose, fructose, galactose, xylose, sucrose, maltose, proteins (casein)
(Porzio and Zasypkin, 2010)	Modified starches, maltodextrins (DE10-DE20), sucrose, maltose, glucose, xylose, fructose, trehalose corn syrup (DE24-DE42), fatty acids, gums, proteins (casein)
(Bhandari et al., 2001)	Soy flour, corn flour, corn starch, β-cyclodextrins
(Benczedi and Bouquerand, 2001)	Sucrose, maltose, fructose, mannitol, glucose, ribose, dextrose, arabinose, sorbitol, xylose, galactose, starch, maltodextrins, gums, modified starch, proteins
(Lengerich, 2002)	Starch, modified corn starches, cyclodextrins, cellulose, polyvinyl alcohol, dextrins, corn syrup, gelatin, sorbitol, casein, carrageenan, alginates, pectins, xanthan, gum arabic, guar gum, fat, chitosan
(Benczedi and Bouquerand, 2003)	Sucrose, maltose, fructose, mannitol, glucose, ribose, dextrose, arabinose, sorbitol, xylose, galactose, starch, maltodextrins, gums, modified starch, protein
(Leusner et al., 2002)	Oligosaccharides (oligofructose), inulin, fructose, sucrose, dextrose, maltose, lactose, medium chain triglycerides
(Kohlus and Pacha, 2004)	

Table 1

Review of all the different wall materials and additives used in extrusion microencapsulation (melt injection and melt extrusion) in chronological order. *(Continued)*

Reference	Wall material
	Sucrose, fructose, maltose, ribose, mannitol, maltodextrins, Xylitol, polybutyl-methacrylate
(Yuliani et al., 2004)	Sucrose, maltose, glucose syrup, glycerine, glucose, β cyclodextrin
(Yuliani et al., 2006)	Corn starch, β cyclodextrin
(Gouin, 2004)	Maltodextrins, starches, fat
(Porzio and Zasypkin, 2010; Zasypkin and Porzio, 2004; Zasypkin, 2011; Zasypkin et al., 2013)	Modified starch, lactose, dextrose, maltodextrins
(Bohn et al., 2005)	Sucrose, maltodextrins
(Valentinotti et al., 2006)	Sucrose, maltose, glucose, lactose, levulose, ribose, dextrose, isomalt, sorbitol, mannitol, xylitol, lactitol, pentatol, arabinose, maltodextrins, gums, hydrogenated starch, cyclodextrins, cellulose
(Bouquerand, 2007)	Maltodextrins (DE8-DE10), lactose, dextrins, pre-gelatinized starch, medium chain triglycerides
(Chang et al., 2010)	Maltodextrins (DE8-DE10), medium chain triglycerides
(Lengerich et al., 2010)	Caseinates, wheat proteins isolates, pre-gelatinized starch, low molecular weight carbohydrates, durum flour
(Benczedi et al., 2011)	

(*Continued on next page*)

Table 1

Review of all the different wall materials and additives used in extrusion microencapsulation (melt injection and melt extrusion) in chronological order. *(Continued)*

Reference	Wall material
	Mono and di-saccharides, citric acid, hydrogenated corn syrup, polysaccharides, gums, maltodextrins, modified starch
(Gregson and Sillick, 2012a)	Erythritol mannitol, sorbitol, maltodextrins (DE10-DE20), gum acacia, alginates, pectins, proteins, hydrogenated starch hydrolysates
(Gregson and Sillick, 2012b)	Maltodextrins (DE10-DE20), modified starch, sucrose, maltose, trehalose, soy lecithin, antioxidants
(M. A. Emin and H. P. Schuchmann, 2013)	Native maize starch
(T. M. Goss Milani et al., 2014)	Soy protein isolate
(Chang et al., 2014)	Modified starch/matodextrin/lecithin
(Tackenberg et al., 2015)	Maltodextrins (DE-12 and DE-17)/sucrose

glass transition is higher, so diffusion of solutes is enhanced. A key feature of most biomaterials and especially of carbohydrates is the fact that the level of water included in the matrix controls T_g. The relationship between water activity and T_g in carbohydrate has been extensively discussed by Slade and Levine[73] and is still the most important factor influencing processability and volatile retention.[14] Water molecules inserted between the polymeric chains, opening the three-dimensional structure of the polymer and breaking interactions between chains. Low energy interactions between water molecules and polymeric chains are thus established, and so the polymeric structure becomes soft and flexible, i.e., the polymer goes from a brittle, glassy state to a plastic, rubbery state (Section 3.4.4). Product stability is governed by the amount of water, both added and already existing inside the system; water is the key factor controlling the stability of biopolymers.[74–77] Kollengode and Hanna[38,55] have demonstrated that a delivery system with low moisture content (9%) showed higher retention of volatiles like cinnamic aldehyde, eugenol, nonanoic acid, and 3-octanone, than delivery system with high moisture content (17%). Gunning et al.[63] have demonstrated in their studies that retention of volatiles is correlated to the glass transition temperature of the system. For instance, in a low water content matrix composed of maltodextrin and sucrose, the highest amounts of volatiles were released when the matrix was above its glass transition temperature. However, water may be a handicap because all the volatile compounds are flashed off when water evaporates during processing. High temperature and pressure inside the extruder barrel make the steam rapidly blow off out to the surface of the matrix dragging the volatiles with it.[78] This is one of the major causes of flavor and fragrance loss during processing. For all of these reasons, controlling the exact formulation prior to extrusion process can be crucial for the final product.[16,69]

3.2. Carbohydrates and Polysaccharides

Carbohydrates were the first polymers used for flavor encapsulation, and are still being used because of their good physicochemical properties (low viscosity, good solubility in water, and excellent barrier properties with respect to volatile organic compounds, at least under dry conditions).[7,79] Presently, starches, modified starches and sugars, either in a glassy or crystalline state, are considered to be the best hydrophilic matrices for entrapment and protection of volatiles. This can be explained by the low solubility of oxygen and volatiles in the matrix and, by the low free volume available for molecular transport.[13] The advantages of amorphous carbohydrate matrices in a glassy state are illustrated in the review by Ubbink and Krüger.[69] Amorphous food powders present great barrier properties against flavor losses and oxidation and are therefore often used for encapsulation and stabilization of complex flavor mixtures.

However, as already mentioned above, the quality of the protection against oxidation and leakage depends strongly on the glass transition temperature, which in turn depends on the water activity in the carbohydrate matrix, and on the surface to volume ratio of the extruded materials, since changing the granule morphology can impact the rate of water uptake and volatile losses.[69]

3.2.1. Maltodextrins. Maltodextrins are obtained by acid or enzymatic hydrolysis of starch and, depending on how they are produced, may differ in their dextrose equivalent (DE) (relative to the degree of hydrolysis, a higher DE means greater hydrolysis), which ranges from 0 (corresponding to long-chain glucose polymers) to 100 (corresponding to pure glucose). The DE is inversely proportional to the average molecular weight of the

Table 2
Composition of delivery systems using only maltodextrins as the main ingredient (nd = not determined).

Reference	Initial formulation composition (% w/w)	Active core (%w/w)	Extrudate moisture content (%w/w)	Encapsulation efficiency (% w/w)	Encapsulation Rate (% w/w)	Technology
(Porzio and Popplewell, 1999)	Maltodextrin DE-10/water (85.6/ 5.3)	Diacetyl (9.1)	8.3	nd	4.9	Melt Extrusion
(Porzio and Popplewell, 2001)	Maltodextrin DE-10/water(81.4/10)	Diacetyl (8.6)	7.6	nd	4.4	Melt Extrusion
(Benczedi and Bouquerand, 2001)	Maltodextrin DE-19/water/lecithin (90/6/1)	Strawberry flavor (3)	nd	nd	nd	Melt Extrusion
(Benczedi and Bouquerand, 2003)	Maldotextrin DE-19/water/silicon dioxide/lecithin (87/7/2/1)	Fragrance (3)	nd	nd	nd	Melt Extrusion
(Bouquerand, 2007)	Maltodextrin DE-10/miglyol/ lecithin (77.6/1/ 0.5)	Ascorbic acid (20.8)	nd	nd	18.9	Melt Extrusion
(Chang et al., 2010)	Maltodextrin/ lecithin/miglyol (75.6/1/0.5) ; (88.4/1/0.4)	Ascorbic acid (18.9); (16.1)	(9.2); (7.9)	(97.2); (97.9)	(18.6); (15.3)	Melt Extrusion
(Benczedi et al., 2011)	Maltodextrin DE-19 ;DE-12 ;DE-6 (83)	Orange oil (nd)	nd	nd	(8.3); (8.1); (7.9)	Melt Extrusion

Table 3
Composition of the delivery systems using only starch as the main ingredient (nd = not determined).

Reference	Initial formulation composition (% w/w)	Active core (%w/w)	Extrudate moisture content (%w/w)	Encapsulation efficiency (% w/w)	Encapsulation Rate (% w/w)	Technology
(Carr et al., 1991)	Corn starch/water (80-95/10)	Atrazine (5–20)	8-25	73 – 96	nd	Melt Extrusion
(Kollengode and Hanna, 1997b)	Corn starch/water (95/nd)	Cinnamaldehyde (5)	nd	24.1	nd	Melt Extrusion (direct injection)
		Eugenol (5)		20.5		
		nonanoic acid (5)		15.1		
		3-octanone (5)		25.8		
(Hau et al., 1998)	Wheat starch/water (67.3-84.1/15.90-32.7)	Diacetyl, 3-methylbutanal, heptane (nd)	19-43	nd	nd	Melt Extrusion
(Ubbink et al., 2001)	Potato starch/capsule/ glycerol/water (64.1/2.4/2.7/25)	Orange oil (5.8)	nd	nd	nd	Melt Extrusion
(Lengerich, 2002)	Semolina/wheat gluten/ wheat starch/vegetable oil/ water (25.1/18/25.1/7.9/1.3)	Various materials (22.3)	nd	nd	nd	Melt Extrusion
(M. A. Emin and H.P. Schuchmann, 2013)	Native Maize starch (nd)	Medium chain triglyceride (4)	18	nd	nd	Melt extrusion

polysaccharide, and the maltodextrins normally found in microencapsulation have a DE varying from 3 to 20.[80] Maltodextrins are the reference wall material in extrusion entrapment of food ingredients due to their film-forming properties, high water solubility, low oxygen solubility, binding characteristics, good protection against oxidation, and low cost.[12]

The influence of the molecular weight and DE of maltodextrins on the behavior of the carriers has been extensively discussed in the so-called "food polymer science" approach.[14,71,73] In fact, molecular weight is the one parameter that is directly linked to physicochemical properties (viscosity, glass transition temperature, solubility, etc.) even though DE can also be correlated to some physicochemical properties, e.g., solubility of the polysaccharide increases when DE increases. Some authors have reported that the retention of flavors decreases with increasing DE[3,7,67,81] and this has been attributed to the fact that, when DE increases, the maltodextrins become more hygroscopic and their solubility in water increases, which does not favor the retention of volatiles. Conversely, when DE decreases, hygroscopicity also decreases, while the molecular weight, the apparent viscosity, the cohesiveness, the glass transition temperature, and the film-forming properties increase, with all of these properties favoring of a good encapsulation.

However, maltodextrins have low emulsifying properties and for this reason some emulsifiers are needed in order to improve the incorporation of the active material, as well as to lower the viscosity and to enhance the flow of the melt inside the extruder. Moreover, by lowering the surface tension of the extrudate, the emulsifiers help to give products with a less sticky and less porous surface[36] which is beneficial to a better encapsulation of volatiles.

Examples of different formulations, as well as some encapsulation rates and efficiency are given in Table 2. In general, compositions of the delivery system are almost the same, and the moisture content of the extrudate is similar for all studies covered, no matter whether the active compounds are flavors, fragrances, or bioactive food compounds.

3.2.2. Starch. Starch is a polysaccharide, consisting of D-glucose chains. It is a mixture of two homopolymers, amylopectin, which is a linear polymer (10–20%) and amylose, which is a crosslinked polymer (80–90%). Amylose and amylopectin are interconnected by 1,4-α and 1,6-α glycosidic bonds, which are part of the ramifications in the molecule's structure. For this reason, the supra-molecular structure of starch is in a semi-crystalline form. Amylopectin is organized in the form of sheets giving the crystalline portion and amylose is in an amorphous form. Under normal conditions of temperature and pressure, starch is insoluble in aqueous solvents.[12,71,82]

Several studies have been conducted to better understand the thermal transitions, and the changes of physical state of starch. The theory mentioned by Donovan[83] allowed a better understanding of what is happening during the changes in the physical state of this material, and particularly for determining in which states the polymeric matrix is when water and temperature are in excess.[84,85] Swelling of the amorphous regions is observed when water is in excess (the hydrogen bonds between the polysaccharide chains are cut, and the starch granules absorb water and swell). This phenomenon is associated with the initiation of the gelatinization temperature (60°C–85°C, depending on the type of starch). The crystalline regions are degraded (dissociation and opening of the amylopectin "propellers") and starch is converted into a gel.

When starch is in a gelatinized state, the phenomenon of retrogradation (reorganization of its crystalline structure) is observed. In this case, the gel is more rigid and tends to

expel water included between the polysaccharides chains (a phenomenon known as syneresis). Starch rearranges itself into a more crystalline and stiff structure. The glass transition of the sample depends on the rate of hydration. Actually pre-gelatinized starch is used for the entrapment of volatiles, due to enhanced diffusion of the latter, and in fact, pre-gelatinized starch is soluble in cold water, which facilitates processing conditions for encapsulation.

Since starch is a more complex molecule than maltodextrins (greater physicochemical properties) more interactions can be established with active compounds. Starch has often been used in extrusion encapsulation (Table 3) due to the stable inclusion complexes of starch forms with flavor.[51] Indeed these inclusion complexes proved to be stable at high temperatures and showed great stability when stored for longer periods of time. Forming these complexes, however, requires conformational changes of the amylose moieties, which require in turn high processing temperatures to counterbalance the relatively low level of water in the extrudate.

Regarding the physicochemical properties of starch, it has been demonstrated that amylose content can affect expansion and in fact, it increases with the amylose content (this is without taking into account temperature and moisture content). It has been found that the expansion ratio increases from 8.3 to 16.4 as the amylose content of native starch increases from 0 to 50%. Above 50% of amylose content, the expansion ratio decreases.[86] As expansion is related to volatile losses, it is assumed that for better retention, starch with low amylose content should be chosen. In addition, Hau et al.[31] have shown that for starch with an amylose/amylopectin ratio of 27/73, water content influences the binding of volatiles. In fact, volatile uptake increases as the water content of the delivery system increases from 19% to 43%, and this could be due to the decrease of viscosity of the melt allowing the volatile compound to be better dispersed inside the carrier. However, when the moisture content increases, the expansion ratio decreases and this tendency is the same for starches with different amylose contents (amylose content varied from 0 to 70%). The maximal expansion ratio of various starches was obtained with a moisture content of 14%.[86]

The extrusion of starch involves its gelatinization, at least partially, with water or a water/plasticizer mixture before or during the initial steps of the extrusion, and the water content ranges typically from 10 to 45%. In some cases part of the water is added together with the encapsulated oil in the form of an emulsion.[40]

3.2.3. Modified Starch. In the context of encapsulation, the term "modified starch" actually includes dextrins, on which octenyl succinate groups have been grafted by esterification of the hydroxyl groups with mono octenyl succinic acid. These products are obtained by acidic or enzymatic degradation of starch and subsequent chemical treatment with the succinic derivate. The modifications are made in order to improve the chemical and physical properties of the dextrin to meet specific needs. The advantage of the so-called starch octenylsuccinate, also known as OSAN (octenyl succinic anhydride), lies in its remarkable emulsifying properties, which are related to the presence of the hydrophobic octenyl moieties that allow better interactions with aroma compounds.[12,82] The roles of these materials on the retention of volatiles in carbohydrate matrices have been discussed in the study made by Zasypkin and Porzio.[30] Clear benefits were found in terms of oil droplet dispersion, viscoelastic properties and surface oil.

It should be noted that there are other ways to modified starches, for example, by oxidation in the presence of sodium hypochloride in order to decrease its viscosity. Or, on the other hand, to improve its viscosity, starch can be modified with propylene oxide. In

Table 4
Composition of delivery systems of oligosaccharides as the main ingredient (nd = not determined), for melt extrusion, examples listed are calculated for one hour of production.

Reference	Initial formulation composition (% w/w)	Active core (%w/w)	Extrudate moisture content (%w/w)	Encapsulation efficiency (% w/w)	Encapsulation Rate (% w/w)	Technology
(Schultz and Calif, 1958)	Sucrose/corn syrup/ water (53.8/26.9/ 14)	Orange oil (5.4)	nd	nd	nd	Melt Injection
(Miller and Mutka, 1987)	Corn syrup/sugar/ water (48/33/nd)	Orange oil (17.5)	5	nd	16.7	Melt Injection
(Saleeb and Pickup, 1989)	Maltose monohydrate/ maltodextrin (24.1/72.5); mannose/ maltodextrin (24/ 72.2)	Ethyl butyrate (3.4); lemon oil (3.8)	3–6	nd	(3.4); (3.3)	Melt Extrusion (single screw)
(Kollengode and Hanna, 1997a)	Corn starch/ β-cyclodextrin (nd)	Cinnamaldehyde, eugenol, nonanoic acid, 3-octanone (nd)	nd	(42); (46) ; (26); (36)	nd	Melt Extrusion (direct injection)
(Black et al., 1998)	Whey protein/ sucrose/ maltodextrin/	Cinnamic aldehyde (nd)	nd	nd	nd	Melt Extrusion

(*Continued on next page*)

	water (50/25/25/ excess)					
(Porzio and Popplewell, 1999)	Maltodextrin/corn syrup/methyl cellulose (72.5/ 20/7.5)	Orange oil (nd)	nd	nd	8.3	Melt Extrusion
(Gunning et al., 1999)	Sucrose/ maltodextrins (52.8/47.2)	Cherry, pepper mint flavors (nd)	(3.5); (5.2)	nd	(10); (7.4)	Melt Injection
(Reifsteck and Jeon, 2000)	Corn syrup/sugar/ flour/starch (nd)	Flavors (nd)	nd	nd	nd	Melt Extrusion
(Zasypkin and Porzio, 2004)	Hi-Cap100/ EmCap12639/ lactose (40/30/ 30); EmCap12634/Hi-Cap100/lactose (40/20/40)	Lemon flavor (10-20)	(7.7); (7.6)	nd	nd	Melt Extrusion

(*Continued on next page*)

Table 4

Composition of delivery systems of oligosaccharides as the main ingredient (nd = not determined), for melt extrusion, examples listed are calculated for one hour of production. *(Continued)*

Reference	Initial formulation composition (% w/w)	Active core (%w/w)	Extrudate moisture content (%w/w)	Encapsulation efficiency (% w/w)	Encapsulation Rate (% w/w)	Technology
(Bohn et al., 2005)	Sucrose/ maltodextrin (nd)	Benzaldehyde (nd)	(4–5.4)	nd	nd	Melt Injection
(Yuliani et al., 2006)	Native corn starch/ β-cyclodextrin (nd)	d-Limonene (nd)	nd	nd	nd	Melt Extrusion (pre-encapsulation by spray drying)
(Gregson and Sillick, 2012b)	Maltodextrin/ trehalose/lecithin/water (35.8/ 35.8/0.8/19.3)	Orange oil (8.3)	5.8	nd	nd	Melt Injection
(Chang et al., 2014)	Modified starch/ maltodextrin/ lecithin	Vitamine E (5-8)	nd	nd	93	Melt Extrusion
(Tackenberg et al., 2015)	Maltodextrine DE12 and Maltodextrine DE-17/sucrose (nd)	Orange terpenes and tocopherol (nd)	nd	nd	67	Melt Extrusion

general, starch properties can be modified according to the final application (i.e., thickening agent, emulsifier, texturizing agent).

3.2.4. Carbohydrate Mixtures. Mixtures of oligosaccharides are often used either in spray-drying or extrusion encapsulation of flavors because they offer wall material with better barrier properties. [14,15,50] As mentioned above, the physicochemical properties of carbohydrates are a key parameter that needs to be taken into account during formulation and processing of delivery systems. In particular, high molecular weight polysaccharide matrices have higher residual porosity, which enhances oxygen uptake and is detrimental to final product shelf life. However, high molecular weight polysaccharides may be easier to process owing to their higher viscosity. As is usual in formulation, a trade-off between both performance indicators can be reached by mixing different molecular weight polysaccharides. And in fact, most of the formulations used for encapsulation of volatiles or other sensitive active materials found in the literature used a mixture of different molecular weight carbohydrates, (see Table 4 below) (starch, maltodextrins, and mono- or disaccharides, e.g., sucrose, mannose, lactose, etc.).

The most recurrent formulations found in the literature are those employing a mixture of high molecular weight polysaccharides (molecular weight greater than 2000 Da) and low molecular weight polysaccharides (molecular weight less than 1000 Da), for example, a mixture of maltodextrin and glucose syrup or maltodextrin and gums, or starch and maltodextrins or disaccharides.[14] Such mixtures (Table 4) allow adjustment of the glass transition temperature, the hygroscopicity, and porosity of the matrix.

Cyclodextrins, and more particularly β-cyclodextrins, are cyclic oligosaccharides which have also been considered as wall material in combination with other oligosaccharides. These materials are obtained from starch by enzymatic conversion and are very resistant to high temperatures (100 to 300°C). Cyclodextrins have a toroid structure, with the inner core less hydrophilic than the surface of the molecule. The advantage of this arrangement is that the inner core can establish inclusion complexes with various hydrophobic substances, while remaining water-soluble. β-cyclodextrins have been used in melt extrusion microencapsulation to pre-encapsulate flavors prior to extrusion; either by forming a flavors/β-cyclodextrins emulsion or by spray-drying the flavors with β-cyclodextrin.[12,38,41,42,78]

3.3. Proteins

Due to their amphiphilic, emulsifying, film forming, and solubility properties, proteins are now used as an innovative raw material for microencapsulation, and those most often employed are sodium caseinate, soy and pea protein isolates. Whey proteins and soy proteins make good wall materials for flavor and essential oil encapsulation due to their good gel-forming, emulsifying, and surfactant properties. Indeed, these protein isolates have been widely used, mainly by spray-drying,[87] in microencapsulation of different types of active materials (i.e., essential oils, flavors, tocopherols, oils rich in polyunsaturated fatty acids, etc.).[71,88]

The major problem related to proteins is that they are not as chemically inert as polysaccharides, and side reactions can take place (Schiff base formation and Maillard reactions). This may result in browning (oxidation reaction between amino-acid groups of proteins and aldehyde groups of the flavor molecule) of the final product.[87,89,90] As a result, interactions between proteins and flavors may cause a loss of flavor perception in the final product or the production of off-flavors. The latter are the result of the reaction

Table 5
Composition of delivery systems using proteins or mixture of proteins and oligosaccharides as the main ingredient (nd = not determined).

Reference	Initial formulation composition (% w/w)	Active core (%w/w)	Extrudate moisture content (%w/w)	Encapsulation efficiency (% w/w)	Encapsulation Rate (% w/w)	Technology
(Sair and Sair, 1980)	Casein/water (43.2/ 45.8)	Orange oil (7.6)	6	92	nd	Silent cutter Autoclave
(Black et al., 1998)	Whey protein/ maltodextrins (lodex-10)/ sucrose/water (nd/ nd/nd/excess)	Cinnamic aldehyde (nd)	nd	nd	nd	Extrusion (not specified if melt injection or melt extrusion)
(Lengerich et al., 2010)	Durum flour/wheat protein/sodium caseinate/ glycerol/ erythrobic/water (35.3/8.8/2.3/12/ 2.4/27)	Oil rich in polyunsaturated fatty acids/vanilla (11.9/ 0.3)	nd	nd	nd	Melt extrusion

of aldehydes with the amino, disulfide, sulphydryl, or thiol groups of the proteins through Van der Waal interactions or hydrogen bonds.[78]

In fact, the determination and understanding of the type of interactions between flavors or fragrances and proteins have raised considerable interest among academic researchers. Landy et al.,[59] have investigated the interactions between aroma compounds and proteins (sodium caseinate) by measuring the vapor-liquid partition equilibrium (by headspace analysis or exponential dilution) in order to understand how these volatiles are retained. They were able to establish that, depending on the concentration of protein and the type of chemical group of volatile compounds, retention can be affected. In some cases, the liberation of active compounds is slowed down or inhibited due to irreversible interactions between some flavor compounds and the protein support (i.e., aldehydes and ketones interact with the amino acids).[91] These interactions result in flavor loss or modification. There are two major problems related to proteins as encapsulating agent;

(i) proteins are highly reactive compounds that can bind irreversibly to flavor molecules inducing loss or modification of the flavor,
(ii) proteins are molecules with different types of chemical groups and structure, thus they can have different interaction sites (i.e., hydrophobic and/or hydrophilic binding sites).

For example, soy proteins do not retain some volatile compounds such as alcohols but they do retain aldehydes and ketones through irreversible interactions and consequently the release rate of these volatiles is very low.

Furthermore, hydrophobic core materials may be more soluble in proteins, because of the presence of hydrophobic moieties in this material, which may lead to enhanced diffusion and leakage of the encapsulated active, especially if the latter is volatile.

Mixtures of proteins and fats, or proteins and oligosaccharides have also been proposed.[23,90] For example, Lengerich et al.[39] used a mixture of protein and flour (durum flour and whey protein) as matrix (Table 5). Alternatively, the pre-encapsulation of the active compound in a water-in-oil emulsion has been proposed in order to improve the barrier properties of the delivery system.[40,92] In this case, the aqueous phase was composed of a solution of sodium caseinate, and the emulsion was injected directly into the second barrel of a seven-section barrel extruder. This latter preparation gave higher encapsulation efficiency than the encapsulation efficiency found in Black's work.[23]

In addition, Black et al. [23] have also determined the release rate behavior of different proteins (gluten, soy protein, egg albumin, acid casein, whey protein concentrate) mixed with a mixture of polysaccharides (e.g., sucrose and maltodextrins) and glycerin as plasticizer. They determined that for cinnamic aldehyde (principal component of cinnamon flavor) gluten had the highest release rate compared to the other proteins, and indeed gluten has better viscoelastic properties than the other proteins cited above.

These results confirm that proteins admixed with polysaccharides or fat are better carriers than a matrix composed only of proteins. As mentioned in Guichard's paper,[90] a solution of sodium caseinate (0,1% in water) and egg albumin decreases the activity coefficient of flavor compounds and ensures better retention. In these types of mixtures, proteins act more as a compatibilizing rather than encapsulating agent; they help to decrease the surface tension of the flavors and the polymer matrix in order to obtain homogeneous blends.

3.4. Additives

3.4.1. Introduction. Additives can be considered as components, which impart specific properties to the final product. For instance hydrophobic coating compounds like waxes or oils are normally employed to enhance oxidative stability and lower releasing rates. Plasticizers are employed to decrease the processing temperature and thus avoiding thermal degradation.[68] Carboxylic acids like ascorbic acid, citric acid, erythorbic acid, and other components such as lecithin, caseinate, and gelatin are used as food preservatives and/or antioxidants.[50,93] However, the most important additives in terms of encapsulation performances are certainly emulsifiers which can be added either to the feed emulsion or to the carrier itself in order to ensure small oil droplets of aroma or fragrance compounds inside the matrix, thereby providing better dispersion in the carrier and higher protection of the core material.[16] Table 1 gives a perfect overview of all the "raw materials" used.

3.4.2. Emulsifiers and Other Compatibilizing Agents. Emulsifiers are used in encapsulation principally to increase the compatibility between the matrix and the active materials. Besides the OSAN modified starch mentioned above, a number of emulsifiers could be used.

Gums, such as gum Arabic, have been proposed and used either alone or in combination with maltodextrins. For example, Jacquot et al.[79] found efficient flavor encapsulation by spray drying a flavor/gum Acacia/maltodextrin (DE18) emulsions, although gums are also claimed to delay water uptake and thereby enhancing the controlled release of the encapsulate.[32] However, these high molecular weight compounds are detrimental to the matrix barrier properties against oxygen and to the protection against oxidation.[94] Therefore, due to these two limitations and also to the fact that gums are rather expensive and suffer from irregular market availability and variable quality, they are preferred as additives and not as a polymer matrix.

Another solubilizer widely employed in microencapsulation is lecithin, soy lecithin being the most used of the range. Lecithin has the additional advantage of acting as a lubricant, thereby improving the flowability of the melt. It helps to decrease the stickiness (especially for maltodextrins and starches) and the structural surface defaults on the surface of the delivery system.[35,36,50,92,93] An additional benefit is the lowering of the extrudate surface tension, which in turn decreases the porosity of the product and provides a better protection against oxygen permeability.

Medium chain triglycerides (MCT) are less well known than gums or lecithin and are synthesized from glycerol and fatty carboxylic acids (i.e., caproic, caprylic, capric, and lauric acids). There are different types of MCT depending on the length of the major fatty acid chain (from C6 to C12) and all are colorless, tasteless, and odorless, hence their use in the food and cosmetics industry. In microencapsulation, they are used as lubricants providing better flowing materials and easier shaping of the molten mixture at the die exit. In addition, they offer protection to the active ingredient by acting as a coating material, thus slowing down release of the active compound.[35,36] Moreover, in some studies, MCT have been used as "solvent vector" in which the flavors or fragrances are dissolved in order to facilitate their handling or to offer an extra protection (formation of an oil/flavor droplets) prior to processing.[16] In recent studies, MCT is employed as a model active-oil compound allowing to determine the dispersion and the mixing efficiency of twin-screw extrusion processing.[19,20] Additionally, they can also act as antioxidant because they are able to reduce the vapor pressure of the active material.[40] According to the references cited before, MCT can be used with any type of carriers, but here they are specially

Table 6
Composition of delivery system and its initial and final moisture content in relation with the glass transition temperature (nd = not determined).

Reference	Initial formulation composition (%w/w)	Core material (%w/w)	Initial moisture content (%w/w)	Extrudate moisture content (%w/w)	Tg (°C)	Technology
(Swisher, 1957)	Corn syrup/brominated vegetable oil/ emargol (88/4.1/0.8)	Orange oil (7.1)	3–8.5	nd	nd	Melt Injection
(Schultz and Calif, 1958)	Sucrose/corn syrup (53.8/26.9)	Orange oil (5.4)	14	nd	nd	Melt Injection
(Sair and Sair, 1980)	Casein (43.2)	Orange oil (7.6)	45.8	6	nd	Silent cutter Autoclave
(Miller and Mutka, 1987)	Corn syrup/sugar (48/ 33)	Orange oil (17.5)	nd	5	nd	Melt Injection
(Saleeb and Pickup, 1989)	Maltose monohydrate/ maltodextrin (24.1/ 72.5); mannose/ maltodextrin (24/ 72.2)	Ethyl butyrate (3.4); lemon oil (3.8)	nd	3–6	50–80	Melt Extrusion (single screw)
(Kollengode and Hanna, 1997b)	Starch (95,2)	Cinnamaldehyde, eugenol, nonanoic acid, 3-octanone: (nd)	15	nd	nd	Melt Extrusion (direct injection)
(Black M., Popplewell L., and Porzio M. 1998)	Whey protein/ maltodextrins (DE10)/sucrose (50/ 25/25)	Cinnamic aldehyde (nd)	Excess	nd	nd	Extrusion (not specified if melt extrusion or melt injection)

(*Continued on next page*)

Table 6
Composition of delivery system and its initial and final moisture content in relation with the glass transition temperature (nd = not determined).
(Continued)

Reference	Initial formulation composition (%w/w)	Core material (%w/w)	Initial moisture content (%w/w)	Extrudate moisture content (%w/w)	Tg (°C)	Technology
(Porzio M. and Popplewell L. 1999)	Maltodextrin (85.6)	Diacetyl (9.1)	5.3	8.3	35–50	Melt Extrusion
(Hau M., Gray D., and Taylor A. 1998)	Wheat starch (67.3-84.1)	Diacetyl, 3-methylbutanal, heptane (nd)	15.9-32.7	19-43	nd	Melt Extrusion
(Gunning et al., 1999)	Sucrose/maltodextrins (52,8/47,2)	Cherry, pepper mint flavors (nd)	nd	(3.5); (5.2)	nd	Melt Injection
(Reifsteck and Jeon 2000)	Corn syrup/sugar/flour/ starch (nd)	Flavors (nd)	nd	nd	nd	Melt Extrusion
(Porzio and Popplewell, 2001)	Maltodextrin DE10 (81.4)	Diacetyl (8.6)	10	7.6	51	Melt Extrusion
(Benczedi and Bouquerand, 2001)	Maltodextrin DE19/ lecithin (90/1)	Strawberry flavor (3)	6	nd	<40	Melt Extrusion
(Ubbink et al., 2001)	Potato starch/capsule E/glycerol (64.1/2.4/ 2.7)	Orange oil (5.8)	25	nd	nd	Melt Extrusion
(Leusner et al., 2002)	Fructooligosaccharide/ Miglyol (65.8/4.9)	Calcium (28)	1.3	nd	nd	Melt Extrusion

(*Continued on next page*)

(Benczedi and Bouquerand, 2003)	Maldotextrin DE19/ silicon dioxide/ lecithin (87/2/1)	Fragrance (3)	7	nd	40	Melt Extrusion
(Zasypkin and Porzio, 2004)	Hi-Cap100/ EmCap12639/lactose (40/30/30); EmCap12634/Hi-Cap100/lactose (40/ 20/40)	Lemon flavor (10-20)	nd	(7.7);(7.6)	(13); (15)	Melt Extrusion
(Bohn et al., 2005)	Sucrose/maltodextrin (nd)	Benzaldehyde (nd)	nd	4–5.4	38–54	Melt Injection
(Yuliani et al., 2006)	Native corn starch/ β-cyclodextrin (nd)	d-Limonene (nd)	nd	nd	nd	Melt Extrusion (pre-encpasulation by spray srying)
(Bouquerand, 2007)	Maltodextrin DE10/ miglyol/lecithin (77.6/1/0.5)	Ascorbic acid (20.8)	nd	nd	35.8	Melt Extrusion
(Chang et al., 2010)	Maltodextrin/lecithin/ miglyol (75.6/1/0,5); maltodextrin/	Ascorbic acid (18.9); (16.1)	(4); (2)	(9.2); (7.9)	<35	Melt Extrusion

(*Continued on next page*)

Table 6
Composition of delivery system and its initial and final moisture content in relation with the glass transition temperature (nd = not determined).
(Continued)

Reference	Initial formulation composition (%w/w)	Core material (%w/w)	Initial moisture content (%w/w)	Extrudate moisture content (%w/w)	Tg (°C)	Technology
	lecithin/miglyol (88.4/1/0,5)					
(Zasypkin, 2011)	OSAN starch/gournd oregano/lactose/ dextrose monohydrate (43.88/ 18.62/25.27/2.65)	Flavor (6.6)	2.4	7.6	44.9	Melt Extrusion
(Benczedi et al., 2011)	Maltodextrin DE19, DE12, DE6 (83)	Orange oil (nd)	25	7.5–15.1	49-54	Melt Extrusion
(Gregson and Sillick, 2012a,b)	Maltodextrin/trehalose/ lecithin (35.8/35.8/ 0.8)	Orange oil (8,3)	19.3	5.8	51	Melt Injection
(M.A. Emin and H.P. Schuchmann, 2013)	Native maize starch	Medium chain triglycerides (4)	18	nd	nd	Melt Extrusion
(Chang et al., 2014)	Modified starch/ maltodextrin/lecithin	Vitamin E (5-8)	nd	nd	30	Melt Extrusion
(Tackenberg et al., 2015)	Maltodextrin DE12 or Maltodextrin DE17/ sucrose	Orange terpenes and tocopherols (nd)	4-5.7	2-12	54-58	Melt Extrusion

employed with maltodextrins, starch and oligosaccharides (oligofructose), as emulsifiers and vectors to enhance the adsorption of the active compound.

Hydroxypropyl methylcellulose (HPMC) is a semi-synthetic polymer employed in some formulations to control the release of flavors when the delivery systems have to be solubilized in water. Porzio and Popplewell[95] have suggested that, when dissolved in water, HPMC rehydrates, thereby increasing the viscosity of the medium and slowing down the diffusion of the flavor in the medium. HPMC is less commonly used than OSAN-modified starch, lecithin, or gums.

Finally, ethyl cellulose is commonly found in the food industry as a colloidal stabilizing agent (E462). In microencapsulation it is also used as a viscosity modifier because it allows decreasing the interfacial tension between the core material and the encapsulating carrier to be lowered, along with the energy required.

3.4.3. Antioxidants. The second group of additives is antioxidants. These are usually employed in the case of microencapsulation of sensitive and readily oxidizable active compounds, e.g., oils rich in polyunsaturated fatty acids, bioactive food compounds like polyunsaturated fatty acids (omega-3 oils), fragrances, and flavor compounds.[25,41,66,96–99] For example, the antioxidants most commonly employed for protection of volatiles or high sensitive core compounds are ascorbic acid, citric acid, erythorbic acid, and mixed tocopherols.[99]

3.4.4. Plasticizers. In the polymer industry, plasticizers are an important class of low molecular weight compounds, whose role is to modify the mechanical properties of polymers, by lowering down the glass transition temperature. Plasticizers reduce the density, the viscosity, the hardness, and the tensile of deformation force of a polymer. And at the same time they render the system more flexible and resistant to fractures[100] and improve the processability of the polymer.

In the case of melt extrusion microencapsulation, plasticizers are required to ensure formation of the melt inside the extruder's barrel. If the carrier employed is in a solid-state, a plasticizer may be necessary; however, for some carrier, depending on the physical state of the core material, the use of a plasticizer may be optional.[23] In general two groups of plasticizers are distinguished in this area, water and polyols (also known as low molecular weight alcohols).

As already mentioned in the preceding sections, water is the most frequently used plasticizer for carbohydrates and is also a key process parameter (Table 6). However, other plasticizers, such as sugar alcohols, polyols, glycols, polyglycols, linear alcohols, glycerin, etc., have been proposed to avoid early losses of volatile by water (or flash) distillation during the process. The sugar alcohols are synthesized from carbohydrates whose carbonyl groups have been reduced to a primary or secondary hydroxyl group. Polyols are low molecular weight plasticizers, characterized by their significant impact on the mechanical properties. They are often employed in the fabrication of biopolymeric films because they improved the mechanical properties of these films in terms of flexibility and elasticity.[101,102] For example, sorbitol, glycerol, erythritol, xylitol, and aqueous-based compositions such as alcoholic solutions of polypropylene glycol, polyethylene glycol, pentanol, and hexanol are used for plasticization of the biopolymer matrix in extrusion microencapsulation.[23,40,99,103] All of these alternative plasticizers are bulkier than water and are supposed to provide matrix materials more ductile and homogeneous in the extruder barrel. One drawback is that such matrices are also more permeable to volatiles, and another is that such alternative plasticizers are not easily removed from the final product. Both drawbacks are detrimental to encapsulation.

Black et al.[23] evaluated the release rate of cinnamic aldehyde using the same type of carrier but changing the nature of the plasticizer: glycerin or water. Modified starch, whey protein, soy protein, and egg albumin were tested for the same amounts of plasticizers. Results showed that flavor release was more important for extrudates plasticized with water than extrudates plasticized with glycerin (and this is true for all the matrices except for the modified starch matrix). Besides, Porzio and Popplewell[95] have used water as a plasticizer, setting very low initial water content around 3 to 5% (w/w), in order to obtain an extrudate glass transition temperature of equal or higher than 40°C.

4. Extrusion Microencapsulation Technologies

4.1. Introduction

A categorization of the extrusion technologies for microencapsulation has been made in recent works,[29,67,68,104] leading to a clear distinction between ram extrusion (also called melt injection) and screw extrusion (also called melt extrusion).

Swisher,[22] and Schultz and Calif [21] defined ram extrusion as a process consisting of a rotating screw inside a heated cylindrical barrel, where the raw materials are introduced in order to be melted. Next, a piston (here called a ram) pressurizes the molten mixtures through a die and transforms them into the desired shape. The main advantage of ram extrusion is the simplicity of the set-up. The major inconvenience is the limited melting capacity of the apparatus, producing poor temperature and composition uniformity in the extrudate.[68] The resulting material has the consistence of a hard candy entrapping the active.

In screw extrusion, the apparatus is composed of a single screw or two co-rotating screws inside a multiple heated barrel section, with inlets in each barrel where the raw material or additives can be introduced. The design of the apparatus allows controlled shear stress and controlled temperature depending on the conditions desired. In addition, according to the screw profile, different conveying, mixing, and shearing zones can be established to treat the materials. The raw materials are then mixed, melted, and transported to a die system where the molten mass is shaped. The advantage of screw extrusion is its versatility in terms of operating conditions. The major disadvantage is the difficulty of accurately controlling the parameters of this complex set-up to ensure the good and constant quality of the final product. On the other hand, to achieve a high quality material trough using an extrusion process, it is important to have a solid background knowledge in the materials science, so that the adequate formulation and the process variables can accurately be chosen.[16,30,67–69]

Co-extrusion consists of a dual fluid stream of immiscible liquid core and shell materials. Coating and core materials are pumped separately through concentric feed tubes and exit through the concentric orifices of the nozzles as a fluid rod or drop under the action of mechanical or sonic vibrations. Thanks to the action of surface tension, the wall material entraps the core material. The wall material is further solidified by a temperature drop or cross-linked in a bath containing suitable cross-linking agents. This technology does not need a pre-treatment of the carriers nor the active compounds.[2,8,105,106] This type of process will not be further addressed in this review.

The process steps of the three technologies used for microencapsulation of volatile organic compounds referred as extrusion encapsulation are described in Table 7. The term extrusion is used here to designate the exiting of a molten mass through an orifice under pressure (either by a mechanical piston, as for melt injection, or forced by an

Table 7

Overview of extrusion microencapsulation processes: melt injection, co-extrusion and melt extrusion (adapted from Zuidam and Shimoni[106]).

Technology	Melt Injection or Durarome	Co-Extrusion	Melt Extrusion
Process steps	1. Melting of the coating material	1. Dissolution or dispersion of the active compound in oil (emulsion)	1. Melting of the coating material inside a twin-screw extruder
	2. Dispersion or dissolution of the active compound in the coating material	2. Preparation of the aqueous or fat coating material	2. Direct introduction of the active compound (pure or in a pre-encapsulated form)
	3. Extrusion of the molten mixture through filter	3. Using of a concentric nozzle, and simultaneously pressing the oil phase through the outer one	3. Dispersion of the active compound into the coating material
	4. Coating and dehydration of the extrudate (cooling solvent)	4. Dehydration of the extrudate by dropping it into a gelling or cooling bath (cooling solvent)	4. Cooling and shaping of the extrudate (ambient temperature)
Morphology	Matrix	Reservoir	Matrix
Load rate (%)	5–20	70–90	5–40
Particle size (μm)	200–2000	150–8000	300–5000

endless screw as in melt extrusion). The three technologies employ similar carrier materials and almost the same operational conditions. However, melt extrusion differs from the two others because it does not involve the cooling step using a dehydrating solvent and in general the melting of the coating material and the injection of the core are made *in situ*. The product delivered by the three methods is a matrix where the active compounds are dispersed inside, usually in the form of droplets.

Melt extrusion is considered nowadays as one of the most promising techniques for microencapsulation of flavors and bioactive compounds because it is a highly flexible process, economical and environmentally friendly. The versatility of the twin-screw extruder allows adapting the conditions and parameters depending on the carrier, core material and the product desired.

4.2. Melt Injection or Durarome® or Ram Extrusion

The first technologies that were developed to encapsulate sensitive and volatile organic compounds relied on the preparation of an emulsion where flavors were finely dispersed in the coating material. Next, the dough was forced to exit through an orifice, and the high mechanical stress and shear allowed a homogeneous, finely dispersed emulsion and a semi-solid matrix to be produced. Finally a cooling step was required to obtain a solid glassy extrudate, and thus the mixture was cooled down in an isopropanol bath (also called a bath of dehydrating liquid) and then shaped into granulates.[10,107,108] These steps are shown in Fig. 5. The aim was only to protect the sensitive active ingredient. These

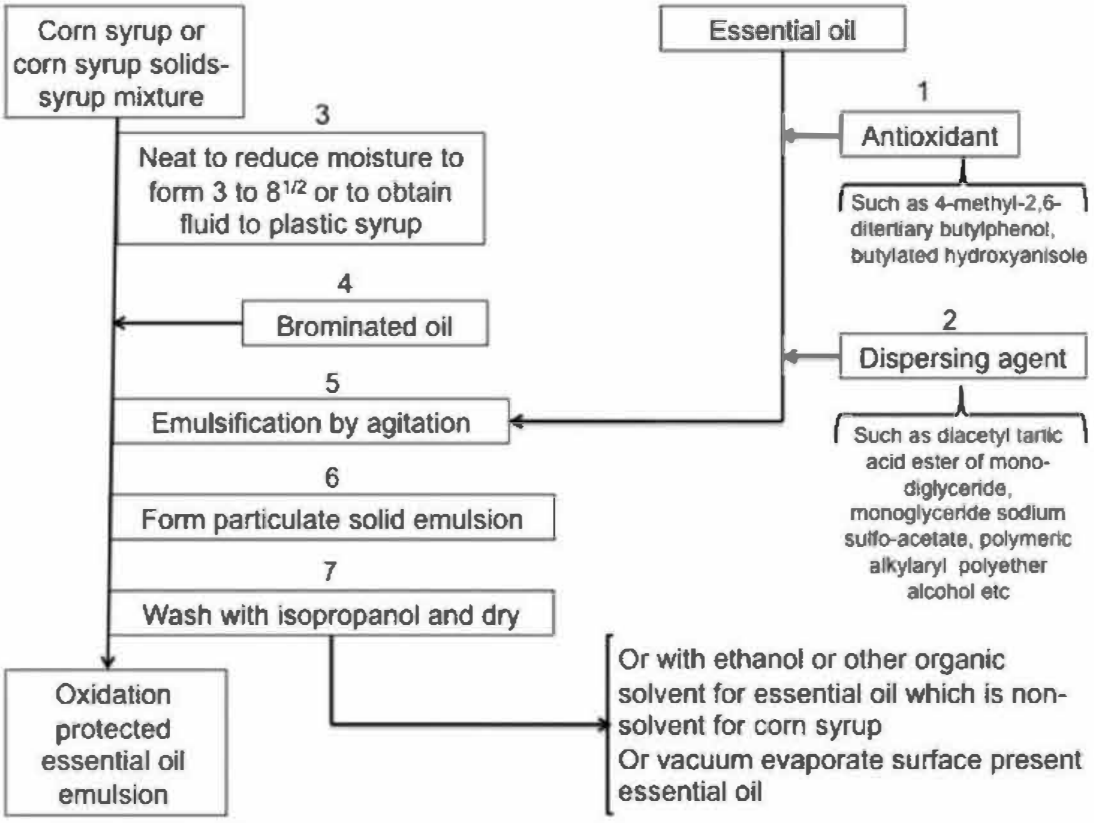

Figure 5. Scheme of extrusion encapsulation method (adapted from Swisher[22]).

Table 8
Extrusion microencapsulation by melt injection or ram extrusion technology: description of all the processing conditions.

Type of apparatus	Emulsification conditions	Cooling conditions	Reference
Steam Jacketed Lenhart mixer	1. Emulsification of the carrier material 2. Emulsification of the core material and additives 3. Melting and mixing between 85 and 125°C	Isopropanol bath (−20°C) and vacuum dried	(Swisher, 1957)
Mixer and heater reactor, with an orifice	1. Emulsification of the carrier material 2. Emulsification of the core material and additives, 3. Melting and mixing between 130 and 150°C	Cold air tunnel	(Schultz and Calif, 1958)
Steam Jacketed stainless vessel with an agitator equipped with a plate with multiple orifices of 0,762 mm of diameter	1. Emulsification of the carrier material 2. Emulsification of the core material and additives 3. Melting and mixing between 125 and 130°C	Isopropanol bath (−20°C) and vacuum dried	(Miller and Mutka, 1987)
nd	1. Melting of the carriers 2. Melting of the core material and additives 3. Emulsification step	Isopropanol bath (−20°C)	(Bohn et al., 2005)

(*Continued on next page*)

Table 8

Extrusion microencapsulation by melt injection or ram extrusion technology: description of all the processing conditions. *(Continued)*

Type of apparatus	Emulsification conditions	Cooling conditions	Reference
Tank reactor with a stirrer and outlet valve with die holes	1.Melting and emulsification of the carriers and additives 2. Emulsification of core material and additives 3. Emulsification of carriers and core material at 70°C	Dehydrating solvent isopropanol or hexane (−4°C)	(Valentinotti et al., 2006)

methods were called "extrusion encapsulation" since they involved in their process the use of a screw (as a stirrer or as a shear stress tool) in order to force a molten carbohydrate mixture to exit through a die or a series of dies.[14,16,21,22,25,41,56,106,107,109]

The process of encapsulation is divided here into three steps; the first step consists of melting the carbohydrate matrix in the presence of a plasticizer (generally water or glycerol), if required. Usually, the melting temperatures do not exceed 140°C in order to avoid thermal degradation of the active compound. Typical melting temperatures lie between 110 and 140°C. The second step corresponds to the addition of the active ingredient into the melt. In cases where the core ingredient is sensitive to oxidation, this step is carried out under an inert atmosphere. From the literature, the active compound is added to the carrier mixture, directly or as an oil-in-water emulsion, and the mixture is strongly stirred so as to disperse the flavor into the melting carbohydrate matrix. The third step is exiting and cooling of the dough. The mixture is forced to exit through a die, which results in the formation of a homogeneous product where the flavor is finely dispersed. The matrix is still in the rubbery state, but it is directly cooled down and dehydrated in isopropanol to induce transition to the glassy state. As shown in Table 8, microencapsulation by melt injection can be carried out in various types of apparatus (steam jacket mixer, tank reactor with an orifice or multiple nozzles). Depending on the type of device, different forms can be obtained (rods, droplets).

The drying step is mandatory every time the extrudate contains high levels of plasticizers and cold isopropanol is often used as a drying agent at this stage. Concomitantly, the extrudate is transformed into a glassy matrix by the dual effect of desiccation and cooling. This drastic shift from a paste to a glassy state fosters the entrapment of the active compound.

The Durarome® process named after the trade name of the first commercially available line of encapsulated flavors made by Firmenich S.A.,[17,48,56] is based on this method and involves the dispersion of the flavor into a sucrose and maltodextrin candy matrix.

However, the cooling step is more considered as a counterproductive stage rather than being an advantage, because it is an extra step in the whole process and increases both the time and the cost of production. This is not to mention the costs due to solvents like isopropanol and the fact that such a process is not compliant with today's food regulations, which tend to limit the use of organic solvent in food production processes.

Nonetheless, it is important to stress that the aim of encapsulation in these early days, was to protect the flavor compounds against oxidation and evaporation, in order to extend the flavored product's shelf life.[21,22,25,26] The controlled release of the active compound is a more recent property that can be adjusted by modifying either the formulation of the microcapsules or the processing conditions. [69]

Different apparatus have been developed since the pioneering work of Swisher to perform ram extrusion. These go from vertical screw-less extruders to multiple needle droplet-generators (also known as a nozzle encapsulation technology), and those mentioned in Uhlemann and Reiss' review.[14] Actually there are six other methods

(i) simple dripping
(ii) electrostatic extrusion
(iii) coaxial airflow
(iv) vibrating jet/nozzle
(v) jet cutting
(vi) spinning disk atomization), which have been recently described in the literature as extrusion encapsulation technologies.

Table 9
Processing parameters for melt twin-screw extrusion microencapsulation:*extruder has 4 temperatures zones, the numbers in brackets correspond to a range of values. SME (= specific mechanical energy).

Type of extruder (ratio L/D)	Feeder rate solid (kg/h)	Feeder rate liquid (kg/h)	Screw speed (rpm)	Temperature profile (°C)	Die diameter (mm)	Pressure die (Pa)	SME (kJ/kg)	Reference
(Coperion) ZSK30 &ZSK57 – 16:1& 34:1	5.4	nd	[50–500]	nd	nd	nd	nd	(Carr et al., 1991)
(Plasticorder) 2803 - 20:1	nd	nd	100	*60,120,110, 100	7	nd	[360–540]	(Kollengode and Hanna, 1997a, 1997b)
(Clextral) BC 21–16:1	3.7	[0.7 – 1.81]	nd	*50, 100, 120, 80	10	nd	nd	(Hau et al., 1998)
nd	6.8	[0.18–0.42]	nd	[93–121]	nd	nd	nd	(Porzio and Popplewell, 2001)
(Clextral) BC 21& BC45- 16:1& 20:1	[5–50]	nd	nd	[90–130]	[0.7–2]	$[1\times10^5 - 50\times10^5]$	< 10	(Benczedi and Bouquerand, 2001)(Benczedi and Bouquerand, 2001)(Benczedi and Bouquerand, 2003)(Benczedi et al., 2011)

(*Continued on next page*)

Table 9
Processing parameters for melt twin-screw extrusion microencapsulation:*extruder has 4 temperatures zones, the numbers in brackets correspond to a range of values. SME (= specific mechanical energy). *(Continued)*

Type of extruder (ratio L/D)	Feeder rate solid (kg/h)	Feeder rate liquid (kg/h)	Screw speed (rpm)	Temperature profile (°C)	Die diameter (mm)	Pressure die (Pa)	SME (kJ/kg)	Reference
(Berstorff) ZE25- 40:1	3.5	nd	nd	[70–120] [a](die 50–70)	7	2.1×10^{6}	nd	(Ubbink et al., 2001)
(Clextral) BC45- 20:1	[25–35]	[0.10–0.481]	175	[140-160] [a](die 185–195)	4	nd	nd	(Boutboul et al., 2002a)
(Coperion) ZSK25&Buhler44- 40:1	4	[0.4-1.1]	[150–200]	[15-120]	[0.5–1]	nd	< 180	(B. H. Van Lengerich, 2002) (Lengerich et al., 2010)
9.6	[3.2-6.8]	80	0.5					
(Buhler) DNDL44- 40:1	9	0.18	nd	[30-160]	[0.25- 1]	nd	< 180	(Leusner et al., 2002)
40:1 & 50:1	[2.16-115]	nd	[50-700]	nd	[0.8-1]	nd	< 180	(Kohlus and Pacha, 2004)
nd	[6-15]	[0.12-0.72]	100	<121	0.79	6.86×10^{6}	nd	(Zasypkin and Porzio, 2004; Zasypkin, 2011; Zasypkin et al., 2013)

(*Continued on next page*)

Table 9

Processing parameters for melt twin-screw extrusion microencapsulation:*extruder has 4 temperatures zones, the numbers in brackets correspond to a range of values. SME (= specific mechanical energy). *(Continued)*

Type of extruder (ratio L/D)	Feeder rate solid (kg/h)	Feeder rate liquid (kg/h)	Screw speed (rpm)	Temperature profile (°C)	Die diameter (mm)	Pressure die (Pa)	SME (kJ/kg)	Reference
(Prism Eurolab) KX16-40:1	0.96	0.4	[158- 242]	[50-167]	2	nd	nd	(Yuliani et al., 2006)
(Clextral) BC 21- 16:1	nd	nd	nd	nd	[1-3]	$[1\times10^5 - 10\times10^5]$	nd	(Bouquerand, 2007)
(Haake Polylab System)- 24:1	3	nd	80	*80, 105, 115, 95	3	$[1\times10^6 - 3.5\times10^6]$	nd	(Chang et al., 2010)
ZSK 26 Mc Coperion 29	10-30	1-3	300-800	140	3	nd	nd	(M. A. Emin and H. P. Schuchmann, 2013)
LTW 26 HB-Feinmechanik GmbH&Co (25:1))	1.50-3.00	nd	[248-748]	105-145	1.25	nd	[920-2115]	(Tackenberg et al., 2015)

However, they correspond more to a co-extrusion encapsulation technology because they are based on the same principles as melt injection.[4,5,11]

4.3. Melt Extrusion or Extrusion Microencapsulation

Melt extrusion encapsulation differs from melt injection encapsulation, not only because the apparatus employed is different but also because no pre- and/or post-treatment is applied to the materials (carriers, active compounds, and extrudate). The major difference between these two processes is the moisture content: in melt injection high levels of water are required so that the slurry can be extruded; while in melt extrusion the melt can take place at low water content levels. The advantage of working at low moisture content is that no post-extrusion drying process after is required, thus the material obtained is more homogenous (has less fractures on the surface). Therefore, melt extrusion encapsulation corresponds to a process allowing a glassy delivery system to be obtained, by melting matrix components and mixing them with the active compounds under specific conditions.

The technology applied is generally a twin-screw extruder, whose flexible configuration allows the melting, addition, mixing, and cooling of the carbohydrate mixture in a continuous system. According to the configuration of the extruder, different barrel temperatures, various inlet ports for liquid injection or solid feed, and screw profiles (conveyance, mixing and nest against) can be set up depending on the active ingredient and the biopolymer matrix.[15,19,20,49] The process is usually divided into three steps (Fig. 6): first of all, the introduction of powder mixture of the carbohydrate into the extruder's first barrel section, plus a plasticizer or additives can be added if required into the barrel next to the solid feed section. Then the heating and mixing zone are established upstream in order to form a rubbery, viscous, and homogeneous mass before the introduction of flavors. Finally, these flavors can be finely dispersed into the molten mass in the last sections of the extruder, via a pump.[16]

The liquid aroma compounds are generally introduced into the extruder's first barrel sections or right at the end. Also, depending on the product's final application, a pre-encapsulation step and/or post-coating of the delivery system can be made in order to increase final product performance.

Single-screw extrusion can also be used here, but the mechanical shear exerted on the molten mass is lower than in twin-screw extrusion, due to the fact that only a conveying screw is used, and this is filled-up all along the extruder barrel. Saleeb and Pickup[27] have employed a single-screw extruder for the encapsulation of orange oil flavor in a maltodextrin matrix. Extrusion temperature was ranged between 98 and 105°C and screw speed was set around 60 rpm. The flavor load obtained in this example was similar to the values found in twin-extrusion encapsulation that are around 5 and 40% (Table 9).

4.4. Key Process Parameters

The processing conditions in extruders are strongly determined by the chemical stability and physical properties of the coating and matrix material (molecular weight, desired glass transition of the final product, melt viscosity, and melting point). All these properties should be taken into account to establish adequate processing conditions. [68] However, depending on the technology applied (ram extrusion, Durarome®, or melt extrusion) process variables are also very important and can directly affect the macroscopic characteristics of the final product, e.g., the texture, aspect, and release properties. Figure 6 shows

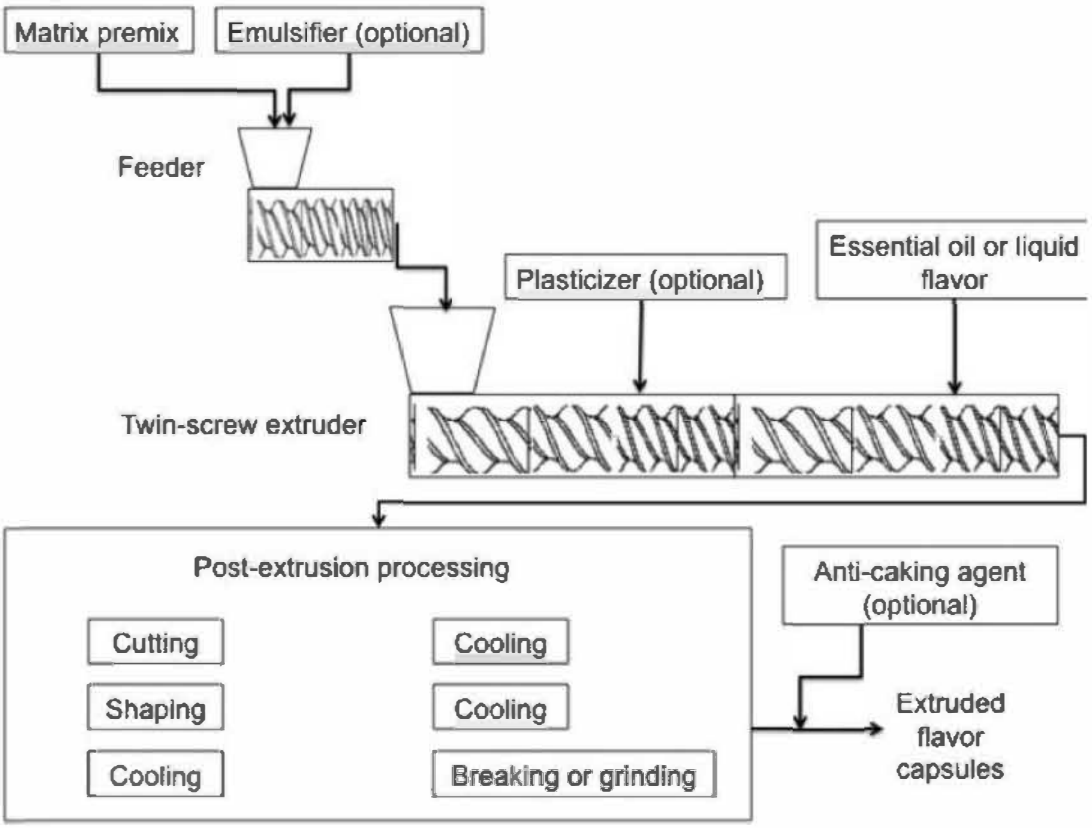

Figure 6. Scheme of flavor encapsulation by melt extrusion using a Twin-screw extruder (adapted from Ubbink and Schoonman[16]).

the different independent processing variables, for melt extrusion, influencing the properties of the final material.[110]

As already mentioned, carbohydrates constitute the mostly used matrix materials in melt extrusion and extrusion encapsulation,[69] and since these materials are essentially glassy and brittle, polar plasticizers are necessary to insure homogeneous melting of the carrier under appropriate thermo-mechanical stress and shear conditions. The preferred plasticizer is water.

The glass transition temperature of the delivery system depends on two important process parameters: extrusion temperature and moisture content. In addition, extrusion temperature and moisture content are directly related to viscosity and in the same way the volatile retention relies on viscosity. For this reason, temperature and moisture content are considered the most important factors affecting volatile retention. Therefore controlling viscosity is critical and thus, measurements of exit die pressure are always made.[94] The examples given in Table 9 show that, in general, pressure at the die exit is in of the same range for the studies presented (1×10^5 and 7×10^6 Pa) and glass transition temperatures for these delivery systems are around 30°C and 50°C. This implies that the moisture contents employed for these formulations are of the same order. And in fact, moisture content of the examples shown in Table 6, are in agreement with the pressure values given in Table 9. Zasypkin and Porzio,[30] Chang et al.,[35] and Benczedi et al.[34] measured pressures at the die's exit of 6.86×10^6 Pa, 3.5×10^6 Pa and 1×10^5 to 50×10^5 Pa and a moisture content of 7.5% (w/w), 9.3% (w/w) and 12.3% (w/w), respectively.

As mentioned earlier, water is the key parameter governing the stability of biopolymers. It influences the crystalline and amorphous structures, the glass transition

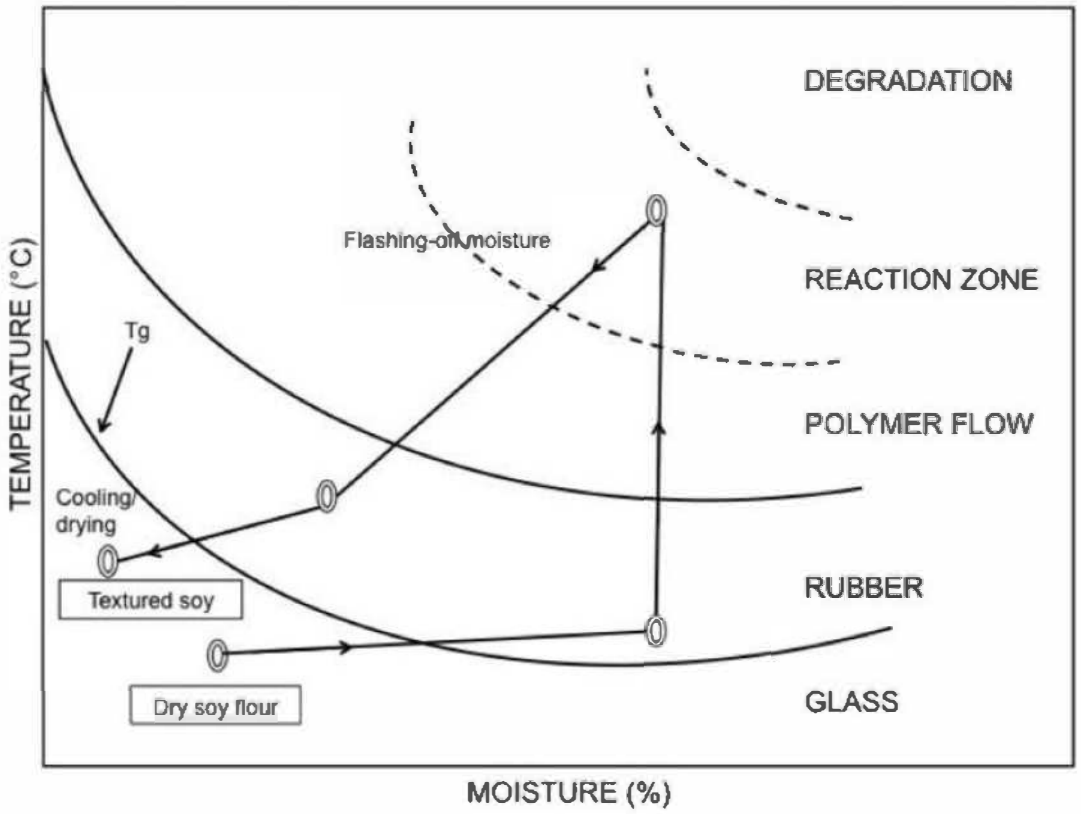

Figure 7. State diagram showing transformations of proteins during the wetting, heating, cooling, and drying stages of extrusion cooking (adapted from Kokini et al.[111]).

temperature and consequently the thermoplastic properties of biopolymers. Increasing the moisture content of a biopolymer increases the chain mobility and the heat capacity, but it decreases the viscosity and the system glass transition temperature. All these physico-chemical properties can be explained by how water interacts with the biopolymer.[74] Understanding water-biopolymer interactions gives a better insight thermo-mechanical processing. Similarly, knowing water-biopolymer interactions allows the processing conditions to be determined in order to better target the final properties of the material.

Glass transition temperature of the biopolymer is correlated to water-biopolymer interactions. Thanks to a combination of mechanical spectrometry and differential scanning calorimetry data, the glass transition temperature of a protein-based matrix can be determined. The results provide a better understanding of the phase transition behavior of amorphous biopolymers at different moisture contents. For instance, Kokini and co-workers[111] determined protein state diagrams, in order to predict physical states and phase transitions of the material during processing conditions (e.g., extrusion or baking). Figure 7 shows the state diagram of proteins under different physical conditions (i.e., cooling, heating, drying, wetting) during extrusion cooking processing. As mentioned above, this diagram demonstrates the importance of moisture content and the temperature conditions that are required to obtain the desired polymeric matrix during a thermo-mechanical process (melt extrusion, melt injection, thermo-molding, etc.).

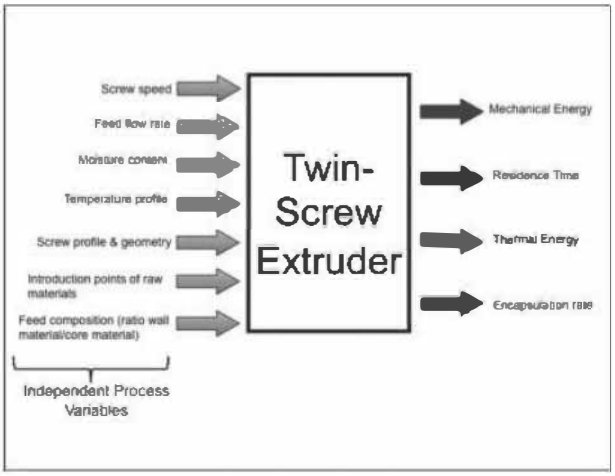

Figure 8. Scheme of Twin-screw extrusion microencapsulation processing variables; on the left the independent process variables and, on the right the measurable responses.

The other main process variables in melt extrusion are the temperature profile, screw profile and geometry, screw speed, feed flow rate, moisture content and feed composition.[19,20,49] The influence of these variables can be evaluated by measuring the mechanical or the thermal energy, the residence time, or other properties of the extrudate like product expansion (axial and radial expansion), breaking strength, encapsulation efficiency and release rate.[35,112,113] The process of melt extrusion encapsulation has different independent variables and measurable responses that must be taken into account (Fig. 8). The most frequently measured responses are encapsulation rate or encapsulation efficiency, and both can be used for discussion.

The processing conditions described in both patents and academic work (Table 9) are quite similar. The temperature profile is more or less the same, but the choice of extrusion temperature depends on the type of matrix and active material. In the case of active materials like sensitive oils rich in polyunsaturated fatty acid, extrusion temperature does not exceed 120°C [39,98]. In fact, the temperature profile retained for melt extrusion does not exceed 160°C in order to avoid thermal degradation of the compounds to be encapsulated (fragrances, flavors, bioactive food compounds, etc.). However, not only the core material, but also the carrier material may be affected by the temperature profile. For example, mixtures of oligosaccharides are more resistant to temperature than maltodextrins, which begin to break down at around 180°C. Hence, Leusner et al.[66] have applied an extrusion temperature of about 160°C to entrap ascorbic acid and calcium in a mixture of oligosaccharides, while Chang et al.[35] applied a temperature no higher than 115° to entrap ascorbic acid, just in maltodextrins.

Although the temperature profile has a great impact on flavors' stability during processing, screw speed is also important to control in order to avoid degradation of the flavors by mechanical shear stress. Indeed, screw speed is crucial because it exerts shear stress into the polymer/active core mixture, modifying its viscosity by involving self-heating through viscous friction, and also determining the residence time of the mixture inside the extruder. Usually a long residence time and high shear stress can cause thermal degradation not only of the active core (flavors, fragrances, bioactive food compounds) but also of the carriers (degradation, polymerization, or offside reactions). Similarly, viscosity decreases when the shear stress exerted increases. For this reason, when the compound to be entrapped is very sensitive to temperature or shear stress, mild extrusion

conditions are required. In the example quoted above, Chang et al.,[35,50] have employed gentle temperatures not above 115°C and a screw speed of 80 rpm for the encapsulation of ascorbic acid in maltodextrin. In the case of proteins used as carriers, screw speed is around 150 rpm, in order to avoid their degradation by mechanical shear.

The screw profile, along with the temperature profile or screw speed, is the major parameter governing the structural transformation of the polymeric matrix (viscosity, expansion, physical changes). Hence, the screw profile can play a central role influencing the residence time inside the extruder. Nonetheless, in some papers, this parameter is not described or studied. In general the screw profile chosen for most of the examples found in the literature consisted of conveying and mixing elements. Reverse pitch screw elements are avoided in order to reduce both shear stress and residence time. Recent works have focused on the influence of screw profile on the polymer-based matrix, but not on the effect that it could have on volatile's retention.[19,20]

The parameter that has been given the most of attention in the literature is the location of the flavor injection port. In fact, depending on the position where the flavor is introduced in the extruder barrel, the retention of volatiles can change, possibly leading to significant losses during the process.[15,55,78,94] Indeed, the location of the injection port directly influences four key factors in the extrusion process, which in turn may impact the retention of volatiles. These factors are: (i) the pressure drop when the extrudate exits the die, (ii) the relative volatility and diffusion (thermodynamic parameters) of the active compounds in the system, (iii) the interactions between the active compounds and the matrix, and (iv) the degradation reactions (oxidation, thermal degradation, polymerization). For example, Lengerich [98] has demonstrated that changing the point of introduction can reduce the losses of active compounds. The highest loss (72,3%) was obtained when active compound was introduced in the first barrel section, whereas when it was introduced into the seventh barrel section of the extruder, losses were about 12,2%. This is because when the active compound is injected into the first barrel, it is exposed to temperatures around 120°C and 140°C for a longer period of time. Conversely, if the active compound is introduced in barrel seven, it is only exposed briefly to high temperatures.

There are three methods to introduce flavors into an extruder. The first consists of pre-incorporation of the flavors into the feed material prior to extrusion, either by preparing an emulsion of carrier/active core, or by spray-drying the flavors with a part of solid carrier and then mixing this with all carrier material. The disadvantage of this method is that since the active compound is added at the beginning of the extrusion process, volatile molecules are more likely to be degraded because of the harsh conditions at the beginning of the extrusion process. The second method is the direct injection of flavors into the extruder, into the last or the middle barrel section. The problem with this procedure is that, even though it leads to better retention rates, flavors are lost due to expansion at the extruder's exit die, due to the pressure increase linked to the reduction in size of the exit die. As a consequence the volatiles are flashed-off at the die level. Finally, the last method is a combination of pre-incorporation and post-coating of the delivery system, this method is highly cost-intensive but it improves the quantity of flavor retained in the matrix and allows the release of the active compounds to be slowed down.

A principal difficulty encountered when encapsulating liquids by extrusion processes is solid-liquid separation, which leads to oil exudation from the extrudate mass and is due to filtration of the phase having the highest mobility through the less mobile phase (for a comprehensive overview of solid-liquid separation in extruder, see Bouvier and Campanella[114]).

Hence, rare are the papers where flavors are introduced directly into the extruder without any pre-encapsulation treatment. Kollengode and Hanna[38,55] were the first to inject pre-encapsulated the flavors directly into the end barrel section of an extruder. In their case, the flavors were pre-encapsulated with β-cyclodextrin and then injected into the extruder. Even though this technique of pre-encapsulation of the core material before extrusion allows having a better protection of flavors against losses, the pre-encapsulation step raises the cost, and even more so if β-cyclodextrin is employed. Using β-cyclodextrin and spray drying are very highly expensive pre-encapsulation techniques.

In more recent industrial patents, direct injection of flavors in the form of an emulsion (i.e. direct injection of flavors in a pre-encapsulated form) has become more and more common in order to minimize losses of volatiles during the extrusion process, vary the release rate and reduce production costs. Core materials are introduced into the extruder as an emulsion of active and additive (plasticizers, compatibilizing agents and antioxidants compounds). Or in other cases, core materials are mixed with a part of the matrix compounds that are in a liquid state (i.e., corn syrup).[35,40,55,66,115]

The use of extrusion as a microencapsulation technology is relatively new and comprehensive engineering models adapted to the behavior of paste-like oil-in-matrix "emulsions" are missing. In this context, the comprehensive exposition of the engineering principles of extrusion technology in food and non-food materials, recently published by Bouvier and Capanella,[114] can be considered as an inspiring source for further work in this area.

5. Conclusions and Future Prospects

Encapsulation of flavors and fragrances, as well as other active compounds (nutraceutics and bioactive food components, pesticides, dyes, enzymes) is a domain that is still in expansion due to the increasing consumer's demands for better quality from the raw materials to the final products.

It is a must to reduce energy consumption, waste production and pollution. Therefore, global policies are focused on leading research and industrial development, into a more environmentally friendly and sustainable domains.[116]

Twin-screw extrusion can be seen as versatile technology that can be employed in different industrial domains, and can contribute with great benefits to sustainable development, i.e., for green extraction of raw materials.[117–119]

As an encapsulation process, twin-screw extrusion technology can be categorized as a green process (if compared with other encapsulation technologies: interfacial polycondesation, suspension and emulsion polymerization, and fluidized bed coating among others). Twin-screw extrusion encapsulation, as it was mentioned before, is a one-pot encapsulation technique, which combines: the formation of the wall material, the dispersion of the active principle, and at the exit of the die the forming of the encapsulated material. All these three different stages take place inside the barrel or the die of the extruder [30]. To compare, spray-drying encapsulation technology needs the prior preparation of the liquid formulation [8,105,107,120,121]. The reducing number of steps in an industrial process contributes to reduce energy consumption. Moreover, encapsulation by twin-screw extrusion does not require a pre- or post-treatment after extrusion unlike most of the other encapsulation methods.

Two other remarkable assets of twin-screw extrusion are the absence use of organic solvents (contrary to the polymerization techniques[122] and fluidized bed coating[123]) and the low amount of water (20% water content) as compared with spray-drying technology

(that requires more than 80% of water). Both of these points involve the reduction of pollution and production costs during the manufacturing process.

To counteract the strong dominance of spray drying in the microencapsulation area, apart from reducing production costs, extrusion encapsulation appears as a versatile and sustainable technique for glassy microencapsulation. Extrusion microencapsulation is presented as a pioneering technology allowing the creation of new delivery systems, providing not only protection of the active compound but also, in some extent, its controlled release.

There remain, however, clear areas of improvement that would help extrusion encapsulation to become a more universal tool. In first rank, increasing the internal, encapsulated liquid phase (payload) in the extrudate would help reducing the material cost and make the technology more affordable for other applications, such as laundry products or agro-formulations. Secondly, there is a strong need for matrices having simultaneously a high encapsulation power and a low hygroscopicity, e.g. for better stability under moist environment. Finally, much remains to be done in the area of triggered release of volatile materials under pre-defined conditions.

Among the different technologies employed in extrusion encapsulation, with all the processing parameters that have to be controlled in order to obtain "the perfect delivery system" with the specific characteristics (T_g, moisture content, encapsulation efficiency...), a lack of understanding of the phenomena occurring during microencapsulation seems to be the major limitation in this domain. For this reason a concerted approach to food material science, materials science, flavor and fragrances chemistry and physical chemistry are required for further progress in this area. Emphasis must be given to determine the type of interactions between the matrix and the encapsulated materials, the state of this matrix, and the extrudate morphology, so as to establish the mechanisms, which control the release of volatile active compounds when and where they are desired.

References

1. Augustin, M. A.; Hemar, Y. "Nano- and micro-structured assemblies for encapsulation of food ingredients", *Chem. Soc. Rev.* **2009**, *38*, 902–912.
2. Dubey, R.; Shami, T. C.; Rao, K. U. B. "Microencapsulation technology and applications", *Def. Sci. J.* **2009**, *59* (1), 82–85.
3. Madene, A.; Jacquot, M.; Scher, J.; Desobry, S. "Flavour encapsulation and controlled release: A review", *Int. J. Food Sci. Technol.* **2006**, *41*, 1–21.
4. Đorđević, V.; Balanč, B.; Belščak-Cvitanović, A.; Lević, S.; Trifković, K.; Kalušević, A.; Kostić, I.; Komes, D.; Bugarski, B.; Nedović, V. "Trends in encapsulation technologies for delivery of food bioactive compounds", *Food Eng. Rev.* **2015**, 7(4), 452–490.
5. Nedovic, V.; Kalusevic, A.; Manojlovic, V.; Levic, S.; Bugarski, B. "An overview of encapsulation technologies for food applications", *Procedia Food Sci.* **2011**, *1*, 1806–1815.
6. Zhu, G. Y.; Xiao, Z. B.; Zhou, R. J.; Yi, F. P. "Fragrance and flavor microencapsulation technology", *Adv. Mater. Res.* **2012**, *535-537*, 440–445.
7. Goubet, I.; Quere, J. L. L.; Voilley, A. "Retention of aroma compounds by carbohydrates: influence of their physicochemical characteristics and of their physical state: A review", *J. Agric. Food Chem.* **1998**, *46*, 1981–1990.
8. Gouin, S. "Microencapsulation: Industrial appraisal of existing technologies and trends: A review", *Trends Food Sci. Technol.* **2004**, *15*, 330–347.
9. Kenyon, M. M. Modified starch, maltodextrin and corn syrup solids as wall materials for food encapsulation. In *Encapsulation and Controlled Release of Food Ingredients*; ACS Symposium Series; Reineccius & Risch, 1995.

10. Risch, S. J.; Reineccius, G. A. *Flavor Encapsulation*, American Chemical Society Symposium.; ACS Symposium Series; Washington D.C., 1988; Vol. 370.
11. Manojlovic, V.; Rajic, N.; Djonlagic, J.; Obradovic, B.; Nedovic, V.; Bugarski, B. "Application of Electrostatic extrusion – flavour encapsulation and controlled release", *Sensors* **2008**, *8* (3), 1488–1496.
12. Wang, X.; Yuan, Y.; Yue, T. "The application of starch-based ingredients in flavor encapsulation", *Starch - Stärke* **2015**, *67* (3-4), 225–236.
13. Quellet, C.; Schudel, M.; Ringgenberg, R. "Flavors and fragrances delivery systems", *Chimia* **2001**, *55* (5), 421–428.
14. Uhlemann, J.; Reiss, I. "Product design and process engineering usin the examples of flavors", *Chem. Eng. Technol.* **2010**, *33* (2), 199–212.
15. Tackenberg, M. W.; Krauss, R.; Schuchmann, H. P.; Kleinebudde, P. "Encapsulation of orange terpenes investigating a plasticisation extrusion process", *J. Microencapsul.* **2015**, 32 (4), 1–10.
16. Ubbink, J.; Schoonman, A. Flavor Delivery Systems. *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: NJ, 2003; Vol. 11, pp. 527–563.
17. Blake, A. "Flavor encapsulation with carbohydrate glasses", *Int. Food Ingred.* **1994**, *3*, 30–34.
18. Benczedi, D.; Bouquerand, P. E. Process for the Preparation of Granules for the Controlled Release of Volatile Compounds. US 6,607,771 B2, 19 **2003**.
19. Emin, M. A.; Schuchmann, H. P. "Analysis of the dispersive mixing efficiency in a twin-screw extrusion processing of starch based matrix", *J. Food Eng.* **2013**, *115* (1), 132–143.
20. Emin, M. A.; Schuchmann, H. P. "Droplet breakup and coalescence in a twin-screw extrusion processing of starch based matrix", *J. Food Eng.* **2013**, *116* (1), 118–129.
21. Schultz, H. T.; Calif, L. Preparation of Solid Flavoring Compositions. US 2,856,291, 14 **1958**.
22. Swisher, H. E. Solid Flavoring Composition and Method of Preparing the Same. US 2,809,895, **1957**.
23. Black, M.; Popplewell, L.; Porzio, M. Controlled Release Encapsulation Compositions. US 5,756,136, 26 **1998**.
24. Levine, H.; Slade, L.; Lengerich, B. V.; Pickup, G. J. Glassy Matrices Containing Volatile And/or Labile Components and Processes for Preparation and Use Thereof. US 5,009,900, 23 **1991**.
25. Miller, D. H.; Mutka, J. R. Solid Essential Oil Flavor Composition. US 4707367, 17 **1987**.
26. Sair, L.; Sair, R. Encapsulation of Active Agents as a Microdispersions in Homogeneous Natural Polymeric Matrices. US 4, 230, 687, 28 **1980**.
27. Saleeb, Z. F.; Pickup, G. J. Fixation of Volatiles in Extruded Glass Substrates. US 4,820, 534, 11 **1989**.
28. Feng, T.; Xiao, Z.; Tian, H. "Recent patents in flavor microencapsulation", *Recent Pat. Food Nutr. Agric.* **2009**, *1*, 193–202.
29. Porzio, M. "Melt extrusion and melt injection: An in depth look at the strengths, limitations and applications of these two processes", *Perfum. Flavorist* **2008**, *33*, 48–53.
30. Zasypkin, D.; Porzio, M. "Glass encapsulation of flavours with chemically modified starch blends", *J. Microencapsul.* **2004**, *21* (4), 385–397.
31. Hau, M.; Gray, D.; Taylor, A. "Binding of volatiles to extruded starch at low water contents", *Flavour Fragr. J.* **1998**, *13*, 77–84.
32. Lengerich, B. H. V. Embedding and encapsulation of sensitive components into a matrix to obtain discrete controlled release particles. US 2002/0044968 A1, **2002**.
33. Porzio, M.; Zasypkin, D. Encapsulation Compositions and Process for Preparing the Same. US 2010/0289164 A1, **2010**.
34. Benczedi, D.; Bouquerand, P. E.; Steinboeck, E. Process for the Preparation of Extruded Delivery Systems. US 8,017,060 B2, 13 **2011**.
35. Chang, D.; Abbas, S.; Hayat, K.; Xia, S.; Zhang, X.; Xie, M.; Kim, J. M. "Original Article: Encapsulation of ascorbic acid in amorphous maltodextrin employing extrusion as affected by matrix/core ratio and water content", *Int. J. Food Sci. Technol.* **2010**, *45* (9), 1895–1901.

36. Bouquerand, P. E. Extruded Glassy Vitamin C Particles. EU 1836902 A1, September 26, **2007**.
37. Kohlus, R.; Pacha, E. F. Process for Producing Structured Materials. WO 2004/099359 A1, 18 **2004**.
38. Kollengode, A.; Hanna, A. "Cyclodextrin complexed flavors retention in extruded starches", *J. Food Sci.* **1997**, *65* (5), 1057–1060.
39. Lengerich, B. H. V.; Walther, G.; Auken, B. V. Encapsulation of Readily Oxidizable Components. US 7, 803,413B2, 28 **2010**.
40. Ubbink, J.; Quellet, C.; Taschi, M. Encapsulated Liquid. US 1116515A2, 18 **2001**.
41. Valentinotti, S.; Armanet, L.; Porret, J. Encapsulated Polyunsaturated Fatty Acids. US 2006/0134180A1, **2006**.
42. Yuliani, S.; Torley, P. J.; D'Arcy, B.; Nicholson, T.; Bhandari, B. "Extrusion of mixtures of starch and d-limonene encapsulated with b-cyclodextrin: Flavour retention and physical properties", *Food Res. Int.* **2006**, *39*, 318–331.
43. Zasypkin, D. Melt extrusion encapsulation of flavors and other encpasulates in a carrier containing spices and herbs. US 2011256199, October 20, **2011**.
44. Duda, J. L. "Molecular diffusion in polymeric systems", *Pure Appl. Chem.* **1985**, *57* (11), 1681–1690.
45. Vrentas, J. S.; Duda, J. L. "A free-volume interpretation of the influence of the glass transition on diffusion in amorphous polymers", *J. Appl. Polym. Sci.* **1978**, *22* (8), 2325–2339.
46. Tackenberg, M. W.; Geisthövel, C.; Marmann, A.; Schuchmann, H. P.; Kleinebudde, P.; Thommes, M. "Mechanistic study of carvacrol processing and stabilization as glassy solid solution and microcapsule", *Int. J. Pharm.* **2015**, *478* (2), 597–605.
47. Tackenberg, M. W.; Thommes, M.; Schuchmann, H. P.; Kleinebudde, P. "Solid state of processed carbohydrate matrices from maltodextrin and sucrose", *J. Food Eng.* **2014**, *129*, 30–37.
48. Benczedi, D.; Blake, A. "Encapsulation and controlled released of flavours", *Leatherhead Food RA Food Ind. J.* **1999**, *2*, 36–48.
49. Tackenberg, M. W.; Krauss, R.; Marmann, A.; Thommes, M.; Schuchmann, H. P.; Kleinebudde, P. "Encapsulation of liquids using a counter rotating twin screw extruder", *Eur. J. Pharm. Biopharm.* **2015**, *89*, 9–17.
50. Chang, D. W.; Zhang, X. M.; Kim, J. M. "Encapsulation of vitamin E in glassy carbohydrates by extrusion", *Adv. Mater. Res.* **2013**, *842*, 95–99.
51. Conde-Petit, B.; Escher, F.; Nuessli, J. "Structural features of starch-flavor complexation in food model systems", *Trends Food Sci. Technol.* **2006**, *17*, 227–235.
52. Heinemann, C.; Zinsli, M.; Renggli, A.; Escher, F.; Conde-Petit, B. "Influence of amylose-flavor complexation on build-up and breakdown of starch structures in aqueous food model systems", *Food Sci. Technol.* **2005**, *38*, 885–894.
53. Nuessli, J.; Sigg, B.; Conde-Petit, B.; Escher, F. "Characterization of Amylose—flavour complexes by DSC and x-ray diffraction", *Food Hydrocoll.* **1997**, *11* (1), 27–34.
54. Nuessli, J.; Conde-Petit, B.; Trommsdorff, U. R.; Escher, F. "Influence of starch flavour interactions on rheological properties of low concentration starch systems", *Carbohydr. Polym.* **1995**, *28* (2), 167–170.
55. Kollengode, A.; Hanna, A. "Effect of low boiling point liquids on volatile retentions in starch extrudates", *Lebensm.-Wiss. Technol.* **1997**, *30*, 814–818.
56. Bohn, D.; Cadwallader, K.; Schmidt, S. Use of DSC, DVS-DSC, and DVS-Fast GC-FID to evaluate the physicochemical changes that occur in artificial cherry durarome® upon humidification. *J. Sci.* **2005**, *70* (2), E109–E116.
57. Cayot, N.; Karbowiak, T.; Savary, G.; Voilley, A.; Dury-Brun, C. "Measurement of transport phenomena of volatile compounds: A review", *Food Res. Int.* **2008**, *41*, 349–362.
58. Druaux, C.; Voilley, A. "Effect of food composition and microstructure on volatile flavour release : Review", *Trends Food Sci. Technol.* **1997**, *8*, 364–368.
59. Landy, P.; Druaux, C.; Voilley, A. "Retention on aroma compounds by proteins in aqueous solution", *Food Chem.* **1995**, *54* (4), 387–392.

60. Boutboul, A.; Lenfant, F.; Giampaoli, P.; Feigenbaum, A.; Ducruet, V. "Use of inverse gas chromatography to determine thermodynamic parameters on aroma-starch interactions", *J. Chromatogr. A* **2002**, *969*, 9–16.
61. Boutboul, A.; Giampaoli, P.; Feigenbaum, A.; Ducruet, V. "Use of inverse gas chromatography with humidity control of the carrier gas to characterised aroma-starch interactions", *Food Chem.* **2000**, *71*, 387–392.
62. Delarue, J.; Giampaoli, P. "Study of interaction phenomena between aroma compounds and carbohydrate matrixes by inverse gas chromatography", *J. Agric. Food Chem.* **2000**, *48*, 2373–2375.
63. Gunning, Y.; Gunning, P.; Kemsley, E.; Parker, R.; Ring, S.; Wilson, R.; Blake, A. "Factors affecting the release of flavor encapsulated in carbohydrate matrixes", *J. Agric. Food Chem.* **1999**, *47*, 5198–5205.
64. Jouquand, C.; Ducruet, V.; Giampaoli, P. "Partition coefficients of aroma compounds in polysaccharide solutions by the phase ratio variation method", *Food Chem.* **2004**, *85*, 467–474.
65. Menzi, H.; Perren, M.; Ringgenberg, R. Aromatic Granulated Material. US 6056949, February 5, **2000**.
66. Leusner, S. J.; Lakkis, J.; Lengerich, B. H. V.; Jarl, T. Oligosaccharide encapsulated mineral and vitamin ingredients. US 6468568 B1, **2002**.
67. Abbas, S.; Chang, D.; Hayat, K.; Xiaoming, Z. "Ascorbic acid: Microencapsulation techniques and trends: A review", *Food Rev. Int.* **2012**, *28*, 343–374.
68. Crowley, M. M.; Zhang, F.; Repka, M. A.; Thumma, S.; Upadhye, S. B.; Battu, S. K. "Review: Pharmaceutical applications of hot-melt extrusion: Part I", *Drug Dev. Ind. Pharm.* **2007**, *33* (9), 909–926.
69. Ubbink, J.; Krüger, J. "Physical approaches for the delivery of active ingredients in foods: Review", *Trends Food Sci. Technol.* **2006**, *17*, 244–254.
70. Renard, D.; Reddy, T. Polymères D'origine Biologique Pour La Microencapsulation. In *Des sciences Aux Technologies;*Vandamme, T.; Poncelet, D.; Subra-Paternault, P., Eds.; Lavoisier: Paris, France, 2007; pp. 175–188.
71. Gaonkar, A. G.; Vasisht, N.; Khare, A. R.; Sobel, R. *Microencapsulation in the Food Industry: A Practical Implementation Guide*; Elsevier; Amsterdam, 2014.
72. Zasypkin, D.; Paranjpe, S.; Reick, M.; Johnson, S. Extrusion Encapsulation of Actives at an Increased Load, Using Surface Active Plant. US 2013243851A1, September 19, **2013**.
73. Slade, L.; Levine, H. Glass Transitions and Water-Food Structure Interactions. In *Advances in Food and Nutrition Research*; Kinsella, J. E., Taylor, S. L., Eds.; Academic Press, 1995; Vol. 38, pp. 103–234.
74. Rouilly, A.; Jorda, J.; Rigal, L. "Thermo-mechanical processing of sugar beet pulp. II. Thermal and rheological properties of thermoplastic SBP", *Carbohydr. Polym.* **2006**, *66* (1), 117–125.
75. Slade, L.; Levine, H.; Reid, D. S. "Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety", *Crit. Rev. Food Sci. Nutr.* **1991**, *30* (2-3), 115–360.
76. Nelson, K. A.; Labuza, T. P. "Water activity and food polymer science: Implications of state on Arrhenius and WLF models in predicting shelf life", *J. Food Eng.* **1994**, *22* (1–4), 271–289.
77. Hancock, B. C.; Zografi, G. "The relationship between the glass transition temperature and the water content of amorphous pharmaceutical solids", *Pharm. Res.* **1994**, *11* (4), 471–477.
78. Bhandari, B.; D'Arcy, B.; Gordon, Y. "Flavour retention during high temperature short time extrusion cooking process: A review", *Int. J. Food Sci. Technol.* **2001**, *36*, 453–461.
79. Jacquot, M.; Madène, A.; Desobry, S. Encapsulation d'arômes Alimentaires. In *Des Sciences aux Technologies*; Vandamme, T.; Poncelet, D.; Subra-Paternault, P., Eds.; Lavoisier: Paris, France, 2007; pp. 227–294.
80. Avaltroni, F.; Bouquerand, P. E.; Normand, V. "Maltodextrin molecular weight distribution influence on the glass transition temperature and viscosity in aqueous solutions", *Carbohydr. Polym.* **2004**, *58* (3), 323–334.

81. Bangs, W. M.; Reineccius, G. A. The influence of dryer infeed matrices on the retention of volatile flavor compounds during spray drying. *Jounral Food Sci.* **1982**, *47* (1), 254–259.
82. Shrestha, A. K.; Halley, P. J. Starch Modification to Develop Novel Starch-Biopolymer Blends: State of Art and Perspectives, Ch. 5. In *Starch Polymers*; Avérous, P. J. H., Ed.; Elsevier: Amsterdam, 2014; pp. 105–143.
83. Donovan, J. W. "Phase transitions of the starch–water system", *Biopolymers* **1979**, *18* (2), 263–275.
84. Zeleznak, K. J.; Hoseney, R. C. "The glass transition in starch", *Cereal Chem.* **1987**, *64*, 121–124.
85. Chabrat, E.; Abdillahi, H.; Rouilly, A.; Rigal, L. "Influence of citric acid and water on thermoplastic wheat flour/poly(lactic Acid) Blends. I: Thermal, mechanical and morphological properties", *Ind. Crops Prod.* **2012**, *37* (1), 238–246.
86. Chinnawasmy, R.; Hanna, M. A. "Relationship between amylose content and extrusion-expansion of corn starches", *Cereal Chem.* **1998**, *65* (2), 138–143.
87. Nesterenko, A.; Alric, I.; Silvestre, F.; Durrieu, V. "Vegetable proteins in microencapsulation : a review of recent interventions and their effectiveness", *Ind. Crops Prod.* **2013**, *42*, 469–479.
88. Goss Milani, T. M.; Cortazzo Menis, M. E.; Jordano, A.; Boscolo, M.; Conti-Silva, A. C. "Pre-extrusion aromatization of a soy protein isolate using volatile compounds and flavor enhacers: Effect on physical characteristics volatile retention and sensory characteristics of extrudates", *Food Res. Int.* **2014**, *62*, 375–381.
89. Charve, J.; Reineccius, G. A. "Encapsulation performance of proteins and traditional materials for spray dried flavors", *J. Agric. Food Chem.* **2009**, *57*, 2486–2492.
90. Guichard, E. "Interactions between flavor compounds and food ingredients and their influence on flavor perception", *Food Rev. Int.* **2002**, *18* (1), 49–70.
91. Gremli, H. A. Interaction of flavor compounds with soy protein. *J. Am. Oil Chem. Soc.* **1974**, *51* (1), 95A–97A.
92. Benczedi, D.; Bouquerand, P. E. Process for the Preparation of Granules for the Controlled Release of Volatile Compounds. 01/17372 A1, March 15, **2001**.
93. Gregson, C.; Sillick, M. Method of Preparing a Granular Delivery System. US 2429313 A1, **2012**.
94. Yuliani, S.; Bhandari, B.; Rutgers, R.; D'Arcy, B. "Application of microencapsulated flavor to extrusion product", *Food Rev. Int.* **2004**, *20* (2), 163–185.
95. Porzio, M.; Popplewell, L. Encapsulation Compositions. US 5897, 897A, 27 **1999**.
96. Auken, B. V.; Lengerich, B. H. V.; Walther, G. Encapsulation of Readily Oxidizable Components. US 2007/055815 A1, **2007**.
97. Kaushik, P.; D.; Barrow, C. J.; Adhikari, B. "Microencapsulation of omega-3-fatty acids: A review of microencapsulation and characterization methods", *J. Funct. Foods* **2014**, 1–14.
98. Lengerich, B. H. V. Encapsulation of Sensitive Components into a Matrix to Obtain Discrete Shelf-Stable Particles. US 6,500,463B1, 21 **2002**.
99. Saleeb, Z. F.; Arora, K. V. Method of Preparaing Glass Stabilized Materials. US 5972395, **1999**.
100. Vieira, M. G. A.; Silva, M. A. da; Santos, L. O. dos; Beppu, M. M. "Natural based plasticizers and biopolymer films: A review", *Eur. Polym. J.* **2011**, *47*, 254–263.
101. Gaudin, S.; Lourdin, D.; Ilari, J. L.; Colonna, P. "Plastisation and mobility in starch-sorbitol films", *J. Cereal Sci.* **1999**, *29*, 273–284.
102. Lourdin, D.; Colonna, P.; Ring, S. "Volumetric behaviour of maltose/water, maltose/glycerol and starch/sorbitol/water systems mixtures in relation to structural relaxation", *Carbohydr. Res.* **2003**, *338*, 2883–2887.
103. Benczedi, D.; Bouquerand, P. E. Process for the Preparation of Granules for the Controlled Release of Volatile Compounds. 2001/0036503 A1, Spring 2001.
104. Wolf, B. "Polysaccharide functionality through extrusion processing", *Curr. Opin. Colloid Interface Sci.* **2010**, *15* (1-2), 50–54.

105. Desai, K. G. H.; Park, H. J. "Recent developments in microencapsulation of food ingredients", *Dry. Technol.* **2005**, *23*, 1361–1394.
106. Zuidam, N. J.; Shimoni, E. Overview of microencapsulates for use in food products or processes and methods to make them. In *Encapsulation Technologies for Active Food Ingredients and Food Processing*; Zuidam, N. J., Nedovic, V., Eds.; Springer: New York, 2010; pp. 3–29.
107. Gibbs, B. F.; Kermasha, S.; Alli, I.; Mulligan, C. N. "Encapuslation in the food industry: A review", *Int. J. Food Sci. Nutr.* **1999**, *50*, 213–224.
108. Risch, S. J. Chapter 1. Encapsulation: Overview of uses and techniques. In *Encapsulation and Controlled Release of Food Ingredients*; Reineccius, G. A., Ed.; ACS Symposium Series; Reineccius & Risch, 1995; pp. 1–7.
109. Vos, P.de; Faas, M. M.; Spasojevic, M.; Sikkema, J. "Encapsulation for preservation of functionality and targeted delivery of bioactive food components: A review", *Int. Dairy J.* **2010**, *20*, 292–302, 8, 853–860.
110. Thiry, J.; Krier, F.; Evrard, B. "A review of pharmaceutical extrusion: Critical process parameters and scaling-up", *Int. J. Pharm.* **2015**, *479* (1), 227–240.
111. Kokini, J. L.; Cocero, A. M.; Madeka, H.; de Graaf, E. "The development of state diagrams for cereal proteins", *Trends Food Sci. Technol.* **1994**, *5* (9), 281–288.
112. Carr, M. E.; Wing, R. E.; Doane, W. M. "Encapsulation of atrazine within a starch matrix by extrusion processing", *Cereal Chem.* **1991**, *68* (3), 262–266.
113. Choudhury, G. S.; Gautam, A. "Screw configuration effects on macroscopic characteristics of extrudates produced by twin-screw extrusion of rice flour", *J. Food Sci.* **1999**, *64* (3), 479–487.
114. Bouvier, J.-M.; Campanella, O. H. The Generic Extrusion Process V. In *Extrusion Processing Technology*; Wiley: NJ, 2014; pp. 393–464.
115. Porzio, M.; Popplewell, L. Encapsulation Compositions. US 6,187,351 B1, 13 **2001**.
116. Morais, A. R. C.; Bogel-Lukasik, R. "Green chemistry and the biorefinery concept", *Sustain. Chem. Process.* **2013**, *1* (18), 1–3.
117. Chemat, F.; Vian, M. A.; Cravotto, G. "Green Extraction of natural products: Concepts and principles", *Int. J. Mol. Sci.* **2012**, *13*, 8615–8627.
118. Rombaut, N.; Tixier, A. S.; Bily, A.; Chemat, F. "Green extraction processes of natural products as tools for biorefinery", *Biofuels Bioprod. Biorefining* **2014**, *8*, 530–544.
119. Clark, J. H.; Budarin, V.; Deswarte, F. E. I.; Hardy, J. J. E.; Kerton, F. M.; Hunt, A. J.; Luque, R.; Macquarrie, D. J.; Milkowski, K.; Rodriguez, A.; Samuel, O.; Tavener, S. J.; White, R. J.; Wilson, A. J. "Green chemistry and the biorefinery: A partnership for a sustainable future", *Green Chem.* **2006**, *8*, 853–860.
120. Gharsallaoui, A.; Roudaut, G.; Chambin, O.; Voilley, A.; Saurel, R. "Applications of spray-drying in microecnapsulation of food ingredeints: An overview", *Food Res. Int.* **2007**, *40*, 1107–1121.
121. Barbosa-Cánovas, G. V.; Ortega-Rivas, E.; Juliano, P.; Yan, H. *Food Powders: Physical Properties, Processing, and Functionality*; Springer: New York, 2005.
122. Rodrigues, S. N.; Fernandes, I.; Martins, I. M.; Mata, V. G.; Barreiro, F.; Rodrigues, A. E. "Microencapsulation of limonene for textile application", *Ind. Eng. Chem. Res.* **2008**, *47* (12), 4142–4147.
123. Teunou, E.; Poncelet, D. "Batch and continuous fluid bed coating-review and state of the art", *J. Food Eng.* **2002**, *53* (4), 325–340.
124. Aguilera, J. M.; Stanley, D. W. *Microstructural Principles of Food Processing and Engineering*; Springer Science & Business Media; NY, 1999.