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Review

Microencapsulation: industrial appraisal of existing technologies and trends

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Controlled release of food ingredients at the right place and the right time is a key functionality that can be provided by microencapsulation. A timely and targeted release improves the effectiveness of food additives, broadens the application range of food ingredients and ensures optimal dosage, thereby improving cost-effectiveness for the food manufacturer. Reactive, sensitive or volatile additives (vitamins, cultures, flavors, etc.) can be turned into stable ingredients through microencapsulation. With carefully fine-tuned controlled release properties, microencapsulation is no longer just an added value technique, but the source of totally new ingredients with matchless properties.

Introduction

The food industry expects increasingly complex properties from food ingredients and such complex properties can oftentimes only be provided by microencapsulation. Microencapsulation has been used in the past to mask the unpleasant taste of certain ingredients and also to simply convert liquids to solids. However, in recent years, the concept of controlled release of the encapsulated ingredient at the right place and the right time has become more and more interesting. Controlled release of the ingredients can improve the effectiveness of food additives, broaden the application range of food ingredients and ensure optimal dosage. With carefully fine-tuned controlled release properties, microencapsulation is not just an added value, but is also the source of totally new ingredients with matchless properties. The growing interest by food technologists in the enormous potential of microencapsulation is demonstrated by the exponential increase in the number of publications (non-scientific and scientific articles and patents) published over the years since the mid 1950s, as illustrated by Fig. 1. Liposome entrapment and spinning disk, as well as coacervation to as lesser extent, have experienced the most rapid growth in interest from researchers and technologists.

Sophisticated shell materials and technologies have been developed and an extremely wide variety of functionalities can now be achieved through microencapsulation. Any kind of trigger can be used to prompt the release of the encapsulated ingredient, such as pH change (enteric and anti-enteric coating), mechanical stress, temperature, enzymatic activity, time, osmotic force, etc. However, cost considerations in the food industry are much more stringent than in, for instance, the pharmaceutical or cosmetic industries. Therefore, the cost-in-use (see Popplewell, 2001, for an excellent theoretical treatment of the cost-in-use concept) of the encapsulated product must be tolerable in the final foodstuff. Some microencapsulation technologies, however scientifically impressive they are, might not be appropriate for all, if any, applications. When microencapsulation is used to prevent excessive degradation of a sensitive ingredient or to reduce flashing off of volatile flavors during baking, in order to save on an expensive ingredient, the cost-in-use must in fact be lower than the non-encapsulated ingredient. However, if microencapsulation provides the ingredient with a unique property that is not achievable without encapsulation, then the cost-in-use can be slightly higher than the non-encapsulated ingredient. As a rule of thumb, the customer will accept a price increase of €0.1 per portion for a new product. Considering that functional ingredients are used at low levels in foodstuffs (1–5%), a maximum cost for a microencapsulation process in the food industry can be roughly estimated at €0.1/kg.

There are a number of excellent review papers on microencapsulation technologies, shell materials and

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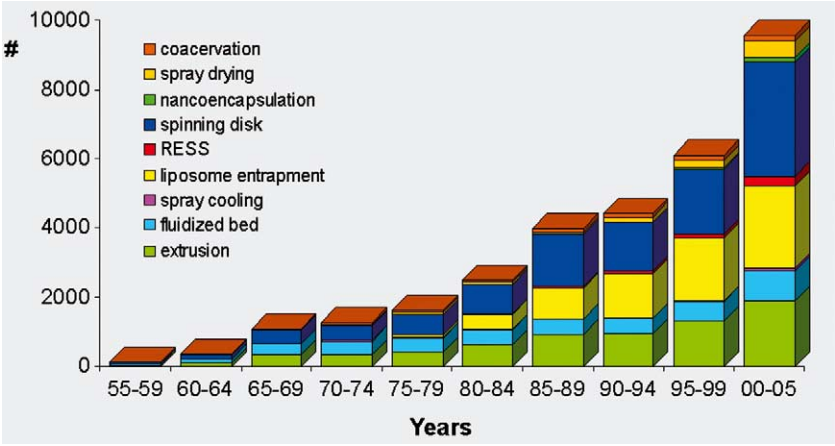

Fig. 1. Trends in microencapsulation technologies. Keywords used were: (Microencapsul* or encapsul* or coating or coated) and 1. extrusion or extruded 2. fluid* bed 3. spray (cool* or chill*) 4. spray dry* 5. coacervat* 6. liposome 7. spin* disk 8. nano-encapsul* or nanoencapsul* 9. supercritical fluid or SCF or RESS for the respective encapsulation technology. Chemical Abstract was the main reference source.

applications of microencapsulated ingredients in the food industry (Benita, 1998; Garcia-Anton *et al.*, 1997; Heintz, Kröber, & Teipel, 2001; Jackson & Lee, 1991; Kondo, 2001; Manekar & Joshi, 1998; Omanakutty & Matthew, 1985; Shahidi & Han, 1993; Sparks & Jacobs, 1999a; Sparks, Jacobs, & Mason, 1999b). The latest review papers include Gibbs, Kermasha, Alli, and Mulligan (1999), Brazel (1999) and Augustin, Sansuansri, Margetts, and Young (2001). The aim of this paper is not to describe technologies and survey applications, but rather to give a critical industrial perspective on the microencapsulation technologies, their advantages, flaws and variations, as well as to review interesting emerging technologies and trends.

Spray drying

Spray drying encapsulation has been used in the food industry since the late 1950s to provide flavor oils with some protection against degradation/oxidation and to convert liquids to powders. Thorough reviews of the technology (Cho, Shin, & Park, 2000; Hecht & King, 2002; King, 1990; Langrish & Fletcher, 2001; Re, 1998; Rosenberg, Kopelman, & Talmon, 1990; Rosenberg, Kopelman, & Talmon, 1990), of the wall material properties (Buffo & Reineccius, 2000; Fäldt & Bergenstahl, 1996; Gascon, Zuritz, Bustamante, De Borbon, & Oberti, 1999; Hogan, McNamee, O'Riordan, & O'Sullivan, 2001; Kim, Morr, & Schenz, 1996; McNamee, O'Riordan, & O'Sullivan, 1998; Moreau & Rosenberg, 1996; Rosenberg & Sheu, 1996; Sheu & Rosenberg, 1998; Wan, Heng, & Chia, 1992) and of the applications of spray dried ingredients (Belghith, Ellouz Chaabouni, & Gargouri, 2001; Favaro-Trinidade & Grosso, 2002; Man, Irwandi, & Abdullah, 1999; Matsuno & Adachi, 1993; Millqvist-Fureby, Malmsten, & Bergenstahl, 1999; Rosenberg & Sheu, 1996; Takeuchi, Yasuji, Yamamoto, & Kawashima, 2002) have been published. The technology is well established, rather inexpensive and straightforward. One limitation of the spray drying technology is the limited number of shell materials available. Since almost all spray drying processes in the food industry are carried out from aqueous feed formulations, the shell material must be soluble in water at an acceptable level. Typical shell materials include gum acacia, matodextrins, hydrophobically modified starch and mixtures thereof. Other polysaccharides (alginate, carboxymethylcellulose, guar gum) and proteins (whey proteins, soy proteins, sodium caseinate) can be used as the wall material in spray drying, but their usage becomes very tedious and expensive because of their low solubilities in water: the amount of water in the feed to be evaporated is much larger due to the lower dry matter content and the amount of active ingredient in the feed must be reduced accordingly. However, the addition of a small amount of these low solubility hydrocolloids has been shown to have some beneficial effect on the stability of encapsulated ingredients (Kim *et al.*, 1996; Matsuno & Adachi, 1993; Re, 1998; Wan *et al.*, 1992). It is noteworthy that hydrophobically-modified polysaccharides (such as octyl-substituted starches) alone have be used as shell material in spray drying to encapsulate up to 50% flavor oils, while still maintaining free-flowing properties. Obviously, with such high amount of volatiles and the high temperatures typically used in spray drying, explosion risks must be carefully considered before scaling up.

Overall, new shell materials for use in spray drying encapsulation have not really emerged in recent years. Few exceptions are noteworthy, though. The investigation of other natural gums and their emulsification and shell properties have been reported. Mesquite gum, for instance, has been shown to give a better stability of the o/w emulsions and higher encapsulation efficiency compared to gum acacia (Beristain, Garcia, & Vernon-

Carter, 1999, 2001). Augustin *et al.* (2001) proposed the use of Maillard Reaction Products (MRPs) obtained by the reaction at high temperature between protein and carbohydrate to encapsulate oxidation-sensitive nutrient such as fish oils. The MRPs are known to exhibit antioxidant properties and form stable and robust shell around the oil phase. The stability of the oil against oxidation was greatly improved compared to non-encapsulated spray dried samples in ordinary shell material. More interesting is the recent development of complex shell formulations for spray drying encapsulation. For instance, aqueous two phase systems (ATPSs), which result from the phase separation of a mixture of soluble polymers in a common solvent due to the low entropy of mixing (ΔS_{mix}) of polymer mixtures, can be used to design double-encapsulated ingredients in a single spray drying step. Millqvist-Fureby, Malmsten, and Bergenstahl (2000) encapsulated *Enterococcus fæcium* in a mixture of PVP and dextran. While proteins exhibit partitioning between the two phases, whole cells tend to concentrate in one of the polymer phases, which make them ideal candidates for ATPS spray drying. The structure of the microcapsule, whether PVP is the outer layer and dextran the inner core or vice-versa, can be controlled by adjusting the ratio and concentration of the two polymers. Encapsulated *E. fæcium* in spray dried ATPS showed a survival rate of up to 45% after 4 weeks at room temperature. Another example is the preparation and spray drying of multiple emulsions, which results a in a double layered microcapsule providing better protection to sensitive materials such as oxidation-probe flavor oils. Edris and Bergmtåhl (2001) have encapsulated orange oil by first preparing a triple emulsion o/w/o/w and then evaporating the outer continuous aqueous phase, which contains sodium caseinate and lactose as shell material, by spray drying. The process leads to a dry free-flowing powder constituting of a double o/w/o, in which the inner orange oil phase is dispersed in an aqueous phase, which is itself dispersed in a oil phase encapsulated in sodium caseinate and lactose. This double emulsion process is not practically more complex than a typical spray drying process that requires an emulsion step anyway. However, preparing a second emulsion implies a dilution of the flavor oil and the much lower payload in the microcapsule (5–10%) is a drawback compared to a typical spray dried flavor oils that have payloads of around 20–25%. The unique protection and delayed release properties obtained with two layers might compensate for the lower payload, but this has still to be demonstrated.

Spray cooling/chilling

Spray cooling/chilling is the least expensive encapsulation technology and is routinely used for the encapsulation of a number of organic and inorganic salts as well as textural ingredients, enzymes, flavors and other functional ingredients to improve heat stability, delay release in wet environments, and/or convert liquid hydrophilic ingredient into free flowing powders. Spray cooling/chilling is typically referred to as 'matrix' encapsulation in the literature because the particles are more adequately described as aggregates of active ingredient particles buried in the fat matrix, while 'true' encapsulation is usually reserved for processes leading to a core/shell type of microencapsules. A matrix encapsulation process leaves a significant proportion of the active ingredient is lying on the surface of the microcapsules or sticking out of the fat matrix, thus having direct access to the environment. Particles produced by a matrix encapsulation process generally release the whole of their content within a few minutes after being incorporated in the food stuff. A non-negligeble proportion of active ingredients can also be found on the surface of a core/shell type of microcapsule, but the bulk of the ingredient is, in that case, encapsulated and much slower release kinetics are typically obtained. However, the distinction between 'true' and 'matrix' encapsulation is indeed blurred, almost obsolete and prone to spark argumentation; performance rather than semantic should indeed be discussed.

Even though the process does not lead to a perfect encapsulate, the properties obtained by spray cooling/chilling are often sufficient to achieve the desired delayed release of the ingredient in the actual application and commercial examples abounds. However, a strong binding of the ingredient to the fat matrix can prevent the release of the ingredient even thought the fat matrix is melted and/or damaged during processing. An illustration of this phenomenon is the improved thermal stability of feed enzymes achieved by spray cooling in monoglycerides, but the non-release and almost quantitative excretion in the feces of the fat-bound enzymes (Gravlsen, 2002).

A common myth concerning spray cooling is that the release of the active ingredient is thought to occur upon the melting of the fat matrix. This fallacy has oftentimes been proven to be inaccurate. First of all, spray cooling/chilling is not a true microencapsulation process, a significant number of active ingredient particles are located at the surface of the microcapsules or have direct access to the environment, as shown in Fig. 2. Therefore, as soon as the encapsulated ingredient is brought into contact with the foodstuff, release begins. Furthermore, other release mechanisms play a significant role in the release kinetics, such as osmotic forces, slow diffusion of water through the shell imperfections, mechanical disruption of the particles, etc. Overall, no matter what the payload or the composition of the fat matrix, it is very difficult to achieve a delayed release of a water-soluble ingredient over 30 min in a foodstuff of relatively high water activity by spray cooling/chilling. Fine tuning or improvement of the release kinetic can be partially

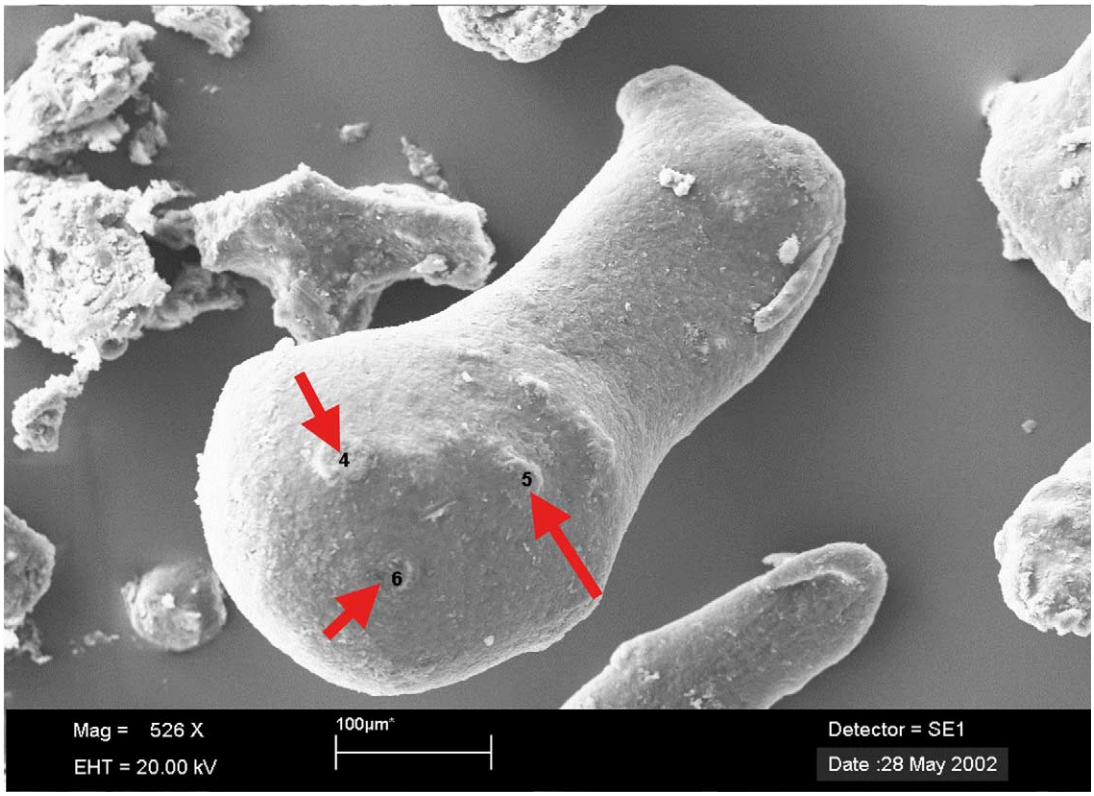

Fig. 2. A spray cooled particle. The red arrows point to active ingredient crystals sticking out of the fat matrix.

achieved by modifying the crystalline structure of the shell material. For example, it is well know that glyceride esters of fatty acids have various crystalline forms (a, b, b′) that exhibit very different crystal sizes, hydrophobicities and densities. A manifest example is the crystallization of fully hydrogenated soybean oil (see Hvolby, 1974) that undergoes a 45% expansion when changing from the instable alpha form to the thermodynamically more stable beta form; one can clearly imagine the effect of such an expansion and the resulting cracking has on the barrier properties of hydrogenated soybean oil in spray cooled microencapsulation. Additives and/or mixtures of glycerides can be used to preferably obtain one crystalline form over another and affect the diffusion rate of water through the matrix, for instance, as well as slow down or speed up the release kinetic of the active ingredient. Despite the obvious interest in investigating the effect of various compositions of glycerides and additives and preferable stabilization of specific crystal forms, very few scientific reports have been published on this crucial issue. In fact, very little innovation has been demonstrated is recent years for spray cooling/chilling. Some exceptions are worth mentioning.

Morgan and Blagdon (1989) have patented a process in which an aqueous solution of an active ingredient (such as corn sirup, solution of vitamins, salts or antimicrobials) is emulsified in melted emulsifiers and/or fats and then spray cooled. This leads to a free flowing powder having a heat-labile shell and a multiplicity of liquid aqueous cores. This process differs from conventional spray cooling since the active ingredient is provided as an aqueous solution distributed in the fat matrix. It also differs from spray cooling of nutritional oils or flavor oils, which usually leads to homogenous particles from which the oil rapidly leak out and may cause lumping of the fat-based powder. The particles produced by the patented process could show some advantages compared to conventional spray cooling in the stability, the ease of processing or the release profile thus obtained. Smith and Lambrou (1974) have double-encapsulated flavor composition by first spray drying a flavor in a gum acacia matrix and then incorporating the powdered flavor into melted fat, followed by spray cooling of the suspension. The resulting powder consists of a fusible fat shell containing dispersed solid flavor particles. The encapsulated flowers can then be incorporated into flour, margarine, eggs, baking powder or other flavoring to achieve delayed release and thermal protection of the sensitive flavor oil. It is important to note that such an encapsulated flavor contains at most 8% w/w flavors (because the already low payload spray dried flavor is further diluted with fat in the spray cooling process). This rather low payload is not very attractive for most applications since dosage of the encapsulated flavor must be increased by a factor of 3

compared to conventional spray dried flavors, and there is therefore a substantial amount of inert shell material (fat and hydrocolloid) that end up in the food stuff and this might have a detrimental effect on the texture, organoleptic properties or the microstructure of the food product.

Spinning disk and centrifugal coextrusion

Spinning disk and centrifugal coextrusion are similar processes in that they are both atomisation methods that can be used in modified spray cooling/chilling encapsulation. Spinning disk involves the formation of a suspension of core particles in the coating liquid and the passage of this suspension over a rotating disk under conditions that result in a film of the coating much thinner than the core particle size (see Sparks, Jacobs, & Mason 1993). Atomization of the mixture at the edge of the disk results in coated core particles and much smaller empty shell material satellites that can be sieved out and recycled in the feed. Centrifugal coextrusion is based on a modified double fluid nozzle where the active ingredient is pumped through the inner part of the nozzle while the shell material is pumped through the outer part of the nozzle. At the edge of the nozzle, Raleigh instabilities leads to the formation of round beads approximately twice the size of the nozzle diameter that are constituted of the active ingredient in the core and a outer layer of the shell material.

From an industrial point of view, spinning disk and centrifugal coextrusion are alternatives to conventional atomization devices such spinning wheels, double fluid nozzles and pressure nozzles to atomize a suspension or an emulsion of an active ingredient in a coating formulation. This equipment can be installed in regular spray towers. The advantage of spinning disk and centrifugal coextrusion lies in the properties and characteristics of the products obtained: the release kinetic of typical ingredients was determined for samples prepared by spray cooling, spinning disk and centrifugal coextrusion using the same shell material. The release kinetic of samples prepared by spinning disk was shown to be intermediate to the release kinetics of the samples prepared by spray cooling and coextrusion, with spray cooling giving faster and coextrusion slower release rates (Gouin, 2002).

Spinning disk is a very promising technology because the throughput is comparable, or even higher, than that of regular spray drying or spray cooling processes, and the processing cost is also very similar. The equipment needed to perform spinning disk encapsulation is also rather simple and can be installed in any existing spray tower. On the other hand, scaling up of centrifugal coextrusion for the large scale production of encapsulated food ingredients would be much more demanding from a engineering perspective, since the scaling up would involve the construction of multi-head nozzles suspended in a spray tower. The small size of the nozzle would also certainly be the source of frequent clogging problems.

Extrusion

Extrusion microencapsulation has been used almost exclusively for the encapsulation of volatile and unstable flavors in glassy carbohydrate matrices (Benczédi & Blake, 1999; Benczedi & Bouquerand, 2001; Blake, 1994; Gunning *et al*., 1999; Qi & Xu, 1999; Reineccius, 1991; Saleeb, 1999). The main advantage of this process is the very long shelf life imparted to normally oxidation-prone flavor compounds, such as citrus oils, because atmosphere gases diffuse very slowly through the hydrophilic glassy matrix, thus providing an almost impermeable barrier against oxygen. Shelf lives of up to 5 years have been reported for extruded flavor oils, compared to typically 1 year for spray dried flavors and a few months for unencapsulated citrus oils. Carbohydrate matrices in the glassy states have very good barrier properties and extrusion is a convenient process enabling the encapsulation of flavors in such matrices. Other processes could, theoretically use glassy carbohydrates as shell material, such as fluidize bed coating for instance, but extrusion remains to most suitable process for such shell materials. The basis of the process was developed by Swisher (1957) and later improved by Schultz (1956). The payload in these systems, however, remained very low (around 8%); higher payloads led to unstable systems, leaking out and fast oxidation of the sensitive flavor oil. Such low payloads in flavor microcapsules are very unattractive, from an industrial point of view, because (1) the cost-in-use becomes unacceptable and (2) the substantial amount of carbohydrate added to the food stuff along with the flavor often requires an undesirable adjustment of the recipe, and might not be appropriate for sugar-free or savory products. However, hydrophobically-modified starches, which have very good amphiphilic properties, have been used instead of simple carbohydrates (Mutka & Nelson, 1988) and allowed the payload to be increased up to 40% while preserving the attractive shelf life. A payload of 40% is more than double the payload of a typical spray dried flavors and while extrusion is a slightly more expensive process than spray drying, the much better shelf life and resistance to oxidation might compensate and give a comparable or even lower cost-in-use. Quellet, Tashi, and Ubbink (2001) have developed a lower-temperature process in which a mass of potato starch, glycerol and water is processed and gelatinized in a twin screw extruder at about 100°C. The mass is then cooled down and the flavor formulation is injected in the last barrel, where the temperature is now approximately 50°C. The exiting ropes are cut into pieces and dried. This process limits the flashing of the volatile flavors in the original mass and might be a better alternative for

sensitive flavors, although the payload in that case is rather low (between 5 and 30%, according to the authors, but most probably below 20% for a stable product).

One of the drawbacks of this technology is the rather large particles formed by extrusion (typically 500–1000 μm), which limit the use of extruded flavors in application where mouthfeel is a crucial factor. Also, a very limited range of shell material is available for extrusion encapsulation. Most of the applications developed so far make use of carbohydrates of various dextrose equivalents (DE), starch, and mixture of additives. Some exceptions are worth mentioning. Van Lengerich (2001) developed a low-temperature extrusion process for the encapsulation of microorganisms and enzyme in a plasticized composite matrix of fat, flour and starch. Basically, all the dry ingredients are mixed together and introduced in the extruder along with about 20% water. The paste is processed inside the double-screw extruder and the exiting rope is cut into pieces (0.5–1.5 mm) and air-dried to yield shelf-stable microcapsules. This process allows the encapsulation of heat-sensitive material, such as *Lactobacillus acidophilus*, which cannot be achieved in a typical carbohydrate matrix because of the much higher processing temperatures typically used. Harz, Heinzl, Schöner, Betz, and Keßler (2000) described a similar relatively low-temperature process using mixtures of corn starch and fat or corn starch and polyethyleneglycol for the encapsulation of enzymes. In this case, the mass is introduced in the extruder at 40°C and treated at 100°C for just a few seconds in barrels 2 and 3 then cooled down to 45°C in barrel up to the die, where the exiting rope is cut into pieces between 500 and 1000 μm. The very low water content in the extruding mass prevents the degradation of the enzyme even at high temperatures for short periods of time.

Fluidized bed

Fluidized bed technology is a very efficient way to apply a uniform layer of shell material onto solid particles. Interestingly, fluidized bed technology is one of the few advanced technologies capable of coating particles with basically any kind of shell material (polysaccharides, proteins, emulsifiers, fats, complex formulations, enteric coating, powder coatings, yeast cell extract, etc.). Therefore, the controlled release possibilities are considerably more versatile with the fluidized bed technology than with any other technologies. Aqueous solutions of hydrocolloids such as gums (Dewettinck, Deroo, Messens, & Huyghebaert, 1998) and proteins (Dewettinck, Messens, Deroo, & Huyghebaert 1999), ethanolic solutions of synthetic polymers (Knezevic, Gosaki, Hraste, & Jalsenjak, 1998; Liu & Lister, 1993; Mehta, Valazza, & Abele, 1986) and melted fats/waxes (Jozwiakowksi, Jones, & Franz, 1990) have all been used as coating formulations in fluidized bed microencapsulation processes. The relevance of the fluidized bed technology as a means to encapsulate microparticles has been extensively discussed (Berk, Dumoulin, & Ghorbel, 1998; Dewettinck and Huyghebaert, 1998, 1999a, 1999b, 2001; Guignon, Duquenoy, & Dumoulin, 2000). A number of food ingredients have been encapsulated by fluidized bed coating, such as ascorbic acid (Knezevic *et al.*, 1998), acidulants for processed meat (Weiss & Reynolds, 1989) and leavening agents (Balassa & Brody, 1968). Spray dried particles, such as spray-dried flavor microcapsules can also be further coated by fluidized bed, with a fat layer, for instance, to impart better protection and shelf life.

The use of melted fats, waxes or emulsifiers as shell materials is a relatively new but very promising and interesting concept. From an industrial point of view, the inherent advantage of hotmelt fluidized bed coating lies in the fact that the coating formulation is concentrated (no solvent as in aqueous-based coating formulation), which means dramatically shorter processing times. The energy input is also much lower than with aqueous-based formulation since no evaporation needs to be done. Very few reports have been published on hotmelt coating by fluidized beds since Jozwiakowksi, Jones and Franz (1990) described the coating of sucrose particles with partially hydrogenated cottonseed oil and analyzed the optimal processing parameters by modified central composite design. A number of patent applications, very similar in processing designs, have been published using fats and emulsifiers of various melting points (Klose, 1992; Pacifico, Wu, & Fraley, 2001; Wu *et al.*, 2002). Tsutsumi, Hasegawa, Mineo and Yoshida (1998) have developed an innovative fluidized bed process for coating particles with fats and waxes using supercritical carbon dioxide as the solvent for the coating formulation. Here again, minimal energy input is needed to 'evaporate' the solvent and the process might lead to lower cost-in-use encapsulated ingredients.

A fascinating advancement in fluid bed coating is reported by Matsuda, Hatano, Kuramoto, and Tsutsumi (2001) for the fluidization and coating of very fine particles by fluidized beds. In conventional fluidised beds, whether it is top-spray, Wurster or rotational, the basic concept of fluidization relies on the compensation of the gravity force experienced by the particles by an upward moving air flow, which ensures complete fluidization of the particles. Typical fluidized bed apparati can efficiently process particles from 100 μm to a few millimeters. However, for very small particles, other forces such as electrostatic forces start to play a major role in the movement of the particles in the fluidizaton chamber and prevent adequate fluidization. Colloidal particle have been used with some success to reduce electrostatic force, but are not much help in the fluidization of very small (sub-micron) particles in a conventional fluidized bed apparatus. In this innovative

process, however, the gravity force is multiplied through the use of a rotating perforated drum that contains the particle. The airflow is then applied tangentially to the rotation of the drum as compensation for the 'gravity force', now a multiple (up to 37 g) of the normal gravitational force. One of the issues remaining to be solved in this process is the atomization of the coating formulation with droplet size one order or magnitude smaller than the fluidized particles. Obviously, achieving fluidization of small sub-micron particles is not enough to make a fluid-bed encapsulation process successful. The atomized coating droplets must be significantly smaller than the particle to be coated in order to achieve uniform and complete coating while avoiding agglomeration. Atomizing droplets at 10–100 nm is a very serious engineering issue and it is uncertain at this moment if actual efficient coating of sub-micron particles can be achieve with this technology.

Coacervation

Coacervation is a unique and promising microencapsulation technology (see Fig. 3) because of the very high payloads achievable (up to 99%) and the controlled release possibilities based on mechanical stress, temperature or sustained release. Coacervation is typically used to encapsulate flavor oils (Arneodo, 1995; Bakker, Gelerna, & Visser, 1999; Chalupa & Calzolari, 1997; Korus, 2001; Korus, Tomasik, & Lii, 2003; Pasla, 1969; Porzio & Madsen, 1996; Soper, 1995), but can also be adapted for the encapsulation of fish oils (Lampretch, Schafer, & Lehr, 2001) nutrients, vitamins (Junyaprasert, Mitrevej, Sinchaipanid, Boonme, & Wurster 2001), preservatives, enzymes (Dubin, Muhoberac, & Xia, 1998), etc.

The basic physical and polymer chemistry behind the coacervation process is well developed and understood (Bakan 1971, 1980; Burgess, 1990; Burgess & Carless, 1984; Dervichian, 1954; Dobetti & Pantaleo, 2002; Passin, 1969; Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998; Thies, 1975). The concept behind (simple or complex) coacervation microencapsulation is the phase separation of one or many hydrocolloids from the initial solution and the subsenquent deposition of the newly formed coacervate phase around the active ingredient suspended or emulsified in the same reaction media. The hydrocolloid shell can then be crosslinked using an appropriate chemical or enzymatic crosslinker, if needed. A very large number of hydrocolloid systems has been evaluated for coacervation microencapsulation (see for example Prokop, Hunkeler, Di Mari *et al.*, 1998; Prokup, Hunkeler, Powers *et al.*, 1998) but the most studied and well understood coacervation system is probably the gelatine/gum acacia system (Aneodo, 1996; Jegat & Taverdet, 2000, 2001; Ijichi, Yoshizawa, Vemura, & Hatate, 1996; Mauguet, Hirech, Brujes, Carnelle, & Legrand, 1999; Porzio & Madsen, 1996; Rabiskova & Valaskova, 1998). However, other coacervation systems exhibit very good properties, such as gliadin (Mauguet *et al.*, 2002), heparin/gelatin (Tsung & Burgess 1997), carrageenan (Patil & Speaker, 1998),chitosan (Babak & Merkovich 2000; Madgassi, Mumcuoglu, Bach, & Rosen 1998; Mi, Sung, & Shyu, 2002), soy protein (Chalupa & Calzolari, 1997), polyvinylalcohol (Han & Hong, 2000), gelatin/carboxymethylcellulose (Bakker *et al.*, 1999; Sovilj, Dokic, Marjanovic, & Trbovic, 1996), starch (Korus, 2001), B-lactoglobulin/gum acacia (Schmitt *et al.*, 2000; Schmitt, Sanchez, Thomas and Hardy, 1999) and guar/dextran (Simonet, Garnier, & Doublier 2002).

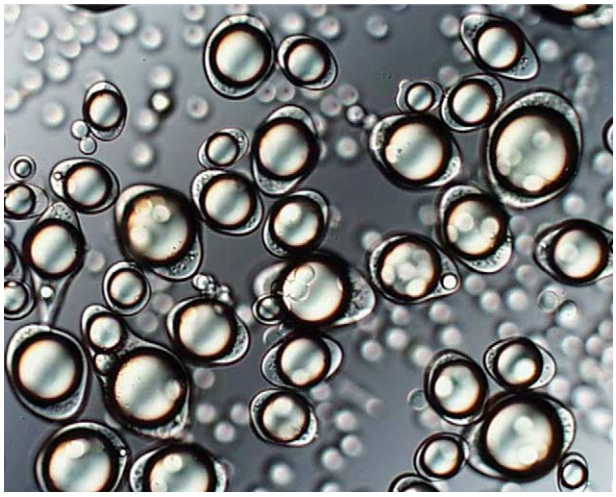

Fig. 3. A coacervated flavor oil.

Innovative and interesting coacervation processes have also been developed in recent years, which can overcome some of the problems encountered during a typical gelatin/gum acacia complex coacervation process, especially when dealing with food ingredients. Arneodo (1996) devised a room-temperature process for the encapsulation of heat-sensitive ingredients such as volatile flavor oils. Basically, the hydrocolloids are mixed and then phase separation (coacervation) is created by adjusting the pH. The newly formed coacervate phase is allowed to separate and sediment, most of the supernatant water is removed and the flavor oil is then added to the mixture kept at 50°C and emulsified rapidly. The initial volume of water is restored with room temperature water, causing a quick drop in the temperature, which means that the flavor oils experience a high temperature for only a few minutes, compared to several hours for a typical coacervation process. Another process, described by Ijichi, Yoshizawa, Uemura, Hatate, and Kawano (1997) involves the formation of a multi-layered coacervated microcapsule. Basically, the process consists of multiple coacervation steps in which a additional layer of shell material is applied to the microcapsule at each passage and the final shell layer can reach a thickness up to 100 μm.

Despite coacervation's intrinsic advantage and unique properties compared to the other common encapsulation processes, major problems face the food scientists when it comes to commercializing a coacervated food ingredient. First of all, the cost of the process is very expensive and rather complex and secondly crosslinking of the shell material usually involves glutaraldehyde, which must be carefully used according to the country's legislation. However, the processing cost can be dramatically decreased by optimizing the isolation procedure at the end of the encapsulation step. It is believed that the usual isolation/dehydration procedure, typically performed by filtration followed by fluidized bed drying (or performed by freeze drying) is responsible for the steep processing cost of coacervation encapsulation. Other methods, cheaper and more straightforward, can be used, such as spray drying (Pearl, Soper, & Wamper, 1993; Porzio & Madsen, 1996) for instance. The problems related to harmful chemical crosslinkers could eventually be solved by using enzymatic crosslinkers instead. Soper and Thomas (2000), for instance, described a process in which a transglutaminase is used to crosslink the proteins in the shell material. The enzyme is added to the microencapsulation tank at 10°C and pH 7 and the reaction is carried out over 16 h, after which a hardened shell of coacervate is formed around the flavor oil droplets. Obviously, this is a rather long processing time that ties up resources and increases the production cost, but these drawbacks might be overshadowed by the fact that enzymes are label-friendly compared to glutaraldehyde and that the low temperature crosslinking step ensures that sensitive and/or volatile active ingredients are not degraded or evaporated during the crosslinking step. While the enzymatic crosslinking of coacervate is not, at the moment, a viable industrial option it is believed that more suitable enzymes are being or will be developed shortly which will make the hardening both efficient and rapid. Kyogoku, Saeki, and Jujikawa (1994) proposed the use of an old Chinese medicine derived from plants to crosslink the proteins in the coacervate shell. The compounds are irridoids extracted from Gardenia jasminoides Ellis and the crosslinking is carried out most quickly at acidic pH, which is a great advantage compared to aldehydes (such as glutaraldehyde which must be used at basic pH).

Alginate beads

Alginate beads have been used extensively in microencapsulation because they are extremely easy to prepare on a lab-scale, the process is very mild, it can be conducted in sterile environments and virtually any ingredient can be encapsulated, whether it is hydrophobic or hydrophilic, sensitive to temperature, a thin liquid or a viscous oil, a solid, etc. However, two major drawbacks limit the use of such microcapsules in the food industry. First, as easy as it is to make small batch using a syringe extruder and a stirred calcium bath, the scaling up of the process is very difficult and processing costs are stupendous. Secondly, the microcapsules thus obtained are very porous and allow fast and easy diffusion of water and other fluids in and out of the alginate matrix. This might be a advantage for the immobilization of live cells and enzymes that are meant to be accessible to their environment, but is definitely a drawback when one is trying to protect or segregate an ingredient from its environment and achieve a longer shelf life than the unencapsulated homologues. However, a few new processes have been proposed to facilitate the large-scale production of alginate beads, which makes it possible to envision a commercial encapsulated food ingredient based on the alginate bead technology. Improvements on the syringe-extrusion process include applying air jet, electrical, potential or vibrating units to the alginate flow, but despite their manifest advantages as far as processing rates and reproducibility, none appears to be reasonably scalable within industrial constraints. However, Mofidi, Aghai-Moghadam, and Sarbolouki (2000) developed an emulsion-based process in which an aqueous alginate solution containing the dissolved or suspended active ingredient is added to a non-aqueous phase, followed by formation of microscopic droplets by homogenization. The emulsified droplets are then crosslinked by adding a solution of calcium chloride and the microapsules are collected by filtration. The process could easily be scaled up and allow formation of better defined particle size, which is difficult to achieve using conventional alginate beads processes. Champagne, Blahuta, Brion, and Gagnon (2000) developed a slightly more complex design to produce up to 50 kg/h of wet alginate beads. The process involves atomising a solution of alginate from a spinning disk onto a rotating vortex bowl containing a recirculating calcium chloride solution. The beads are hardened upon contact with the solution in the rotating vortex bowl and discharged into a large container underneath when the vortex reaches the edge of the bowl. The calcium chloride solution from the container is continuously recycled to the vortex bowl. This very ingenious process allows for the production of rather large quantity of alginate beads on a continuous basis, which is a great industrial advantage compared to the other existing batch methods.

Liposomes

Liposome microencapsulation has been used mostly in pharmaceutical applications to achieve, for example, targeted delivery of paramagnetic contrast agents for cancer cell detection by MRI or in cosmetic applications for the stabilization of skin nutrients in cosmetic cream products. However, the technology has evolved in recent years to the point that it is now conceivable for liposome encapsulation to become a routine process in the food industry (Gregoriadis, 1987; Kim & Baianu,

1991; Kirby & Law, 1987). Methods of liposome formation now exist that do not make use of sonication (Batzri & Korn, 1973; Kirby & Gregoriadis 1984; Peel, 1999; Zhang, Hu, & Lu, 1997; Zhang, Liu, Lu, & Hu, 1997a,b) or of any organic solvents (Frederiksen, Anton, Hoogevest, Keller, & Leuenberger, 1997; Zheng, Alkan-Onyuksel, & Wasan, 1999) and allow the continuous production of microcapsules on a large scale. This paper does not intend to give a detailed explanation of the different liposome stuctures and of the thermodynamic of liposome formation (please refer to Annesini, 1998; Lasic, 1993). However, it is important to reiterate that large unilamellar vesicles (LUV) are the most appropriate liposomes for the food industry because of their high encapsulation efficiency, their simple production methods and good stability over time. The great advantage of liposomes over other microencapsulation technologies is the stability liposomes impart to water-soluble material in high water activity application: spray dried, extruded and fluidized beds impart great stability to food ingredients in the dry state but release their content readily in high water activity application, giving up all protection properties. Another unique property of liposomes is the targeted delivery of their content in specific parts of the foodstuff. For example, it has been shown that liposome-encapsulated enymes concentrate preferably in the curd during cheese formation while non-encapsulated enzyme are usually distributed evenly in the whole milk mixture, which leads to very low (2–4%) retention of the flavor-producing enzymes in the curd (Fresta & Puglisi, 1999; Kheadr, Vuillemard, & Deeb, 2000). Lee, Jin, Hwang, and Lee (2000) have prepared bromelain-loaded liposome for use as meat-tenderizer to improve stability of the enzyme during the processing of the food and subsequently improve the availability of the enzyme. Benech, Kheadr, Laridi, Lacroix, and Fliss (2002) showed that lipsome-entrapped nisin retained higher activity against *Listeria innocua* and had improved stability in cheese production, proving a powerful tool to inhibit the growth of Listeria I in cheese while not preventing the detrimental effect of nisin on the actual cheese-ripening process. Kirby, Whittle, Rigby, Coxon, and Law (1991) have developed a process to stabilize vitamin C in the aqueous inner core of liposomes. Encapsulation of vitamin C gave significant improvements in shelf-life (from a few days to up to 2 months) especially in the presence of common food components which would normally speed up decomposition, such as copper ions, ascorbate oxidase and lysine. Liposomes can also be used to deliver the encapsulated ingredient at a specific and well-defined temperature: the liposome bilayer is instantly broken down at the transition temperature of the phospholipids, typically around 50°C, at which temperature the content is immediately released.

The main issues in liposome encapsulation for the food industry are (1) the scaling up of the microencapsulation process at acceptable cost-in-use levels and (2) the delivery form of the liposome-encapsulated ingredients. The development of a cost-effective drying method for liposome microcapsules and development of a dry liposome formulation that readily reconstitutes upon rehydration would ensure a promising future to liposome encapsulation of food ingredients. The recent advances in liposome technology have most probably solved the first issue: microfluidization has been shown to be an effective, cost effective and solvent-free continuous method for the production of liposomes with high encapsulation efficiency. The method can process a few hundred liters/h of aqueous liposomes on a continuous basis. The process has been reported by Zheng *et al.* (1999), Vuillemard (1991) and Maa and Hsu (1999). The other issue concerns the aqueous form in which the liposomes are usually delivered. Most of the time, if not always, liposome formulations are kept in relatively dilute aqueous suspensions and this might be a very serious drawback for the large scale production, storage and shipping of encapsulated food ingredients. Dry liposome microencapsules can be obtained by freeze-drying the liposome suspension, but the considerable cost of large-scale freeze-drying processes can only be carried out by high price encapsulated ingredients in a niche market. Moreover, not all liposome formulation can be freeze-dried and the reconstitution of the wet formulation is not always straightforward and usually requires complex steps and processes (Lasic, 1993). If the liposomes are kept and used as an aqueous suspension, the shelf life is a important factor to be considered: stabilization with anti-microbials might disrupt the liposome structure while storage and shipping a low temperature adds an extra cost that might not be acceptable for most low-cost food ingredients.

Also very interesting is the replacement of rather expensive phospholipids in the production of liposomes for a mixture of high and low HLB glyceride-based emulsifiers. Roux, Degert, and Laversanne (1996) report the production of liposome-like structures using a mixture of hydrophobic emulsifiers (HLB between 3 and 7) such as mono- and di-glycerides or lactate, acetate or citrate esters of monoglycerides and hydrophilic emulsifiers (HLB between 8 and 15) such as sucroesters and/or stearoyl lactilates. The emulsifers used in this process sell for less than a hundredth of the cost of typical phospholipids used in the formation of conventional liposomes. The very simple process basically involves dissolving the shell material and the active ingredients at temperatures above 60°C and cooling the mixture to obtain a paste which can be readily dispersed in water or in oil.

In another attempt to avoid the use of organic solvent in the production of liposomes, Frederiksen *et al.* (1997)

proposed the use of supercritical carbon dioxide as the solvent for the phospholipids. Basically, the process involves the solubilization of the phospholipids under supercritical condition followed by release of the supercritical mixture into a aqueous phase containing the dissolved active ingredient, which results in the formation of liposomes containing the active ingredient in their aqueous cores. Although this method is scientifically interesting, the encapsulation efficiency reported by the authors, at this moment, is limited at 15%, which would have to be dramatically improved for this technique to become interesting from an industrial point of view.

RESS/SAS

Supercritical fluids exist above the critical point and exhibit properties intermediate between those of liquids and gases: low viscosity, low density, high solvating power, high diffusivities and high mass transfer rates. Basically, supercritical fluid can be regarded as dense, solvating gases or a low-viscosity, low density liquids. A number of compounds can be brought to a supercritical state, such as carbon dioxide, water, propane, nitrogen, etc. However, keeping in mind the particular considerations in the food industry, carbon dioxide is probably the most interesting candidate for use in microencapsulation processes, because it is the second most abundant and the second least expensive solvent on earth. Supercritical fluids have recently been used for encapsulation of heat-sensitive material in a process very similar to spray drying. Basically, the same equipment (nozzle, spray tower) and similar concepts are used, but SC fluids are used for the solubilization/swelling of the shell material and the core material instead of water as in spray drying. The main advantage here is the absence of water and the very mild process ($T < 30^{\circ}C$ throughout the process). Encapsulation of sensitive materials (enzymes, very volatile flavors, sensitive ingredients) could benefit from SC fluid-based spray drying.

Various microencapsulation processes based on supercritical fluids have been developed using slightly different concepts. Rapid Expansion of Supercritical Solutions (RESS) microencapsulation takes place when a pressurized supercritical solvent containing the shell material and the active ingredient is released through a small orifice; the abrupt pressure drop causes the desolvation of the shell material and the formation of a coating layer around the active ingredient. Depending on the processing parameters, sub-micron particles, films or fibres can be obtained through this process. Shell layer thickness anywhere between 100 μm and a monomolecular layer are possible to achieve through RESS. The Centre de Microencapsulation in Angers (France) has developed and published a number of patents and papers on microencapsulation of food ingredients (Benoit, Rolland, Thies, & Vandevelde 1996; Richard, Thies, Gajan, & Benoit, 1998), such as vitamin C, xylitol and potassium chloride, with a thin layer of beeswax, hydrogenated vegetable oil derivatives, paraffin wax, stearic acid or stearoyl acohol, among others. The process involves intimately mixing the shell material and the active ingredient in an autoclave at temperatures between 35 and 45°C and at a pressure of 110 bars. The mixture, after equilibrium has been reached, is then released through a small orifice to yield coated microcapsules and the wetting and/or dissolution were shown to be much slower compared to the uncoated ingredients. Dissolution kinetic studies showed a release rate for the coated ingredient to be about 5 times slower than the uncoated ingredient. More interesting is the absence of the unfavorable initial burst, which is typical of matrix encapsulation for example.

A collaboration between the same Centre de Microencapsulation and Washington University (Ribeiro, Dos Santos, Richard, Thies, Pech, & Benoit, 2003; Ribeiro, Dos Santos, Thies, & Richard, 2003; Thies *et al.*, 2003), led to a new microencapsulation process, with better control over the resulting microcapsules. Basically, the same concept is used, but the resulting mixture, after solvating the shell material in the SC fluid, is slowly cooled down and de-pressurized at controlled rates, compared to an abrupt pressure release as described before. The controlled temperature and pressure decrease leads to a slow deposition of the shell material and a more uniform shell around the active ingredient. Depending on the processing parameters and the particle size of the active ingredient, a range of release kinetics can be achieved using the same shell material, in that case a mixture of glycerides and fatty acid esters.

Shine and Gelb (1998) have developed a slightly different process in which the shell material is not dissolved, but swollen by the supercritical solvent. This approach broadens considerably the applicability of RESS microencapsulation since a wider range of shell materials can be used — materials that do not dissolve but only swell in SC fluids. Carbon dioxide has no dipolar moment and has a low polarizability, which means that only hydrophobic shell materials (fats, glyceride fatty esters and waxes) dissolve in SC carbon dioxide. However, hydrophilic polymers such as proteins (gelatine, whey proteins, etc.) and polysaccharides (cellulose, HPMC, CMC, etc.) can swell in SC carbon dioxide and be used as the shell material, as Shine and Gelb suggest. The process involves intimately mixing the active material, the shell material and the SC fluid in an autoclave. The SC fluid penetrates and swells the shell material, acting as a plastiziser lowering the glass transition temperature (T_g) of the polymer considerably. The temperature is elevated slightly above the T_g, which causes the liquefaction of the polymer, and the pressure is then released abruptly to cause the precipitation of the polymeric shell material onto the active ingredient.

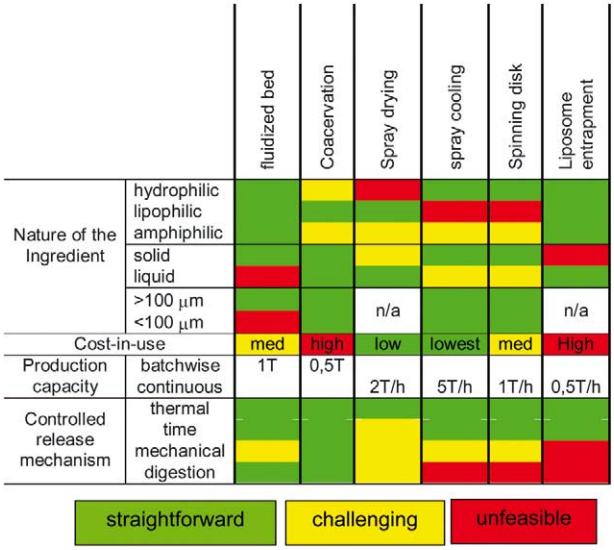

Fig. 4. Summary of the characteristics of common microencapsulation technologies.

Inclusion encapsulation

Inclusion encapsulation generally refers to the supramolecular association of a ligand (the 'encapsulated' ingredient) into a cavity-bearing substrate ('shell' material). The encapsulated unit is kept within the cavity by hydrogen bonding, VDW forces or by the entropy-driven hydrophobic effect. In the food industry, commercially-available molecular entities having suitable molecular-level cavities are uncommon. Examples include the six, seven, or eight-membered cyclic glucose molecules called cyclodextrins, which are produced from starch by enzymatic process using cyclodextrin glycosyltransferase. Cylcodextrins are hollow truncated cone-shaped molecules having an inner diameter of approximately 5–8 Å, sufficient to hold typically 6–17 molecules of water. Small organic molecules can displace the water from the inner cavity and form thermodynamically stable complexes (binding constant up to 100). Characteristics of cyclodextrin and their use as encapsulating material have been extensively described (Hedges & McBride, 1999). For food application, flavor components have been encapsulated within cyclodextrins (Lofstsson & Kristmundsdottir, 1993; Reineccius, Reineccius, & Peppard, 2002; Reineccius & Rish, 1986). Other ingredients such as hydrophobic vitamins (A, E or K) would also be good options for inclusion encapsulation. The main advantage of the cyclodextrin encapsulation is the unique release characteristics and the thermal and chemical stability imparted to the flavor compounds while entrapped within the cyclodextrin. The cyclodextrin complexes are thermodynamically stable up to 200°C. However, the flavor compounds contained in the cavity will be released whenever a better substrate becomes available and displaces the flavor from the cavity and form an even more stable complex with the cyclodextrin. The release can be triggered by the presence of various biological components naturally present in the mouth, for instance, and it has been reported that a flavor burst can be achieved with cyclodextrin-encapsulated flavors (Pagington, 1985). Drawbacks include the low payload typically achieved with cyclodextrins. The six-unit membered of the dextrin family, β-cyclodextrin, is the most studied cyclodextrin for encapsulation and has a molecular weight of 1135 g/mol. The size of the cavity is such that it could hold a flavor compound of about 150 g/mol: this means a theoretical maximum payload of 11% w/w. Payload between 6 and 15% has been reported for artificial flavors (Heath & Reneiccius, 1985). It is important to note, however, that any flavor compounds significantly larger than the cavity would not 'fit in' and would therefore be left unencapsulated. This leads to the problem of segregation during the encapsulation process, where some components are prefereably encapsulated over others. This is, however, a problem not only associated with inclusion encapsulation, but can also take place in coacervation, for instance. Another drawback is the rather high cost of the cyclodextrins: a recent report suggest that the cost of cyclodextrin could never reach a level below $6/kg. All this considered, it seems rather unlikely than cyclodextrin-encapsulation will become a commercially-viable technology for flavor oils in the near future.

Trends

Fig. 4 summarizes the pros/cons, the distinctive features and the similarities of the major microencopsulation technologies discussed in the previous sections. New microencapsulation technologies are relentlessly devised and invented by academics and industrial researchers: in 2002, over 1000 patents were filed concerning various microencapsulation processes and their applications and over 300 of these patents were directly related to food ingredient encapsulation. Some of these new processes have very little industrial relevance because of extremely high cost-in-use, difficult scale up and/or narrow applicability range. However, some of these processes stand out as being promising, sensible and likely to be scaled up in the near future for the encapsulation of food ingredients. Mandralis and Tuot (2001) developed a microencapsulation process based on the gellation of proteins at high pressure. Basically, an aqueous phase containing a dissolved protein such as egg albumin or whey protein and the active ingredient is dispersed in an oil phase and high pressure is applied to the system until the protein has gelled and the ingredient has been encapsulated. The process was used to encapsulate vitamins and the inventors showed a high recovery of vitamins after the pressure treatment, although the release rate is rather fast and 50% of the content is released after just a few minutes followed by a

very slow release of remainder over several days. This might indicate an over-representation of the vitamins on the surface of the microcapsules, which provide little or no protection of delayed release in the foodstuff. Lee and Rosenberg (2000) developed a similar process in which the protein is denatured not by high pressure but by heat. An O/W/O double emulsion is first prepared, in which the inner oil phase contains the active ingredient and the aqueous phase contains the denaturing protein. Heat is the applied (85°C for 20 min) and the resulting microcapsules are separated by filtration and dried. The outer morphology of the microcapsules, depending on processing parameters such as the pH of the aqueous phase, is impressively smooth, spherical and uniform and exhibits small pores of about 100 nm. This contrasts remarkably with spray dried microcapsules where water-evaporation causes the shell to collapse which leads to dents and imperfections and probably to a lesser encapsulation efficiency. Both the Mandralis and Tuot (2001) and Lee *et al.* (2000) processes are closely related to coacervation microencapsulation, but pressure in the former and heat in the latter are used to bring about the phase separation of the protein. Ripoli, Ganan-Calvo, Loscertales, and Bon (2002) describe a microencapsulation process capable of producing capsules of nanometric size using two electrified coaxial jets of two immiscible liquids. The two immiscible liquids are atomized together from a concentric nozzle and an aerosol of charged and structured droplets form because of capillary instability. The inventors suggest that the process might be appropriate to encapsulate, for instance, a lactose composition (injected in the inner par of the nozzle) inside an enteric coating (injected in the outer part of the nozzle) to prevent side effects in lactose-intolerant individuals and ensure that lactose combines with the lactase enzyme in the intestinal tract. The unique potential of this microencapsulation process is its possibility to produce, on a continuous basis, nanomeric size capsules while at the same time tremendously decreasing the probability of nozzle clogging commonly experienced when dealing with very small concentric nozzles.

A straightforward way to develop new encapsulated food ingredients is to adapt microencapsulation processes developed for other applications and turn them into food-grade processes. Many microencapsulation processes that have been developed for pharmaceutical, agricultural or chemical applications could readily be used in the food industry for the encapsulation of food ingredients. Other microencapsulation processes would have to be adapted, substituting food-grade shell material and processing aids for their non-food grade homologous used by our colleagues in other application fields. In any case, food scientists and technologists should search for inspiration in other fields and not be put off by what seems to be, at first sight, a completely unrelated process non applicable in the food industry. With deep knowledge of chemistry, thermodynamics, physics and some imagination, almost any non-food process can be turned into an innovative food-grade microencapsulation process.

Dinsmore *et al.* (2002) published a very interesting microencapsulation technology, based on pioneering work by Velev *et al.* (Velev, Furusawa, & Nagayama, 1996; Velev, & Nagayama, 1997), that produced microcapsules coined 'colloidosomes' because of their resemblance to liposomes, while using colloid particles as shell material. The technology involved the surface tension-driven deposition of solid colloidal particles onto the surface of the inner phase, which contains the active ingredient, of a w/o or a o/w emulsion. The colloidal particles are then fused together by physical (sintering) or chemical (crosslinking) means to yield a complete shell around the active ingredient. The properties of the microcapsules, such as elasticity and selective permeability, can be precisely controlled by choosing the appropriate particle size of the shell material. Fig. 5 shows very clearly the self-assembly of colloidal particles onto the droplet of active ingredients. Interestingly, the extent of crosslinking/sintering determines the porosity and selective permeability of the shell: with a low crosslinking/sintering, a narrow bridge connects two adjacent particles, leaving a very well-defined mesh of defined geometry, while at high sintering a complete and impermeable shell is formed around the droplet. Introducing a needle in the microcapsule, which results in the deformation of the membrane as well as a subsequent burst at high enough pressure, shows the elasticity of the shell material. Despite the fact that most colloidal particles used by the authors in this process are not food grade (such as polymethylmethacrylate and polystyrene) or that the fusing step could not be applied in the food industry (such as sintering of silica particles at high temperature), there is no reason why this process could not be adapted to the food industry using food-grade colloidal polymeric particles and food-grade crosslinkers.

In most microencapsulation processes, the shell material is dissolved or suspended in an appropriate solvent in order to facilitate the formation of a uniform and complete coating of the active ingredient, followed by crosslinking of the shell material or by drying of the solvent which leads to the formation of a continuous barrier around the active ingredient. However, solid-solid interactions in the dry state, which are mostly electrostatic in nature, can in some instances be sufficient to form a self-assembly of smaller particles around a larger one in a uniform and continuous fashion. For example, Tsutsumi *et al.* (1998) mixed together, in a fluid bed, glass beads and silica particles with average sizes of 130 and 1 μm respectively, and shortly after starting fluidization obtained a self-assembly of the

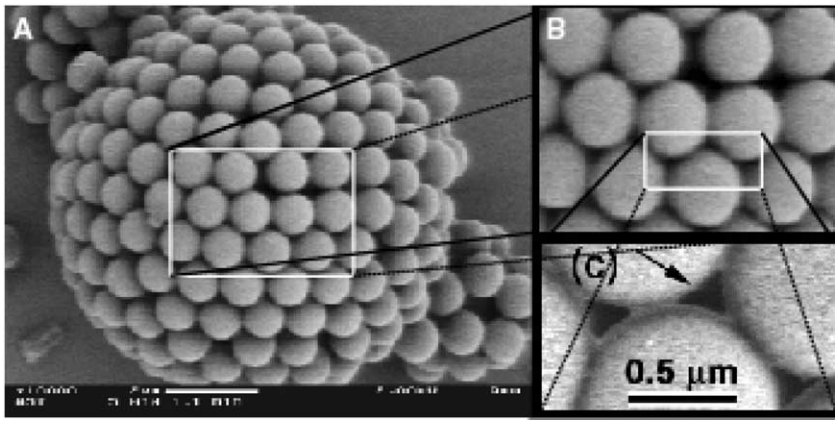

Fig. 5. Colloidosome microcapsule. Reprinted with permission from *Science, 298*, 1006–1009 (2002). ©2002, American Association for the Advancement of Science.

silica particles by 'dry coating' the glass beads. In their case, the self-assembly was stabilized by spraying a coating formulation onto the beads in order to trap the silical/glass bead assembly. Researchers at Nara Machinery Co. in collaboration with the University of Tokyo (Honda, Kimura, Matsuno, & Koishi, 1991; Ishizaka, Honda, & Koishi, 1993; Matsuno, Watanabe, Ono, & Koishi, 1996; Yoshihara, 1999) have developed a hybridization microencapsulation technology based on the self-assembly of smaller particles onto larger active material particles. However, in this process, the binding is achieved by embedding the coating layer into the active ingredient by applying enormous impact force for a few minutes under controlled conditions. The relatively simple apparatus is made of a stator, a rotor and a recycling line. The resulting particles exhibit slow release properties and altered wettability, depending on the nature of the coating particles.

Microencapsulation, in its broader sense, can include the production of molecular complexes exhibiting controlled release or targeted delivery properties of the active ingredient. The term 'nanoencapsulation', coined by pharmaceutical scientists, is more of a marketing tool than a description of the process, which involves the formation of a complex between a polymeric active ingredient (typically a protein) and a polymeric vector, without the actual coating of the active ingredient by a shell layer, as the term above suggests. The said complex often exhibits very different solubility and stability characteristics and also sometimes has an increased uptake rate by the epithelium, which results in an overall increase in the bioavailability of the active ingredients. The relevance of such processes for the food industry can be seen in the targeted delivery of probiotics or nutrients in the intestinal tract or in the modification of solution properties of proteins and other hydrocolloids. Chitosan nanoparticles of polypeptides, DNA or synthetic polymers were prepared by Janes, Calvo, and Alonso (2001) and the resulting particles showed improved uptake through mucosal cells compared to non-encapsulated ingredients. Carino, Jacob, and Mathiowitz (2000) developed nanoparticles of insulin complexes with various biodegradable polymers such as polyesters and polyanhydride. The nanoparticles are shown to be relatively stable in the gastric tract and reach the intestinal tract to be absorbed through the epithelium. The ''encapsulated'' insulin can therefore be administrated orally and maintains its effectiveness, while unencapsulated insuline must be administrated *sub cutaneous* because of its instability in the gastric tract. Similarly, Li, Wang, and Wu (1998) prepared gelatin-encapsulated BSA nanoparticles by an emulsification method. The release of the BSA was shown to be diffusion-driven and temperature-dependant.

A microencapsulation process coming from the ceramic industry is the sol-gel process, which can be regarded as an interfacial inorganic polymerization encapsulation process. As the name implies, sol-gel encapsulation involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids usually consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are the most popular because they react readily with water and in the food industry alkoxysilanes such as tetramethoxysilane (TMOS) and tetraethoxysilane seem the most appropriate because of the low toxicity of the side products and the fact that the resulting microcapules are basically just glass (for a treatment of food application and toxicological implication of silicon dioxide, see Villota & Hawkes, 1986). The sol-gel process can be performed in such as way as to encapsulate an active ingredient inside otherwise

hollow microcapsules with very thin walls. The microcapsules can be anywhere between sub-micron size to a few tens of microns. The process can also produce filled microparticles entrapping the active ingredient in the solid glass matrix. The most popular use of the sol-gel microencapsulation process is the production of immobilized biomaterials such as enzymes and microorganisms (An, Jones, & Foglia, 2002; Brinker, Ashley, Bhatia, & Singh, 2002; Heichal, Rappoport, & Braun, 1995; Inama, Dire, Carturan, & Cavazza, 1993; Kato, Gong, Saito, & Yokogawa, 2002; Reetz, Zonta, & Simpelkamp, 1996), which in some instances increase the enzymatic activity and/or increase the thermal stability and shelf life of the biomaterial. It is believed that the sol-gel microencapsulation process could be used for any food ingredients such as flavors, preservative agents, vitamins and nutrients. The main advantage of this particular process is the very mild processing condition (room temperature, slightly acidic or basic pH), the small particle size achievable, and the relatively affordable raw material. From an industrial point of view, the sol-gel process could be scaled up even considering the tight cost-in-use constraint characteristic of the food industry.

Conclusion

Despite the wide range of encapsulated products that have been developed, manufactured and successfully marketed in the pharmaceutical and cosmetic industries, microencapsulation has found a comparatively much smaller market niche in the food industry. The technology is still far from being fully developed and has yet to become a conventional tool in the food technologist's repertoire for several reasons. First of all, the development time is rather long and involving requires multidisciplinary cooperation. Secondly, the low margins typically achieved in food ingredients and the relative inertia of well-established corporations are an effective deterrent to the development and implementation of novel technologies that could result in truly unique food products, whether for more effective production, food fortification, neutraceuticals, improved organoleptic properties or development of ''novelties' food products. However, the most important aspect of R&D, from the very first lab-bench tests, is an understanding of the industrial constraints and requirements to make a microencapsulation process viable, from the transition to full-scale production to the marketing of the final product.

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