Nano- and micro-structured assemblies for encapsulation of food ingredients

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This *tutorial review* provides an overview of the science of food materials and encapsulation techniques that underpin the development of delivery vehicles for functional food components, nutrients and bioactives. Examples of how the choice of materials, formulation and process affect the structure of micro- and nano-encapsulated ingredients and the release of the core are provided. The review is of relevance to chemists, material scientists, food scientists, engineers and nutritionists who are interested in addressing delivery challenges in the food and health industries.

1. Introduction

Microencapsulation is the packaging of small particles of solid, liquid or gas, also known as the core or active, within a secondary material, also known as the matrix or shell, to form small capsules. The contents of the capsule are isolated from the surrounding environment and are released in response to a trigger such as shear, pH or enzyme action, thus enabling their controlled and timed delivery to a targeted site. Microencapsulation technology has applications in the medical, pharmaceutical, cosmetics, chemical, agricultural and food industries.[1–6]

Food ingredients perform a variety of roles when they are formulated and processed into food products. Apart from their nutritive value, food ingredients contribute to flavour and texture. Some food ingredients (*e.g.* vitamins, minerals, folic acid, phytochemicals and functional lipids, probiotic bacteria, amino acids and proteins) also have a physiological role. These ingredients, also known as bioactive food ingredients, are used in the development of functional foods—which are foods that have a role beyond normal nutrition.[7] Bioactives need to be protected during storage of the bioactive ingredient, processing and storage of the functional food and also during gastrointestinal transit until they reach the desired site in the body after ingestion.[8–11]

Encapsulation protects sensitive food ingredients (*e.g.* flavours, polyunsaturated oils, vitamins) against heat, moisture and pH until they are required to be released. Encapsulation can mask the taste of nutrients such as mineral salts that are added for the purpose of food fortification. Examples of where encapsulation offers benefits for controlled release include encapsulated flavouring agents in chewing gums released on chewing, encapsulated leavening agents released during baking and encapsulated probiotic bacteria which are protected from the harsh gastric environment and released in the small intestine. Encapsulation may also simply serve to transform liquid ingredients into free-flowing powders for the

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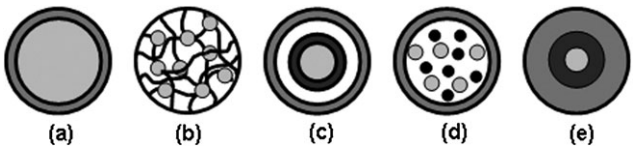

Fig. 1 Morphologies of microcapsules: (a) single-core capsule, (b) dispersed core in polymer gel, (c) multi-layer capsule, (d) dual-core capsule and (e) single-core–multi-shell capsule.

convenience of improved handling and incorporation into dry food systems.

In the food industry encapsulation is used to deliver a range of food ingredients within small capsules when direct addition of the food ingredient compromises the quality of the manufactured food product. Capsules that are less than 100 nm have been classified as nanocapsules, whereas those in the order of microns are termed microcapsules. Although strict classifications may vary, the capsules are built by manipulation of matter at the nanometre scale. As the core is protected from other components in the food and from the environment, the use of encapsulation can improve the nutritional content of food without affecting the taste, aroma or texture of food, mask off-flavours, and enhance the shelf-life and stability of the ingredient and the finished food product.

Nano- and micro-structured assemblies including emulsion-based systems formed with food-grade ingredients including food biopolymers (proteins, carbohydrates), fats, low molecular weight surfactants and co-polymers (protein–carbohydrate conjugates) have been employed to deliver a range of functional ingredients into foods. [4,8,9,12] The structure of encapsulated ingredients can broadly be classified into capsules with (a) a core that is surrounded by a shell of the matrix material or (b) a core that is entrapped within a continuous network of the matrix material. Variations of these include capsules with multiple cores or multi-layered capsules (Fig. 1).

The ability to manipulate food components at the nanometre scale has enabled food formulators and processors to develop encapsulated ingredients to enhance the quality of traditional foods and address challenges in delivering bioactives aimed at improving the health of consumers. This tutorial review considers the design of encapsulated food ingredients. We will examine the formulation and technology for construction of supramolecular assemblies from natural and processed food materials into architectures that protect ingredients until they are released by the desired trigger event or external stimulus.

2. Encapsulated food ingredients—understanding requirements for design

Each encapsulated ingredient has to be tailored to match its end application. Food ingredients have a multiplicity of inherent chemical, physical and nutritional functions. The expression of functionality required of the food ingredient is often specific to its end application. Even when identical ingredients are used in different applications, the stage at which its release is desired may be different depending on the particular function required of the ingredient in that food application.

Encapsulation is typically applied to solve problems relating to stability of food ingredients and their performance in a final food application. Hence, the definition of the purpose for encapsulation is necessary for developing suitable encapsulation solutions. It could be that encapsulation is required to overcome physical or chemical instability of the ingredient, physical incompatibility of ingredients in a formulation, undesirable interactions of the ingredient with other components of the food matrix or premature release of flavour or bioactive ingredients.

Triggers for the release include shear stress such as that encountered during food processing or chewing, degradation of matrix material resulting in erosion of the protective layer, diffusion of the core which is governed by partitioning coefficients between the matrix and the environment or swelling of the matrix due to absorption of fluid when placed in a compatible medium and melting of the matrix or coating.

It is essential to understand the purpose of encapsulation and the mechanism for ingredient release. This knowledge guides the rational design of encapsulated ingredients, from selection of the appropriate matrix material and formulation to the processing of the microcapsule to obtain structures that protect the core and respond appropriately to the desired external stimulus for release of the ingredient.[13]

3. The active core—the encapsulated molecules

Among the traditional food ingredients that have been encapsulated are (a) flavouring agents (*e.g.* sweeteners, seasonings, spices, essential oils), (b) food acids and bases (*e.g.* citric acid, sodium bicarbonate), (c) lipids (vegetable oils, milkfat), (d) food additives (*e.g.* preservatives, pigments), (d) minerals (*e.g.* calcium and iron salts) (e) vitamins (*e.g.* carotene) and (f) colours.[2,4] More recently, there has been growing interest in encapsulation of bioactive ingredients, particularly omega-3 oils,[14] plant phytonutrients,[15] and probiotic bacteria[6,16] because of their associated health benefits. All these food ingredients vary widely in their chemical, physical and physiological properties. The retention of the food ingredient core within a microcapsule and its stability are dependent on many factors: the chemical nature, molecular weight, polarity and volatility of the food ingredient, its interaction with the matrix material and its location within the structure of the microcapsule until its release is triggered by an external stimulus.

4. Materials for the encapsulant matrix—the building blocks

The materials used for encapsulation of ingredients have to be food-grade if the ingredients are to be used for the manufacture of foods. The food materials commonly used as encapsulants can be selected from a diverse range of natural biomaterials or allowed food additives that have been granted GRAS (generally regarded as safe) status. Commonly used in the formulation of encapsulated ingredients are food biopolymers (proteins, carbohydrates), fats, low molecular weight surfactants and co-polymers.[8,9]

The molecular structure of these materials and how they can be assembled into physical microstructures dictate their

usefulness as encapsulants. The functional properties of food ingredients that make them useful as matrix materials are their emulsifying properties and their ability to build viscosity and to form gel networks.

The ability of the matrix material to undergo a reversible phase transition (solid to liquid) in response to an environmental trigger is also useful. The most obvious example is the solidification of fat on cooling and melting on heating. Active cores can be embedded in the solid fat and these are released when the temperature is raised above the melting point of the fat.

Another example is the formation of a glass (*i.e.* amorphous solid) of hydrophilic molecules by rapid dehydration of a dispersion of a biopolymer. Glassy states may also be achieved by rapid cooling of concentrated sugar solutions and plasticised mixtures of sugar and hydrophilic biopolymers (polysaccharides and proteins). The temperature at which the phase transition occurs is termed the glass transition temperature. The glass transition temperature is influenced by the molecular weight of the sugar and the water content as well as other components in the formulation. Increasing molecular weight generally increases the glass transition temperature. Water is a very effective plasticiser, enhancing the mobility of the system and depressing the glass transition to a lower temperature. Simple sugars exhibit a glass transition over a narrow temperature range while biopolymers have a broader temperature range for the glass transition.[17] Active cores can be dispersed in sugars or biopolymers at a temperature above the glass transition temperature of the system. Cooling results in entrapment of the core and its stabilisation due to the marked reduction in molecular mobility in the glassy state. The cores are released on increasing the temperature or the moisture content of the system due to the plasticisation of the matrix above the glass transition temperature.

There are recent reviews on the functional properties of food materials which discuss the mechanisms underlying the formation of structured food materials and how they can be manipulated on the nanometre scale by process-induced modifications to alter their properties and their subsequent functionality on a macroscopic scale.[18–20]

4.1 Food proteins

Food proteins including soy proteins, milk proteins—caseins and whey proteins, egg proteins, zein or hydrolysates of these proteins are commonly used as encapsulant matrices. Their properties are influenced by their amino acid composition, conformation and charge as well as their denaturation temperature. Proteins, because of their amphiphilic nature, are prone to self-assembly.

Aggregation and gelation of proteins enable the development of networks with embedded ingredients. When different conditions are used to direct the assembly of the proteins, the relative contribution of hydrogen bonding, hydrophobic interactions, electrostatic interactions and van de Waals' interactions to the formation of a three-dimensional network varies. The assembly of proteins into gelled structures may be triggered by acidification, which neutralises the charge on the protein as the pH approaches the isoelectric point (pI) of the protein, or by heating which causes unfolding and exposure of hydrophobic groups. Gelation of certain proteins (*e.g.* caseins) is facilitated by addition of ions such as calcium. The microstructure of protein gels is also dictated by the conditions of gelation (Fig. 2). For example, fine-stranded (fibrillar) structures are formed at pH away from the pI and particulate gels are formed at pH near the pI of the protein.[19,21] The gel structure formed becomes the matrix for embedding active cores.

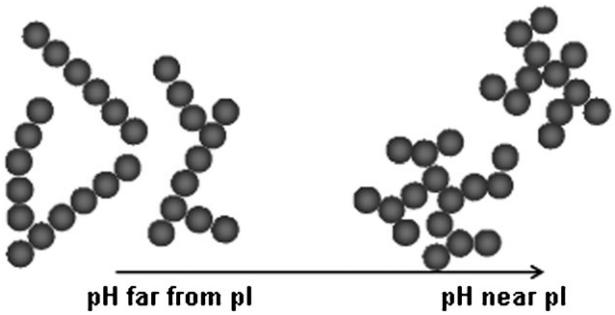

Fig. 2 Schematic representation of filamentous or particulate protein aggregates under different pH conditions. pI is the isoelectric point of the protein.

Proteins have the ability to assemble at interfaces. The type and robustness of an interface depends on the proteins used to form the emulsion. For example, caseins, which are random coil proteins, form an entwined layer of flexible chains while the globular whey proteins form strong dense assemblies at the interface. Both the structure and the rheological properties of the interface have a significant impact on the stability of the emulsion.[22] Their surface-active properties and ability to build viscosity have been exploited in emulsion-based encapsulation systems.[8]

Proteins may serve as an effective transporter of bioactive molecules because of their ligand binding properties. For example, the casein micelle in milk, itself a self-assembled nanoparticle, is an effective carrier for calcium.[23] Another milk protein, β-lactoglobulin, which belongs to the lipocalin family of proteins, has high affinity for hydrophobic molecules such as fatty acids and retinol. Recent studies have shown that the binding of surfactants causes denaturation of the protein but does not affect the conformation of β-lactoglobulin in the region of the retinol binding site.[24]

Proteins may be modified by a number of physical, chemical and enzymic modifications which alters their properties,[25] with consequent effects on their functionality as encapsulants. For example, hydrolysis of proteins alters their emulsifying properties, with the effect being dependent on the degree of hydrolysis. Hydrolysis may expose buried hydrophobic groups leading to increased surface activity. However, excessive hydrolysis yields small peptides which lack an adequate distribution of hydrophobic and hydrophilic sites that result in reduced emulsifying capacity. In addition, small peptides are not able to form cohesive films, unlike peptides with higher molecular weight that can have multiple anchor points at an interface. Research on the effect of hydrolysis of whey protein concentrates showed that at a degree of hydrolysis of between 10–27%, emulsifying properties were improved but further

increases in the extent of hydrolysis resulted in inferior emulsifying properties.[26]

Heating promotes the formation of protein–carbohydrate conjugates *via* the natural Maillard reaction. The attachment of the carbohydrate can decrease the pI of the protein and increase its solubility under acidic conditions. Cross-linking of proteins can also occur. The Maillard reaction affects the solubility, gelling and emulsifying properties of proteins.[27,28] For example, the attachment of carbohydrates (*e.g.* maltodextrin) to β-lactoglobulin results in the formation of a block co-polymer. In emulsions, the protein is anchored at the interface and the carbohydrate protrudes into solution. This increases the interfacial thickness of the steric layer and enhances the colloidal stability of the protein-based emulsion.[29]

4.2 Food carbohydrates

Sugars (*e.g.* glucose, sucrose, oligosaccharide, glucose syrup) and polysaccharides (*e.g.* starch and starch products—low and high-amylose starch, dextrins; non-starch polysaccharides—alginate, pectin, carrageenan, gum arabic, chitosan, cellulose derivatives, cyclodextrin) are often used as constituents of the encapsulating matrix. One of their useful properties is their ability to form kinetically metastable amorphous glassy solids[30] where they can provide structural support for the delivery system. Their ability to bind specific molecules is complementary to their structural role.

Sugar and starch products are important components of encapsulated ingredients in powder formats because of their ability to be the carrier medium for active cores prior to dehydration and for their ability to form glassy solids in which the active is entrapped upon dehydration.[17,30] The dextrose equivalent of the maltodextrins, which is related to the number average molecular weight, has been used to guide the selection of maltodextrins in applications. However, the molecular weight distribution is a better predictor of the glass transition temperature and also of the viscosity in aqueous solutions.[31]

When sugars are used in combination with proteins in formulations that are dried, the sugar also stabilises proteins during dehydration by hydrogen bonding. The stabilisation provided is dependent on the structure of the sugars. Trehalose, a non-reducing sugar, has a superior stabilising effect compared to other simple sugars in stabilising proteins in the dry state but the protection afforded depends on the protein that is dried.[32] However, the use of high concentrations of low molecular weight sugars in formulations intended for drying can lead to sticky powders due to their low glass transition temperature.

Starch and maltodextrins have a number of applications as encapsulants.[33] Maltodextrins, because of their low viscosity at high solids, are useful in formulating dehydrated encapsulated systems where it is desirable to achieve a high solids concentration prior to drying. Maltodextrins provide structural integrity to the final product and their incorporation in place of simple sugars in formulations reduces stickiness during drying, an effect that is due to their higher glass transition temperature.

Starch is composed of two main polysaccharides—amylose and amylopectin. The chain lengths and the ratio of these components affect its phase behaviour and its structure forming properties.[34] High amylopectin-rich starch gels have poor mechanical properties and are more prone to chemical and enzymic degradation compared to high amylose-rich gels.[35] *In vitro* studies demonstrated that the use of high-amylose starch in combination with resistant starch improved the resistance of starch coatings to enzymic digestion.[36]

Polysaccharides form gels, although gelation occurs at lower concentrations than with proteins. The chemical structure of the carbohydrate, its molecular weight, the degree of branching and the functional groups all contribute to the balance of forces keeping the polysaccharide network together. Different polysaccharides have different mechanisms of formation.[37] For example, gels can be cold-set where they are formed on cooling heated dispersions (*e.g.* starch, agar, gellan gum), heat-set (*e.g.* curdlan, a food-grade bacterial polysaccharide) or cross-linked by calcium ions (*e.g.* alginate, low methoxy pectin).

Food carbohydrates play an important role in emulsion stabilisation due to their ability to increase the viscosity of the continuous phase of emulsion systems. However, most food carbohydrates are not surface-active and have to be used in combination with other ingredients with good emulsifying capacity (*e.g.* proteins or low molecular weight surface-active ingredients) when formulating emulsion-based encapsulation systems. The notable exception is gum arabic. With polysaccharide and proteoglycans as its principal components, gum arabic fulfils a surface-active role in addition to providing structural stability to both wet and dry encapsulation systems. An example of the encapsulating properties of gum arabic is illustrated when the gum is used for the stabilisation of soy oil emulsions.[38]

Specific biopolymer–molecular interactions may also be capitalised upon for encapsulation. An example is the formation of helical inclusion complexes of flavour compounds with the amylose component of starch. The flavour compound may be released at high temperature or high water activities.[39] This ability of starch-based material to bind, protect and retain flavours in an amorphous carbohydrate glass which is released in the mouth on contact with saliva is an example of the carbohydrate matrix playing a multi-functional role.

Starch can be chemically modified with *n*-octenyl succinic anhydride to improve its emulsifying properties. Spray-dried sea buckthorn kernel oil powders using octenyl succinylated corn starch as the encapsulant did not contain surface oil, whereas powders made with maltodextrins had lower encapsulation efficiencies. However, the storage stability of the oil powders was not related to encapsulation efficiency but oxidation of the oil was increased with increased humidity, suggesting the importance of the physical state of the matrix.[40]

4.3 Lipids

A wide range of lipids (*e.g.* natural fats and oils, mono- and di-glycerides, phospholipids, glycolipids, waxes—beeswax and carnauba wax) may be used for encapsulation.

Most food fats (*e.g.* milkfat, soybean oil, cocoa butter) have triglycerides as their major component (~98%). These

non-polar lipids are the obvious carriers of lipophilic bioactives in emulsion systems.[8] The chemical and physical properties of fats govern their microstructural characteristics, their colloidal stability, rheological properties and moisture barrier properties. A decrease in the length of the hydrocarbon chain attached to the glycerol backbone or increase in the degree of unsaturation of the fatty acid chains lowers their melting point and decreases their moisture barrier properties. The polymorphic form of fat crystals (*e.g.* α, β, β′) also influences these properties.[41] Active cores may be embedded in a solid fat matrix and released on increasing temperature. In this case, the physical properties of the fat have to be matched to the trigger temperature for release of the encapsulated active.

Fats, with their good moisture barrier property, are also useful as encapsulant materials in systems which require protection against moisture ingress. Fats perform a moisture barrier function most effectively where they are used as a secondary coating but also they can retard water transport when emulsified with other encapsulant materials. The water vapour permeability through fat barrier films is reduced when the fat used has a high solid fat content in addition to having a more organised crystalline state. Fat crystals with a smaller domain size provide better barrier properties. In addition, the film must be malleable for low water vapour permeability as brittle films are more prone to cracking.[42] For emulsion-based films, the water vapour barrier properties are affected by lipid water vapour permeability and the viscoelasticity of the film. Milkfat and beeswax emulsion films were found to have superior water barrier properties to films made with lipids (carnauba or candlilla wax) with lower water vapour permeabilities.[43]

Polar lipids (*e.g.* monoglycerides, phospholipids, glycolipids), because of their amphiphilic properties, are surface-active and can be used to stabilise emulsions containing active food ingredients. Polar lipids interact with water and self-assemble into supramolecular liquid crystalline structures. This self-assembly behaviour of polar lipids can be employed to protect sensitive molecules, to solubilise flavours and bioactives and control their release. Understanding the molecular properties of the polar lipids, their inherent phase behaviour and how this is modified by the introduction of a food ingredient (core) underpins development of novel structures for delivery of ingredients.[44]

5. Microencapsulation techniques

Various processes may be used to produce encapsulated ingredients. Many of these have been adapted from the chemical and pharmaceutical industries. Recent reviews cover the processes and technologies commonly used in the food industry.[4,45]

An understanding of the physico-chemical properties of the core and factors that control the interfacial and aggregation behaviour of the matrix materials is needed to choose suitable processes for producing encapsulated ingredients.

5.1 Spray drying

Spray drying is a well-established process in many sectors of the food industry. It is a commonly used encapsulation method because it is more cost-effective than other techniques. Dried ingredients are valued for their convenience and shelf-life stability.

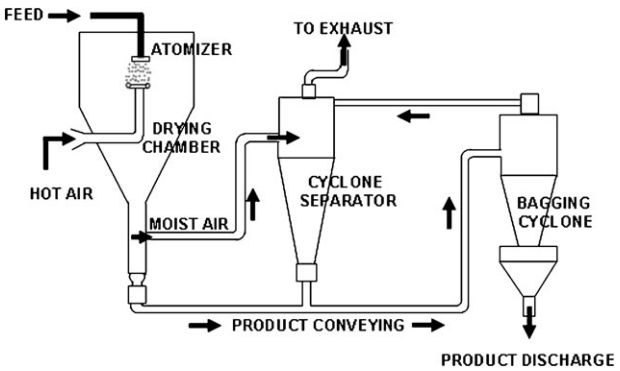

Fig. 3 Schematic of the spray drying process.

The basic process for production of a spray dried encapsulated ingredient involves dissolving the core in a dispersion of the matrix material. The dispersion is atomised into heated air to facilitate the rapid removal of water as the droplets are mixed with the hot air in the drying chamber. The powder particles are then separated from the drying air at the outlet at lower temperatures (Fig. 3).

Only aqueous-based dispersions are used in the food industry. Hence the matrix material requires good solubility in water. The ability to achieve high solids at low viscosity, and good film and emulsifying properties are desirable. The glass transition temperature of the matrix material has to be high enough to avoid the formation of sticky powders during drying. Both hydrophilic and hydrophobic cores can be incorporated into the dispersion prior to drying. Hydrophobic cores are usually dissolved in the oil phase and an oil-in-water emulsion is formed prior to drying. Hydrophilic cores are dispersed in the aqueous phase which contains the water-soluble matrix material (sometimes called the wall material). Matrix materials such as gum arabic, milk proteins, soy proteins, modified starch and maltodextrins have typically been used. When water-soluble core ingredients are entrapped within the powder particle, the release occurs when the powder is reconstituted in water. When a stable oil-in-water emulsion containing an oil or oil-soluble core is dried, the core is surrounded by the interfacial membrane and its release is dependent on the trigger that destroys the integrity of the membrane.

Spray drying is used for the production of many encapsulated food ingredients—vitamins, minerals, flavours, polyunsaturated oils, enzymes and probiotic microorganisms. It is notable that spray drying may be used for heat sensitive and volatile ingredients (*e.g.* flavours) as the wall material protects the core and limits losses of volatiles. This is because of the short exposure time to the hot air in the dryer and rapid water evaporation which keeps the temperature of the core low. A comprehensive review on the use of spray drying for production of microencapsulated ingredients has been published.[46]

5.2 Spray cooling

In spray cooling, an active core dispersed in a liquefied coating material (matrix) is atomised into a cool environment such as

cool air.[45] Usually high melting fats are used as the matrix material. On cooling, the fat solidifies and the core is immobilised. Various water-soluble ingredients including mineral salts, enzymes, flavours, food acids and protein hydrolysates have been incorporated into solid fat particles (lipospheres) to delay the release of the core. These ingredients find applications in dry products but are not suited for incorporation into high moisture foods. Only limited delayed release of a water-soluble active core in high moisture foods can be achieved as some of the core molecules are at the surface of the particle.

5.3 Freeze drying

Freeze drying may be used for very heat sensitive ingredients. However, commercial application of freeze drying is restricted to very high value ingredients such as probiotic bacteria. This is because spray drying is less costly and a more rapid process for water removal than freeze drying. Freeze dried powders have a more porous structure than spray dried powders and this adds to transport and storage costs.

5.4 Fluid bed coating

A fluidised bed is used to coat solid particles of the core. The solid particles are suspended in air and the encapsulant material is sprayed onto the particles, forming a coating.[45] The encapsulant material may be a concentrated solution or dispersion, a hot melt or an emulsion. Most encapsulant materials (*i.e.* fats, carbohydrates, emulsifiers, proteins) may be employed in this process, allowing particles with very different controlled release properties to be developed. This method can be used to give spray dried powders containing sensitive cores (*e.g.* polyunsaturated oils) a secondary coating for added protection.

5.5 Extrusion

In a simple extrusion process, pressure is applied to force a hot biopolymer mass containing the dispersed active core through an orifice into a hardening bath. This process has been used extensively to microencapsulate flavours in glassy carbohydrate matrices. The flavour is injected into a hot mass of the biopolymer melt and extruded into a hardening bath, usually with isopropyl alcohol.[4] An alternate process, syringe-extrusion, is typically used for the formation of alginate beads. An alginate solution containing the active core is extruded as droplets into a calcium chloride solution and beads are formed. This process can be carried out at lower temperatures.

Another extrusion-based process is the spinning disk. Core particles suspended in a solution of the matrix material are passed over a rotating cylinder to form microparticles. In centrifugal co-extrusion a double capillary is used, with the core within the inner capillary and the matrix material on the outer.

5.6 Microencapsulation processes based on supercritical fluids

In these processes, the core ingredient is dispersed in matrix material solubilised in a supercritical fluid (usually carbon dioxide). Removal of the carbon dioxide results in the core being encapsulated within the matrix material. In rapid expansion of supercritical solutions (RESS), the dispersion is sprayed through a nozzle and a particulate material containing the core is formed. Developments in the use of supercritical fluids for encapsulation are provided in a recent review.[45]

5.7 Coacervation

The phase separation of a single polyelectrolyte or a mixture of polyelectrolytes from a solution and deposition of the agglomerated colloidal particles (*i.e.* the matrix material) on an immiscible active core results in the formation of a simple coacervate or a complex coacervate (Fig. 4), respectively. Complex coacervates of oppositely charged biopolymers have been used in the food industry for encapsulation of active food components such as flavours, water-soluble actives and oils.

When a solution of biopolymers of opposite charge is mixed, a complex is formed. Many factors including the biopolymer type (molar mass, flexibility and charge), pH, ionic strength, concentration and the ratio of the biopolymers affect the strength of the interaction between the biopolymers and the nature of the complex formed.[18,47,48] Although electrostatic interactions are considered to drive the interaction between biopolymers of opposite charge, hydrophobic interactions and hydrogen bonding can also contribute significantly to the complex formation.[48]

Depending on the conditions and the biopolymers involved, a one-phase or two-phase system can result. When a two-phase system is formed, one of the phases is depleted in both biopolymers while the other is enriched in both biopolymers in a precipitated form or as a complex coacervate.

Coacervates may be formed when a protein at a pH below its isoelectric point (*i.e.* when it carries a positive charge) is mixed with a polyanion. Examples are mixtures of whey protein or gelatine with gum arabic at pH below the isoelectric

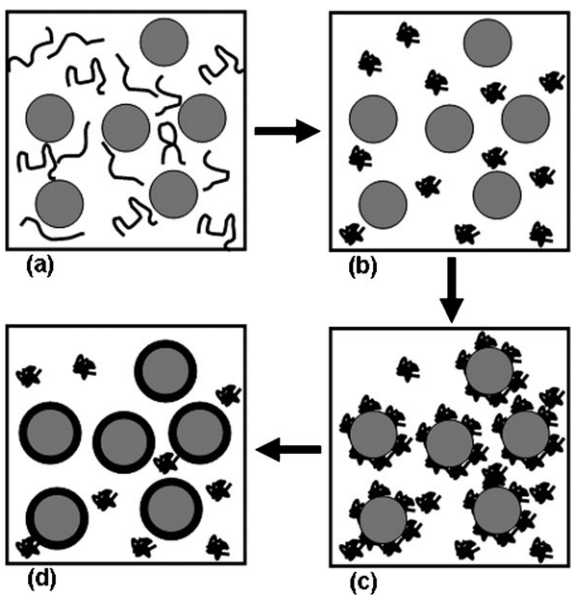

Fig. 4 Example of complex coacervation involving (a) dispersion of the core in gelatine, (b) initial coacervation of gelatine after addition of coacervation agent (*e.g.* absolute ethanol), (c) coacervation of gelatine on the surface of the core and (d) formation of the cross-linked shell by reticulation of the interface.

point of the respective proteins. Similarly, solutions containing a cationic polysaccharide (*e.g.* chitosan) and an anionic polysaccharide (*e.g.* alginate) have the ability to form coacervates.[47,48]

One of the factors that limit the use of coacervates in encapsulation is their sensitivity to pH and ionic strength. To increase the robustness of coacervates, they may be cross-linked. Glutaraldehyde is an effective cross-linker but there are legislative issues with its use. Enzymic cross-linkers, such as transglutaminase, are more acceptable in the food industry and recently plant polyphenols have been used to cross-link gelatine-based coacervates.[49]

5.8 Liposomes

Liposomes are spherical bilayer vesicles that are formed by dispersions of polar lipids in aqueous media. Liposomes have been used widely in the pharmaceutical industry for target delivery of drugs but their application in the food industry is still limited because it is a costly process. Uni-lamellar or multi-lamellar liposomes can be formed. Phospholipids have typically been used to prepare liposomes.

Liposomes can be used as carriers for both hydrophilic and lipophilic molecules. The entrapped actives are stabilised against changes in the environment (pH, temperature, ionic strength). The core contents are released when the gel to liquid transition temperature of the phospholipids used in the formulation is reached. At the transition temperature the ordered packing structure of the bilayer is lost as the hydrocarbon chains melt. The transition temperature is increased with longer hydrocarbon lengths. Cholesterol may also be added to improve the rigidity of the structure and to improve the resistance of the liposomal system to degradation under *in vitro* and *in vivo* conditions.[50]

5.9 Molecular inclusion complexes with cyclodextrins

Cyclodextrins, cyclic oligosaccharides of α-(1,4) linked glucopyranose units, are used in microencapsulation for their ability to form molecular inclusion complexes. Cyclodextrins have a hydrophobic interior and a hydrophilic exterior. The internal size of the hydrophobic cavity that hosts hydrophobic molecules is dependent on the number of glucose units, with α-, β- and γ-cyclodextrins being composed of six, seven and eight glucose units, respectively (Fig. 5).

Complex formation with a hydrophobic molecule is driven because displacement of water from the interior of the cyclodextrin is energetically favourable. Complexation increases the solubility of hydrophobic guest molecules in water and the ingredient is protected against degradation. Unpleasant flavours and odours may be masked. The guest molecule is usually displaced by heating.[51]

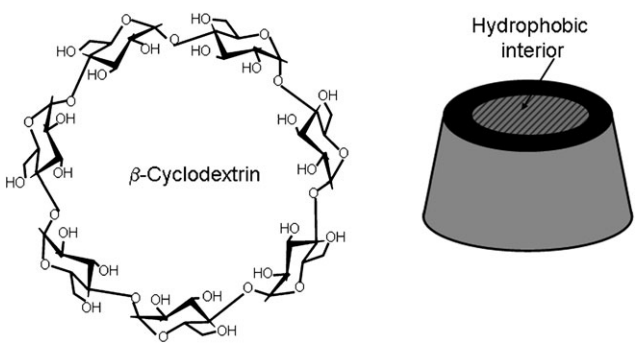

Fig. 5 Structure of β-cyclodextrin.

6. Developments in structured assemblies for encapsulation of food ingredients

Developments in encapsulation of food ingredients have been directed at designing more robust functional encapsulation systems with finer control of release mechanisms. This has been achieved through the construction of various supramolecular structures by manipulation of matter at the nanometre scale.

6.1 Emulsion-based systems

Emulsion-based systems with various structures have been used for delivery of lipophilic food ingredients (*e.g.* omega-3 oils, carotenes, tocopherols). The water phase of the emulsions can also serve to deliver water-soluble food ingredients. Control over the properties of emulsion-based encapsulation systems has been achieved by tailoring the characteristics of the dispersed phase (*i.e.* size, charge, interfacial properties of droplets) as well as the microstructure of the emulsions.[8] Emulsions may be supplied in liquid, gelled or powdered formats.

Conventional emulsions. A range of food ingredients may be used as the building blocks for conventional emulsions. When proteins are used in combination with sugars to produce microencapsulated oil powders, increasing the dextrose equivalent (DE) of the sugar component improves microencapsulation efficiency (*i.e.* less surface oil or less oil easily accessible to organic solvents). This effect was attributed to the powder with higher DE sugars being less porous and having more uniform matrices.[52] Improvement in the oxidative stability of microencapsulated polyunsaturated oil powders has been achieved by using glycated proteins formed by heating aqueous protein–sugar mixtures (*i.e.* Maillard reaction products) as encapsulating matrices.[53]

Multi-layered emulsions. To improve the physical stability of emulsions, multi-layer emulsions may be formed by using layer-by-layer adsorption of oppositely charged polyelectrolytes onto a primary emulsion droplet. This enhances the robustness of the interface, protects sensitive actives against degradation and allows more influence over mechanisms for control of core release compared to conventional unilayer emulsions.[8]

Nanoemulsions. Nanoemulsions are metastable dispersions of nanoscale droplets less than of 100 nm made by application of high shear. The rupture of droplets may be achieved by ultra-sonication or microfluidisation. The amount of surfactant required to stabilise nanoemulsions is greater than that required for microscale emulsions.[54] Kinetically stable nanoemulsions of triglyceride oils may be achieved by using very high pressure homogenisers such as microfluidisers, low molecular weight surfactants and a co-solvent for stability of the oil phase.[55]

While microscale emulsions scatter light, the nanoemulsions are optically transparent. This property is of interest to the food industry as it enables the delivery of lipophilic flavours and bioactive ingredients in clear emulsions. Smaller size droplets also have the potential to improve the bioavailability of the core because of the increased surface area of nanoemulsions compared to conventional emulsions.

Microemulsions. These are thermodynamically stable transparent isotropic dispersions of nanodroplets with a size ranging from 5 to 100 nm. Microemulsions have a large solubilisation capacity for lipophilic and hydrophilic molecules. This protects the solubilised ingredients from degradation. The nanodroplets in a microemulsion are stabilised by a set of surfactants, generally in conjunction with a co-surfactant, such as short and medium-chain alcohols, which are required to further lower the interfacial tension. The application of microemulsions in food formulations has been limited by the toxicity of surfactants and co-surfactants used.

In the last two decades, effort has been dedicated to developing food-grade microemulsions free of co-surfactants, with a mixture of non-ionic surfactants. However, the removal of the medium-chain alcohol co-surfactant results in the decrease in the amount of solubilised oil and in the instability of the microemulsion upon dilution.[56]

Self-assembled polar lipid structures. Mono- and di-glycerides are extensively used in many food applications to control emulsion and foam stability. A peculiar characteristic of monoglycerides is their capacity to form various self-assembly structures when dispersed in water (Fig. 6). Lamellar phases can be dispersed in water in the form of vesicles or liposome structures. The use of stabilisers such as amphiphilic block co-polymers can also stabilise the dispersion of the cubic and hexagonal phases in water into dispersed bicontinuous cubic particles and bicontinuous hexagonal particles, generally termed cubosomes and hexosomes, respectively.

The dispersion of self-assembled lipid structures in water results in nanostructured particles that can be used as delivery systems in food applications. Their successful application depends on their capacity to incorporate the guest molecules within the various phases in appropriate amounts and to disperse these within a complex food matrix without losing the self-assembly structure. Food-grade applications of self-assembled structures are used to control release of aroma and to structure food products and as reactors for the creation of flavour compounds using the Maillard reaction.[57]

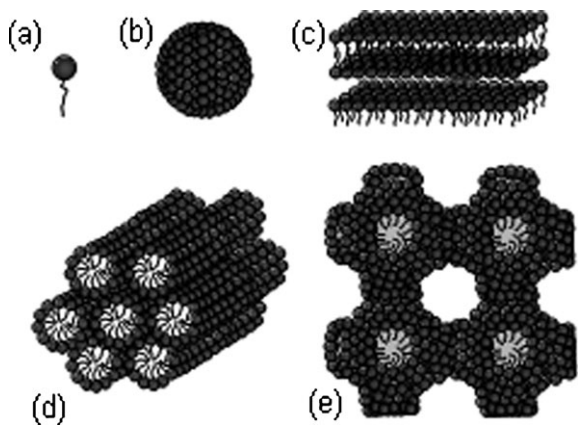

Fig. 6 Self-assembly structures: (a) individual lipid molecule with a polar head, (b) micelle, (c) hexagonal phase, (d) cubic phase and (e) lamellar phase.

Solid lipid emulsions. These include solid lipid nanoparticles and nanostructured lipid carriers. Emulsification is carried out in the presence of an emulsifier at a temperature above the melting point of the fat and the emulsion is cooled to solidify the fat containing the lipophilic active core.

The loading of the active and its stability within the lipid matrix are dependent on the type of lipid used, the melting point of the lipid and the type of crystal network formed on cooling. The lipid network of a purified lipid has a more perfect crystalline nature than a blend of lipids (normally a solid and liquid fat). A benefit of a lipid blend is the imperfections in the network, which can accommodate a higher loading of an active ingredient and anchor it more securely within the fat matrix.[58]

Double emulsions. Water-in-oil-in-water (W/O/W) double emulsions provide the possibility of entrapping a hydrophilic food ingredient in the inner water phase and delaying the release of this core when the emulsion droplet is in an aqueous environment. A hydrophobic emulsifier, typically polyglycerol polyricinoleate, is used to stabilise the inner aqueous phase of the W/O emulsion. This primary emulsion is then emulsified into water with a hydrophilic emulsifier.

Biopolymers and biopolymer hybrids (*e.g.* electrostatic complexes of whey protein and xanthan) are preferred as the external phase emulsifier as they provide better stability than low molecular weight emulsifiers.[59] Stability may be further enhanced by using a protein–carbohydrate conjugate (*e.g.* sodium caseinate–dextran) in place of the protein as the O/W emulsifier. This improves the stability of the particle against coalescence and the release of a water-soluble vitamin from the inner water phase is decreased.[60] Furthermore, these emulsions may be dried and the integrity of the double emulsion is maintained when the powder is reconstituted.[61]

6.2 Biopolymeric particles

Biopolymer-based gels have the ability to trap molecules, provide protection to the entrapped active cores and to reduce the diffusion rate of the active until an external stimulus is applied to weaken the gel network.

Hydrogels and micro-particles. By controlling the conditions for the assembly of polymer molecules, gels with different structural and release properties may be obtained. Alginate gel particles are often used for the delivery of probiotics. Another example of a hydrogel is cold-set whey protein gels for the delivery of iron salts, where the release of iron is dependent on whether the gel network is filamentous or particulate. The filamentous gels release more iron under *in vitro* intestinal conditions than particulate gels. This example and others are discussed in a recent review.[12]

Recently it has been shown that the casein micelle can be re-assembled with a hydrophobic core (vitamin D2), demonstrating the potential of self-assembled proteins to act as delivery vehicles for lipophilic molecules.[62]

Biopolymer complexes. Protein–polysaccharide complexes are widely used for delivery as hydrogel beads or core–shell nanoparticles. They include protein–anionic complexes (*e.g.* gelatine–gum acacia, whey protein–xanthan) and protein–cationic complexes (*e.g.* whey protein–chitosan). By coating microspheres of whey proteins (with oleoresin as a model hydrophobic core) with calcium alginate, a water-insoluble delivery system is obtained that protects a core against degradation and allows its controlled release in food systems.[63] Similarly coating of whey protein hydrogels containing a model drug (caffeine) with alginate reduces the swelling of the particle and influences the release of the drug.[64]

Acidification procedures and polymer ratios used for production of whey protein isolate–low methoxy pectin complexes influence the size, structure and zeta potential of the complexes formed and their ability to entrap vitamin B1 (thiamine).[65] This study highlights an additional lever that may be used to construct different structures for encapsulation of food ingredients.

6.3 Glassy matrices

Glassy states have the ability to entrap and protect sensitive food ingredients. At temperatures below the glass transition, the mobility of molecules is extremely slow, due to the high viscosity of the glassy matrix and this enables active cores to be trapped.[30] As the mobility of molecules (*e.g.* water, oxygen) through a glassy matrix is also arrested, sensitive cores can be protected from degradation.

However, some studies have indicated that factors other than the glass transition temperature may have a role in stability of the core. For example, the oxidation of polyunsaturated lipid in a waxy maize starch matrix was higher in glassy state extrudates than when the system was in a rubbery state. The presence of surface oil and micro-cracks on the surface of glassy state extrudates contributes significantly to higher rates of oxidation.[66] This demonstrates that microstructure plays a role in determining the stability of the oil.

The release of food ingredients entrapped in glassy state capsules may be triggered by transfer of the capsule into an aqueous environment or by increasing the temperature.

7. Functionality of encapsulation systems in food matrices

For an encapsulated ingredient to be successful in the market place, it has to meet several demands. The functionality of an encapsulated ingredient has to be tested in the final food product, taking into account the storage stability of the encapsulated ingredient, its compatibility with the food matrix, the processing stresses it has to withstand during food manufacture when it is in intimate contact with other ingredients and how it breaks down when consumed.

With respect to the storage stability of the encapsulated ingredients, powdered formats in the glassy state have advantages of convenience, ease of transport and improved storage stability over equivalent liquid formulations. Microencapsulated powders can be used for blending with other dry ingredients or incorporated as powders into some food products at various stages during the manufacturing process (*e.g.* encapsulated omega-3 oil powders in infant formula, breakfast bars and yoghurt) or reconstituted prior to incorporation into liquid products.

In dry blends, there may be exchange of moisture if there are differences in water activity of the microencapsulated ingredients and those of other dry ingredients in the blend. As formulations in their glassy state are most stable, it is important to consider the effects of changes in moisture and temperature on the effect of glass transition temperature of the powder composition under its conditions of storage.

When microencapsulated ingredients are mixed with other ingredients and processed, the encapsulated ingredient may be exposed to high temperature, increased moisture content and shear forces. Under conditions where the matrix material undergoes a phase change from a glassy state to the rubbery state because of high temperature and moisture, or is ruptured by shear or degraded by enzymes, the barrier properties of the encapsulating matrix are compromised. As a result active cores are less protected from undesirable interactions with other ingredients in the food formulation and the environment (*e.g.* low pH, oxygen) and there may also be premature release of the core. Hence, the development of encapsulated ingredients has to be tailored with the end application in mind.[13]

The target release of microencapsulated ingredients after ingestion is a challenge for the delivery of bioactives in functional foods. *In vivo* studies with humans that demonstrate the effect of the incorporation of the microencapsulated ingredients in food for a health outcome is necessary to ensure the bioavailability of the encapsulated core as the food matrix can also alter the release profile of a nutrient. Consumption of tuna oil-enriched bread prepared with microencapsulated tuna oil increased omega-3 fatty acids in the plasma, indicating that the encapsulated omega-3 fatty acids were bioavailable.[67] Trials with humans on the iron absorption from milk fortified with a liposomal preparation of ferrous sulfate showed that the encapsulated iron salt was bioavailable.[68] In both these examples above, microencapsulation was considered as a necessary first step to enable the incorporation of the active into the food product without detracting from the sensory properties of the food product. The demonstration of an effect *in vivo* in the food vehicle of choice was necessary to provide the proof of the bioavailability of the encapsulated ingredient.

8. Conclusions

The ability to manipulate food components at the nanometre scale has enabled food formulators and processors to develop encapsulated ingredients to enhance the quality of traditional foods and address challenges in delivering bioactives aimed at improving the health of consumers. Advances are being made in understanding how the physiological effects of food

ingredients are affected by food processing, the food matrix and how food is digested and metabolised, as well as the individual's genetic predisposition.[69] As the food industry becomes more integrated with nutritional sciences, it is expected to guide and facilitate new approaches, including encapsulation technology, for the targeted delivery of bioactive food ingredients.

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