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REVIEW

Oil encapsulation techniques using alginate as encapsulating agent: applications and drawbacks

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ABSTRACT

Oils are used in agriculture, nutrition, food and cosmetics; however, these substances are oxidisable and may readily lose their properties. To reduce their degradation or to mask certain undesirable aspects, one strategy consists in encapsulating the oil in inert structures (capsules). The capsules are classified according to the morphology, the number of cores and size, can be produced by several techniques: jet-cutting, vibrating jet, spray-drying, dispersion and millimicrofluidic. Among the polymers used as a membrane in the capsules, alginates are used in oil encapsulation because of their high gelling capacity, biocompatibility and low toxicity. In the presence of calcium ions, the alginate macromolecules crosslink to form a three-dimensional network called hydrogel. The oil encapsulation using alginate as encapsulating material can be carried out using technologies based on the external, internal or inverse gelation mechanisms. These capsules can found applications in areas as cosmetics, textile, foods and veterinary, for example.

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Alginate; encapsulation; extrusion; microcapsules; microencapsulation; mixing

Introduction

Oils are compounds widely used in agricultural (pesticides), nutritional (vitamins, fish oil), foods (flavour, essential oils, lipids, dye) and cosmetics (vegetal oils, fragrance) industries (Table 1). However, these substances are chemically unstable and susceptible to oxidation when exposed to oxygen, light, moisture and/or temperature (Goula and Adamopoulos, 2012). The lipid oxidation brings losses to the quality of food due to vitamins and proteins degradation or modification in the texture and flavour by the formation of volatile compounds (Ferrari, 1998).

Besides the oxidation, unpleasant taste/smell or high volatility can compromise the oils application in several domains (Peniche et al., 2004; de Paula et al., 2010). Oils with nutritional properties, such as the Omega-3 sources, show important nutritional and therapeutic properties. Nonetheless, the unpleasant smell and taste of these compounds limit their acceptance by consumers (Lee and Ying, 2008).

In order to decrease the oil degradation or mask some undesirable aspects, a strategy is to encapsulate oil in inert shell or matrix to isolate it from external environment (Risch and Reineccius, 1988).

Oil encapsulation has various uses including protection against moisture or oxygen, prevention of chemical reactions between two active species, modification of density, colour, shape or photosensitivity, increase of stability and controlled release of actives (Figure 1). Due to these advantages, encapsulation techniques have been largely employed in various industries such as the pharmaceutical, food, cosmetics and fragrances areas (Table 1).

In a practical example, the encapsulation of larvicidal oil allowed better preservation and handling of active (de Paula et al., 2010; Santos et al., 2014). In addition, the encapsulation promoted prolonged oil release, demonstrating to be a promising strategy to control tropical diseases transmitted by mosquitoes (de Paula et al., 2010).

In food processing, the flavour encapsulation is used to protect the oily ingredient against deterioration, volatile losses or interaction with other substances (Ziani et al., 2012; Carneiro et al., 2013; Nakagawa et al., 2013). Encapsulated flavour is frequently used to reinforce the organoleptic characteristics of foods as chewing gum, confectioneries, bakery products and powdered foods/beverages (Nakagawa, 2014).

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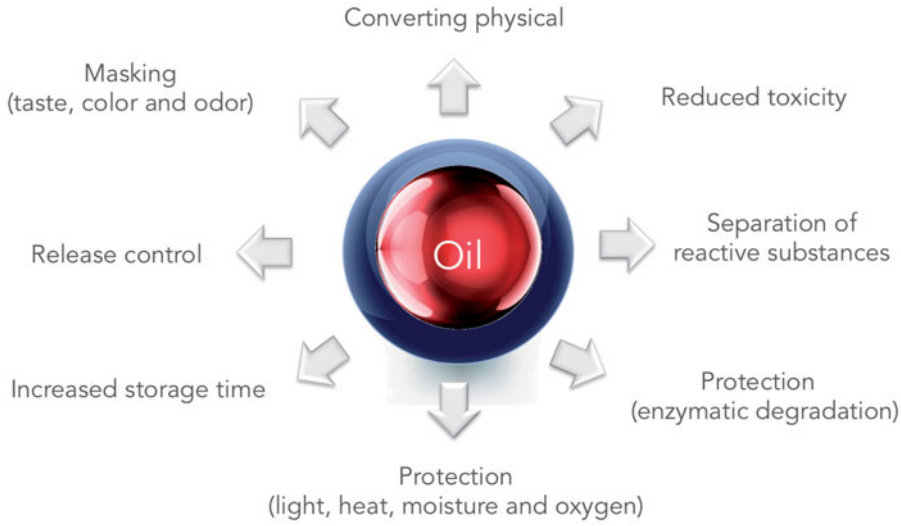


Figure 1. Benefits associated to oil encapsulation.

Table 1. Encapsulated oils used in different industrial fields.

Cosmetic	Berry oil; Argan oil; Caprylic/ Capric Triglyceride; Geranylgeranylisopropanol; Apricot kernel oil; Raspberry oil; Ginkgo biloba oil; Moringa oil; Pistacia Lentiscus oil; Vitamins A and E; Rose hip oil; Camellia oil; Black wheat oil; Jojoba oil; Soybean oil	Alginate	Attractive presentation, Protection of active, marketing and controlled release in skin and hair care products	AVEKA (2015) and CAPSUM (2015)
Food	Olive oil; coriander essential oil; flaxseed oil; fish oils; Vitamin A and E; basil oil; caraway oil; carrot oil; garlic oil; lemon oil; mustard oil; onion oil; orange oil; mint oil Mustard oil	Alginate; Chitosan; Modified starch; sodium caseinate; maltodextrin; caseinate; egg white protein; Pectin; Gelatin; Cyclodextrin; Genipin	Attractive presentation in molecular cuisine; masking of taste and protection of nutritional supplements; control release of flavour; control release of food preservative	Lee and Ying, (2008), Fu et al. (2014), Marques (2010) and Peng et al. (2014)
Textile	Rosemary oil	Ethylcellulose	Control release of fragrance in textiles	Voncina et al. (2009)
Pharmaceutical	Lipiodol; linolenic acid; Miglyol 810; soya bean oil; medium chain triglycerides	Amine-reactive PEO-PPO-PEO; Dextran; Alginate; Chitosan; EUDRAGIT®; Methacrylicacid; Amidated pectin	Cancer cell targeted delivery; insulin targeted delivery	Bae et al. (2007) and Cárdenas-Bailón et al. (2014)
Agriculture	Neem oil; linalool	Polyethylene glycol; cyclodextrin Alginate; Chitosan	Control of volatility and release of insecticide and pesticide	Jerobin et al. (2012) and Lopez et al. (2012)

In pharmaceutical industry, encapsulated oily anti-oxidant and vitamins are used to modulate the oxidative stress that is related to cardiovascular diseases, arteriosclerosis and cancer (Sabliov and Astete, 2008).

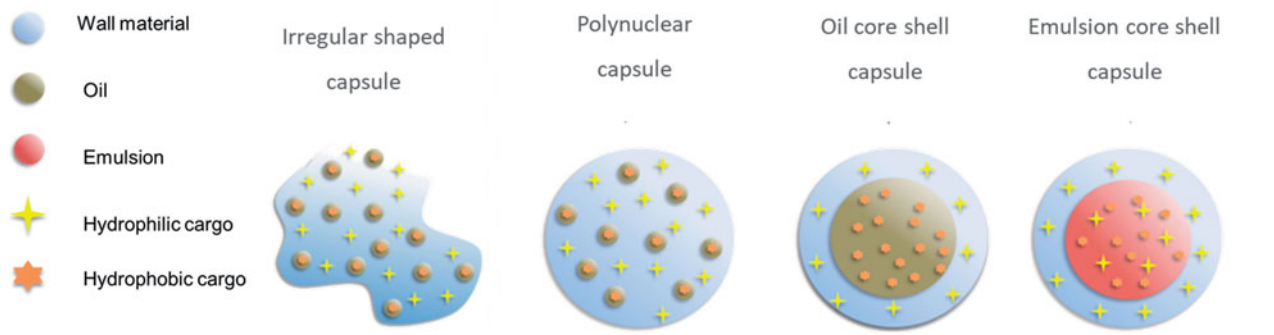
In human nutrition, fish oils are regularly promoted due to their beneficial roles for health and disease prevention. The encapsulation of salmon, shark, tuna and sardine oils promotes both the masking of fishy aroma/taste and the reduction of the oil sensitivity towards oxidation (Lee and Ying, 2008; Hosseini et al., 2013).

In textile area, the oil encapsulation is used to prolong and control the fragrance release in home care products, such as bed linen and perfumed sachets for clothes. In addition, encapsulated essential oils as eucalyptus and citronella can be incorporated in textiles to repel mosquitoes or other insects.

For veterinary applications, encapsulated vitamins are used in animal feed with the aims of taste-masking and ensure that vitamins reach the intestines in their intact form (Brownlie, 2007).

In cosmetic industries, oils are largely used due to their anti-oxidant, nourishing and moisturising properties (Table 1) (CAPSUM, 2015). The encapsulation provides better protection of active compound and grants attractive visual aspect to final product.

Encapsulated fragrances are frequently applied in perfumes, creams and other body care products;



	Irregular shaped capsule	Polynuclear capsule	Oil core shell capsule	Emulsion core shell capsule
Size	0.5 µm – 3.0 mm	200 µm - 5 mm	200 µm - 3.5 mm	200 µm – 7.0 mm
Oil loading*	1– 60 % w/w	30 % v/v	10 - 90 % v/v	30 - 40 % v/v
Efficiency of encapsulation**	74 -92 % v/v	79 -90 % v/v	90 -100 % v/v	> 90 % v/v
	Gharsallaoui et al., 2007 *McNamee et al., 2010* *Beindorff & Zuidam, 2010*	*Chan, 2011* *Zuidam & Shimoni, 2010*	*Ren et al., 2010* *Whelehan & Marison, 2011* *Hoad et al., 2011*	*Abang et al., 2012* *Martins et al., 2015* *Martins et al., 2017* *Martins et al., 2017b*

Figure 2. Morphology of the oil capsules. *Oil in the core (volume or weight)/capsule (volume or weight); **volume of encapsulated oil/volume of total oil.

however, their application is not only restricted to cosmetic. A recent and promising segment of market has used encapsulated fragrances to aromatise environments and graphic materials with the finality to create a consumer olfactory memory. This concept consists in associating a trademark, logo, product or point of sale with a specific fragrance creating an olfactory identity that can be easily exploited as marketing strategy (Table 1).

A wide range of techniques and materials are used to encapsulate oil. The choice of the encapsulation technique and material will depend on several factors including yield of the technique, size of the capsules and cost/process ratio.

In this review, the main techniques used in oil encapsulation, spray-drying, dripping, dispersion and millifluidic will be presented in more details. Between the possible polymers used as encapsulating agent, special attention will be given to alginates due to their versatility and broad applications in several industrial fields.

Oil capsules

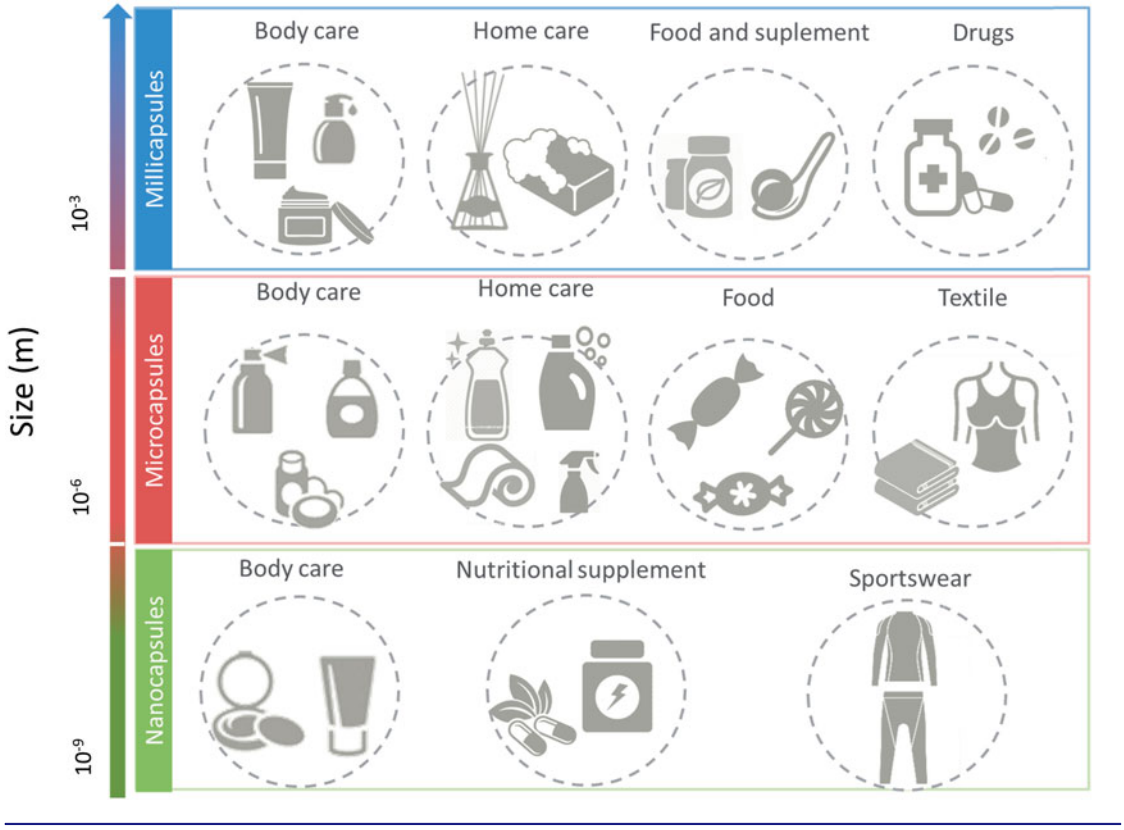
The oil can be the principal active compound encapsulated (flavour, pesticide, fragrance) or acts as carrier of hydrophobic cargos such as drugs and bioactive substances (Hernandez, 2008) (Figure 2). On the other hand, the wall material can be water soluble which can support the incorporation of hydrophilic cargos such as proteins, hydrophilic pigments and plant extracts, as example (Martins et al., 2017a) (Figure 2).

These oil reservoirs can be classified according to their morphology (irregular shaped or spherical), number of cores (single or multi-cores) and size (nano, micro, milli and capsules). In general, the capsule structure depends on the encapsulation technique and/or the mechanism of reticulation of the wall material (Gharsallaoui et al., 2007). Irregular shaped capsules are structures with an ill-defined shape and generally composed by several small oil cores entrapped within the wall material (Figure 2).

Polynuclear capsules have a structural organisation similar to the irregular shaped capsules; however, the wall material has a well-defined spherical shape (Figure 2). The principal inconvenient associated to polynuclear capsules is the low oil loading (<30% v/v). In addition, oil cores can be located at the capsule surface, facilitating the degradation and loss of oil during the storage or drying of the capsules.

Oil core-shell capsules are spherical structures made by a single oil core covered with a shell of wall

Table 2. Use of nano, micro and millicapsules in several industrial applications.



material (Figure 2). These structures are useful when no active material is desired at the particles surface or when high oil loading (>90% v/v) is required (Figure 2).

Emulsion core-shell capsules also contain a single core covered with a shell; however, in this case, the core is filled by an emulsion (Anderson et al., 2005; Martins et al., 2015; Martins et al., 2017b). This particularity allows the simultaneous encapsulation of hydrophilic and hydrophobic cargos in the core, which can be interesting for encapsulation of proteins and oily compounds in cosmetic applications (Martins et al., 2017a).

The capsules can vary in size between few micrometres to few millimetres depending on the technique used for oil encapsulation. A precise definition of milli, micro or nanocapsules is not yet a consensus in the literature, and for this reason, in this review, a precise range of sizes was established to classify the capsules (Table 2).

The term millicapsules (Lidert, 2005) is applied to oil reservoirs bigger than 1 mm and are used in applications where the capsule visualisation is desired. Besides protection of the oil against oxidation, millicapsules guarantee an attractive appearance to final product and are frequently used as marketing strategy (CAPSUM, 2015). Products containing millicapsules include skin creams, shower soaps, room deodorisers, decorative capsules, molecular cooking, dietary supplements and medications (Table 2).

Microcapsules are capsules whose size is between 1 and 1000 μm and are usually used in products whose texture and appearance do not have to be drastically altered. In some cases such as in skin/hair creams, shower soaps and household cleaners, visible microcapsules are intentionally added to make the product more attractive. Microcapsules are also found in body deodorants, perfumes, varnishes, perfumed papers, bed linens, clothes, candies and chewing gums (Table 2).

Contrary to millicapsules, precise systems of actives release can be elaborated from microcapsules. The general rule applying to microcapsules is that by decreasing their size, more actives are released from microcapsules in less time (Vasisht, 2014). It means that by controlling microcapsule size during the process, it is possible to determine the actives release kinetics.

Nanocapsules gather all capsules whose size is between 1 nm and 1000 nm and are usually used in applications where the capsule needs to be injected or do not be perceived in the final product. Nanocapsules are applied in pharmacology, cosmetic,

food, textiles, building materials, electronics, mechanics and chemistry (Perez et al., 2012).

The oil nanoencapsulation is used in the formulation of skin creams and this technology offers advantages to help in the repairing and strengthening of the skin deeper layers, to increase the active stability and to release favourable doses of active compound (Schmaltz et al., 2005).

In textile, nanoencapsulated compounds can act as an adjuvant in different types of treatments such as muscle aches, skin hydration, localised fat, natural repellent of mosquitoes and antimicrobial. The high anchoring of the nanocapsules on the textile fibres allows resistance of up to 20 washes and gradual active release by friction, which is ideal for sportswear applications.

In food packaging, nanocapsules are incorporated in plastic films to improve the properties of packaging, to add antimicrobial compounds and to incorporate nanosensors for monitoring and reporting on the food quality (Perez et al., 2012).

Encapsulation market

The market of encapsulation can be divided into three large fields: macro-, micro- and nanoencapsulation. Macroencapsulation market includes all production and marketing of millicapsules whereas microencapsulation and nanoencapsulation are devoted to the production/marketing of micro and nanocapsules, respectively.

In general, the microencapsulation market is wide and diversified and responsible of large financial flow around the world. In 2012, around 12 billions of dollars (Table 3) were injected only by the global food microencapsulation market. In 2017, it is expected that this market reaches 17 billions of dollars (MarketsandMarkets, 2012). The assessment indicates that the microencapsulation area will represent more than 40% of the global food encapsulation market in the next years.

Key factors driving the global microencapsulation market include rising demand for functional foods, increasing acceptance of detergents and growth of the pharmaceutical industries (Transparency Market Research, 2015). Between these segments, the global pharmaceutical market stands out accounting for over 65% share of the global microencapsulation market in 2013 (Transparency Market Research, 2015).

Table 3. Global food encapsulation market income, 2010–2017 ($billions).

Axis	2010	2011	2012	2017
Microencapsulation	10.9	11.6	12.3	17.2
Nanoencapsulation	7.7	8.1	8.6	11.3
Macroencapsulation	3.3	3.5	3.7	4.6
Hybrid technologies	5.5	5.8	6.1	8.8
Total	27.4	29.1	30.8	42.0

Source: MarketsandMarkets (2012).

As well as the food and pharmaceutical segments, new consumers for cosmetics markets have emerged in Asia and South America. Only in 2014, around 250 millions of euros were invested in beauty products around the world with an increasing consumption of cosmetics in countries such as China (32.6 M€), Brazil (32.6 M€) and India (8 M€) (ADDIACTIVE, 2015).

As described previously, encapsulated oils are used in pharmaceutical, nutritional, food, cosmetic, veterinary and agricultural segments. Although there are no data in the literature, it can be assumed that encapsulated oils have a large financial contribution in the global encapsulation market income.

The oil encapsulation market is actually boosted by the discovery of new vegetable oils with medicinal or cosmetic properties associated with the development of the encapsulation technologies. The combination of these two factors has opened the doors for the creation of more efficient and innovative products.

Techniques of oil encapsulation

Drop formation

The oil encapsulation is based on techniques of drops formation that can be divided into two main groups: liquid–air and liquid–liquid techniques (Figure 3).

In liquid–air techniques, a liquid phase is extruded through a nozzle and drops are dispersed in the air. Depending on the liquid extrusion rate, different regimes of drop formation can be created: dripping, jetting or spraying (Figure 3).

As a general rule, using low liquid extrusion rates, the drop formation occurs by dripping regime (Figure 3). A liquid pendant drop grows at the capillary tip until the surface tension force no longer supports the weight of the drop (Tate, 1864; Chan, 2011). Under gravity, millimetric liquid drops detach from the tip and their sizes are controlled by the properties of liquid (viscosity, surface tension and density) and by tip diameter (Bremond et al., 2010; Chan et al., 2009).

By increasing the liquid extrusion rate, the liquid flows through the nozzle in laminar jet regime (Figure 3). In this case, drops are generated by a physical cutting of the liquid jet using rotating wires or vibration methods (Schwinger et al., 2002).

On one hand, laminar jet techniques are more complex compared to the dripping techniques as it is

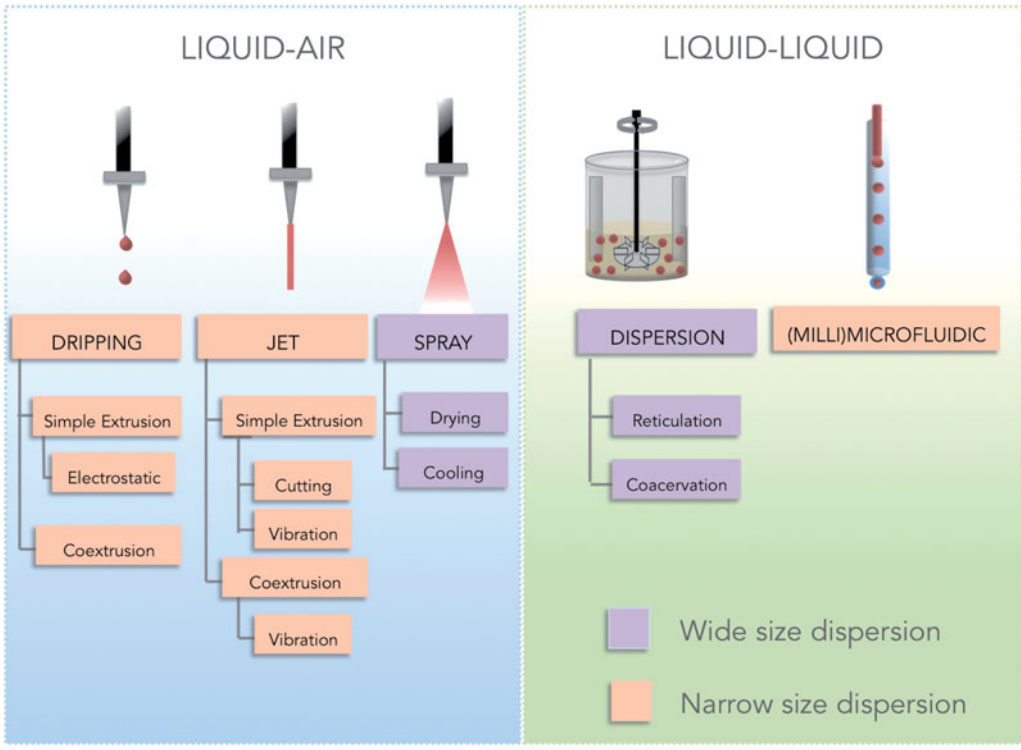


Figure 3. Liquid–air and liquid–liquid techniques of oil encapsulation.

necessary to incorporate an external apparatus to produce the drops. On the other hand, higher number of drops is produced per hours and the drop diameter can vary from micrometres to millimetres.

Using higher liquid extrusion rates, the drops are formed by a spray regime that can be characterised by a dispersion of micrometer liquid drops in the air (Figure 3). This method allows the manipulation of higher liquid volumes per hour and the creation of smaller drops compared with dripping and jet regimes; however, the drops show wide size dispersion (Figure 3).

The liquid–liquid techniques gather all methods based on the emulsification technology (Figure 3). To simplify, two immiscible liquids are put in contact and drops are formed under stirring (dispersion, Figure 3) or shear forces (milli or microfluidic, Figure 3).

In dispersion techniques, oil and aqueous solution are mixed forming oil-in-water (O/W) or water-in-oil (W/O) emulsions depending on the volume fraction of each phase, the stirring rate and the type of emulsion stabilisers used. The size of the drop formed can vary from micrometres to millimetres, the size being essentially determined by the stirring rate (Martins et al., 2015). This technique is advantageous because it allows a high productivity of drops; nonetheless, it does not guarantee precise control of drops size.

In (milli)-microfluidic techniques, immiscible liquids are extruded and put in contact within capillary tubes. By the action of shear forces exerted between the two liquid phases, due to specific capillary tubes geometry, drop of a liquid is dispersed in the other liquid corresponding to the continuous phase resulting in the continuous production of O/W or W/O emulsions (Sun et al., 2014). Contrary to dispersion techniques, this technique allows the control of the size, composition and structure of the generated drops by tuning the fluids flow rates and/or by the design of the (milli)-microfluidic device (Theberge et al., 2010; Schmit et al., 2014).

The next step for oil encapsulation consists in the addition of wall material to entrap the oil phase. Wall materials can be made by polysaccharides (alginate, chitosan, pectin), proteins (casein, albumin, gelatine), lipids (tristearin, stearic acid, cholesterol, cetylpalmitate), resins (Shellac) and synthetic polymers derived from esters of acrylic and methacrylic acid (Nikam et al., 2011; Assis et al., 2012; Patel et al., 2013). The choice of the wall material will depend on the mechanism of polymer cross-linking and the technique of oil encapsulation chosen.

In the next section, the main techniques of oil encapsulation will be detailed taking as example polysaccharides as wall materials. However, the principle of

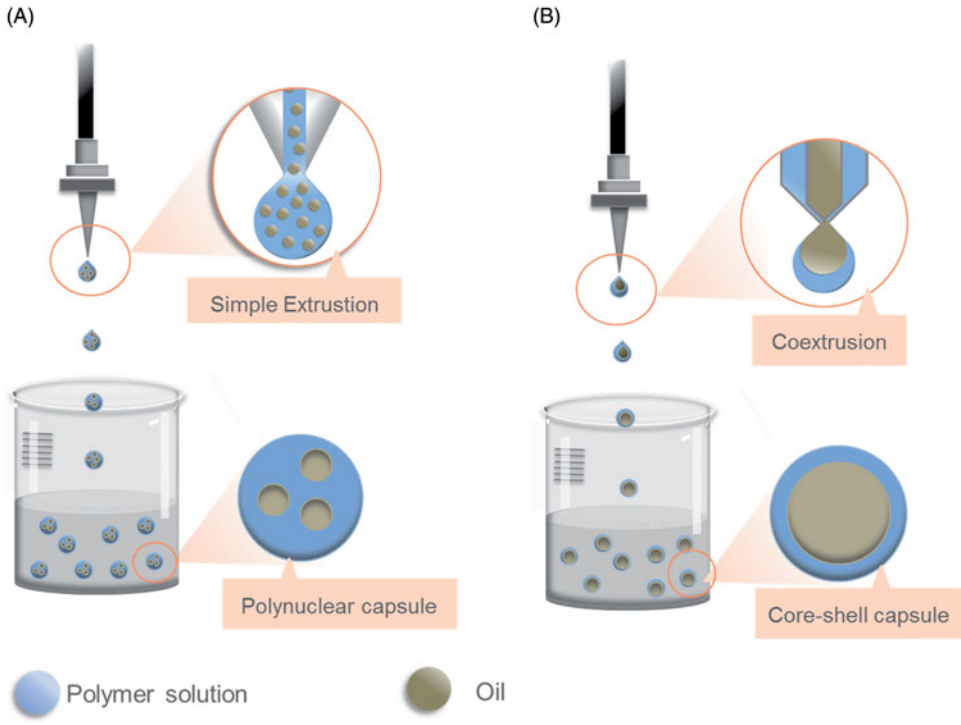


Figure 4. Oil encapsulation by simple (A) and coextrusion (B)-dripping techniques.

the techniques can also be applied to other wall materials.

Extrusion-dripping technique

For the encapsulation of oil in polysaccharide matrix, oil is dispersed in polymer solution forming an emulsion. Next, the emulsion is extruded through a nozzle and added dropwise into a collecting/hardening bath where the polymer is cross-linked (Figure 4(A)). As a consequence, oil droplets are embedded in the polymer matrix forming irregular shaped or polynuclear capsules (Figure 4(A)). This technique is known as simple extrusion-dripping technique as a single nozzle is used during the extrusion of the liquid phases. The procedure is easy to perform and does not require sophisticated equipment, which makes it the most classic and popular technique to encapsulate actives (Chan et al., 2009). The main drawback of this technique is that it is generally used to produce polynuclear capsules with an oil loading rather limited (Figure 4(A)).

In order to produce capsules with higher oil loading by extrusion-dripping, a strategy consists in the use of concentric nozzles to generate the drops. In this method, oil and polymer solution are extruded simultaneously through concentric nozzles (Figure 4(B)). The oil and polymer solution flows in the internal and external nozzles, respectively, and are added dropwise into a bath (Figure 4(B)). After polymer cross-linking, core-shell capsules are formed (Figure 4(B)). As the method of co-extrusion is applied, this technique is known as coextrusion-dripping technique.

The main advantage of the co-extrusion-dripping technique compared with simple extrusion is the capacity to generate capsules with high oil loading (≈90% v/v). However, co-extrusion requires more equipment and a higher number of parameters to optimise for a good efficiency of oil encapsulation.

Under gravitational force, millimetric drops are generated resulting exclusively in millicapsules (2–7 mm) generation. To reduce the capsule size, electrostatic method is frequently applied (Figure 5).

In electrostatic dripping, oil/polymer solution is extruded through a nozzle submitted to an electrical potential difference (Figure 5(A)). Electrostatic forces pull the droplets off the orifice (nozzle) at a considerably faster rate compared to the classical dripping process, where removal is only based on gravitational force (Whelehan and Marison, 2011). Droplets fall into colleting bath where the polymer is cross-linked (Figure 5(A)). This technique is able to produce small capsules compared to gravitational dripping (≥50 μm in diameter) with uniform size and shape (Manojlovic et al., 2006). The microcapsules size basically varies as a function of needle diameter, charge arrangement (electrode geometry and spacing) and strength of electrical field (Bugarski et al., 1994). By increasing the

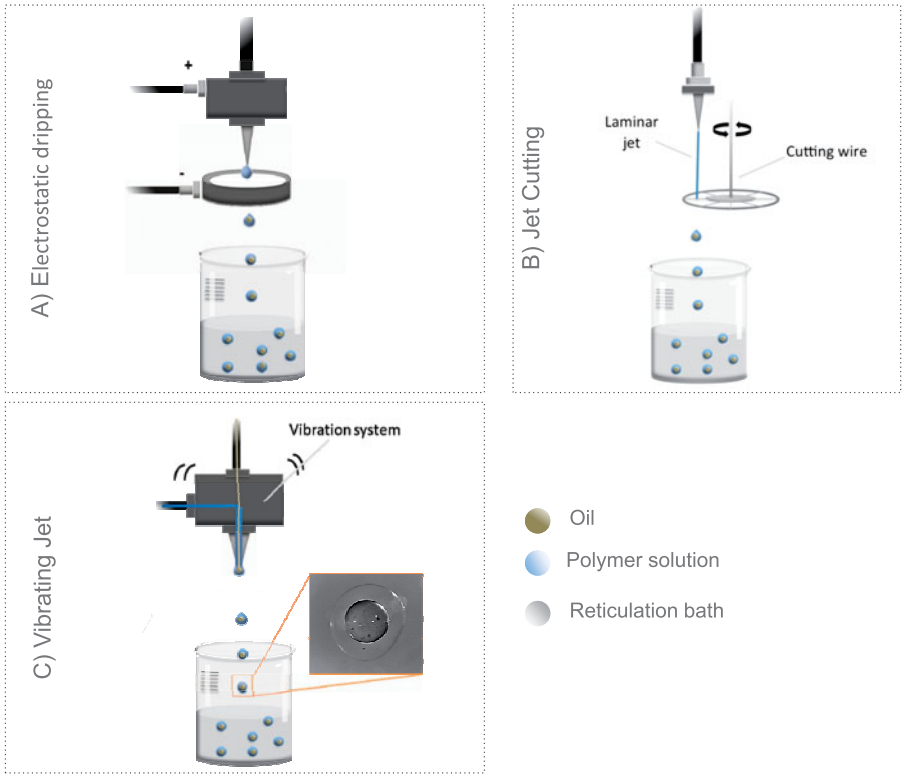


Figure 5. Oil encapsulation by electrostatic dripping (A), jet cutting (B) and vibrating jet (C) techniques.

strength of the electrical field, the dripping regime is replaced by a spray regime leading to smaller droplets with however a high size dispersion (Figure 5(A)).

Jet cutting and vibrating jet techniques

In oil encapsulation by jet cutting, an emulsion of oil-in-polymer solution is extruded at high rate through a single nozzle forming a laminar jet (Figure 5(B)). The jet is then fragmented by mechanical impact of a cutting wire originating droplets that are collected and hardened into a cross-linking bath (Figure 5(B)) (Prusse and Vorlop, 2004). This technique is easy to operate but the extensive loss of membrane and encapsulated material remains the biggest disadvantage (Whelehan and Marison, 2011).

In vibrating jet techniques, a vibrating nozzle system is used to produce drops from laminar jet. For oil encapsulation, oil and polymer solution are coextruded through concentric nozzles and the jet is break-up in droplets due to axisymmetric disturbances caused by vibration (Figure 5(C)). The jet break-up in homogeneous droplets depends essentially on the jet diameter and the fluid properties (viscosity, density and surface tension) (Lord Rayleigh, 1878; Weber and Flussigkeitsstrahles, 1931). The droplets (Figure 5(C)) are collected in a bath and, after polymer cross-linking, core-shell capsules are obtained (Figure 5(C)).

By the vibration methods, the capsules diameters range from 200 μm to 3.5 mm with a narrow size distribution (Hoad et al., 2011; Whelehan and Marison, 2011b). The main drawback of these methods is that the shell materials originate only from low-viscous polymer solutions, the nozzles being frequently clogged using viscous materials interrupting the process of drop generation.

Spray-drying technique

This technique consists in the emulsification of oil in an aqueous solution of carrier material, followed by spraying of the mixture into hot chamber (Zuidam and Shimoni, 2010). During this process, droplets of the mixture are put in contact with hot air in order to remove water by evaporation (Figure 6). The carrier material generates a film around the oil phase forming irregular shaped or polynuclear capsules (Figure 6).

Spray-drying encapsulation has been used in the food industry since the late 1950s to provide flavour oils with some protection against degradation/oxidation and to convert liquids to powders (Gouin, 2004).

Since almost all spray-drying processes in the food industry are carried out from aqueous feed

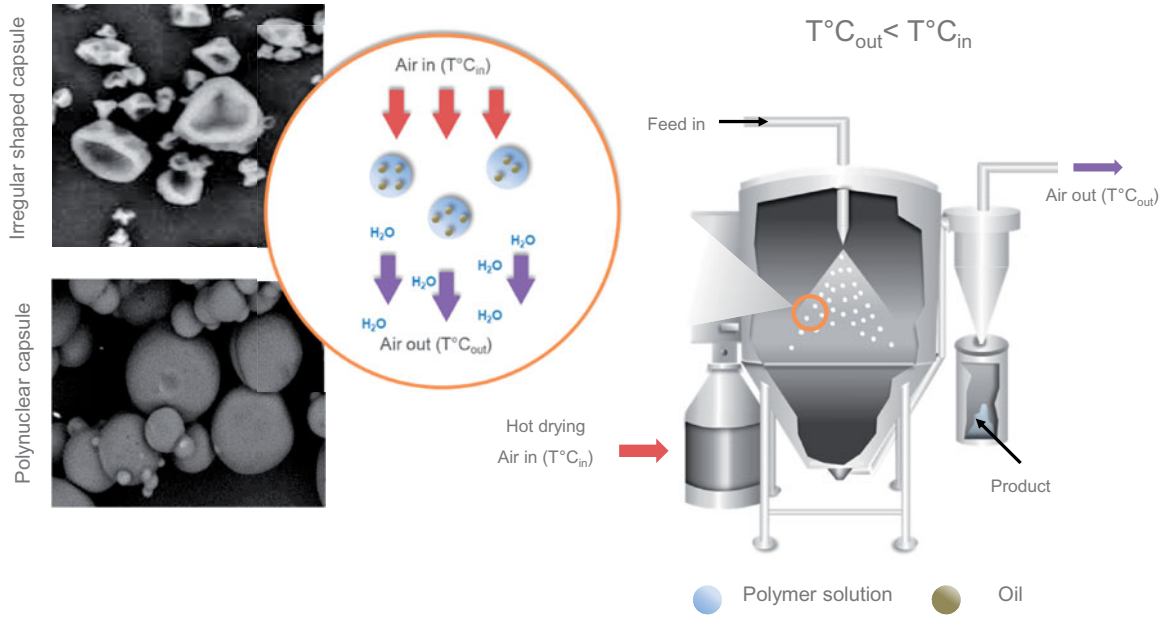


Figure 6. Scheme of spray-drying technology. T_{in} (°C): temperature of air in; T_{out} (°C): temperature of air out.

formulations, the shell material must be soluble in water at an acceptable level (Gouin, 2004). Shell materials include gum acacia, maltodextrins, modified starch, alginate, carboxymethylcellulose, guar gum and proteins.

The advantages of spray-drying technology include availability of equipment, high-production capacities (up to 4000 kg/h), wide choice of carrier solids and production of capsules with a range of size comprised between 0.5 and 1 μm (McNamee et al., 2010; Reineccius, 2001; Gharsallaoui et al., 2007; Beindorff and Zuidam, 2010).

Among drawbacks, it can be listed: high acquisition cost of spray dryer apparatus, large size dispersion of capsules and oxidation or volatilisation of temperature sensitive oils.

Dispersion-cross-linking and dispersion–coacervation techniques

As previously described, dispersion techniques consist in the generation of droplets by dispersion of a liquid in another liquid using stirring forces. In oil encapsulation process, droplets are first formed then hardened to entrap the oil phase. The process of droplet hardening can be provoked by two different mechanisms: cross-linking or coacervation.

In procedures of oil encapsulation by dispersion-cross-linking, oil-in-water emulsion is formed by emulsification of oil and polymer solution (Figure 7(A)). The O/W emulsion is then dispersed into oil bath by mechanical stirring resulting in an oil-in-water-in-oil (O/W/O) secondary emulsion (Figure 7(A)). In the last stage, the secondary emulsion is mixed with a cross-linking agent solution, resulting in the cross-linking of the polymer chains. After complete polymer cross-linking, the capsules formed settle by gravitational or centrifugal forces (Figure 7(A)).

In the dispersion–coacervation technique, oil is emulsified with a solution of charged polymer (polymer 1) forming an oil-in-water emulsion (Figure 7(B)). A solution of another charged polymer (polymer 2) is then added to the emulsion (Figure 7(B)). The pH of the mixture is decreased and the polymer 2 acquires a net charge opposite to the polymer 1. The polymers interact with each other forming complexes that settle around the oil droplets (Thies, 2001; Yan and Wei Zang, 2014). The oil droplets remain entrapped by the polymeric complexes forming very small capsules (2–50 μm) with a core-shell structure (Jyothi et al., 2010).

The couple of polymers generally used in this process are gelatine/gum Arabic, gelatine/carboxymethylcellulose, alginate/polylysine, alginate/chitosan and albumin/gum Arabic (Lee and Wong, 2014; Peng et al., 2014).

The dispersion-based techniques have high-encapsulation efficiency and allow the production of small capsules; however, the greatest limitations of the technique include the excessive use of solvent and the difficult recovery and solubility of the actives in the solvent that can make such processes highly uneconomical (Poncelet et al., 1992; Yan and Wei Zang, 2014).

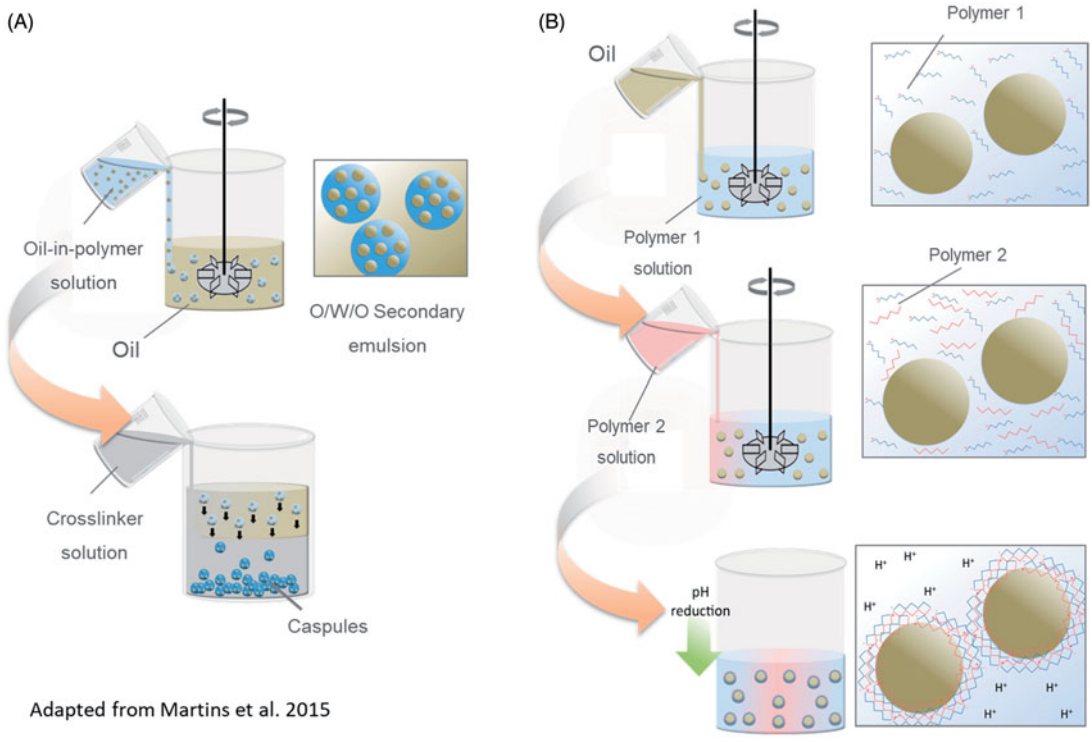


Figure 7. Oil encapsulation by dispersion-cross-linking and dispersion–coacervation techniques.

Droplets (milli)-microfluidic techniques

In droplets (milli)-microfluidic devices, droplets are generated when a liquid phase is introduced through a capillary or needle into the co-flowing continuous phase (Sun et al., 2014). Based on this principle, emulsions with controlled droplets size are produced and used as templates to design capsules (Theberge et al., 2010; Pawlik, 2012; Schmit et al., 2014).

In (milli)-microfluidic (micro)-channels, the droplets size is influenced by the liquid properties (interfacial tensions, viscosities and densities), flow parameters (flow rates of dispersed and continuous phases), geometry (inner diameter of capillary tube; length, width and height of microchannels) and surface-active materials (surfactants, emulsifiers, or proteins) (Erni et al., 2009). By increasing the viscosity or the flow rate (i.e. velocity) of the continuous phase, smaller droplets are obtained (Umbanhowar et al., 2000; Erni et al., 2009) (Figure 8(A)). Another way to reduce the droplets size consists in the use of capillary tubes with narrower inner diameter or in the reduction of the interfacial tension of the liquid by addition of surfactant in the continuous phase (Fischer and Erni, 2007; Erni et al., 2009).

Millifluidic assemblies made of co-axial flow focussing geometries connected to each other via glass capillaries or commercial tubing offer a greater versatility with respect to wetting conditions and modularity (Schmit et al., 2014; Martins et al., 2017). Using these devices, fluids are manipulated to form capsules with size comprised between hundreds of micrometres and few millimetres (Martins et al., 2017). On the other hand, microfluidic assemblies enable the control of smaller volume of fluids. Among the advantages of this technology, it can be listed: the reduction in reagent quantity, the ability to manipulate small droplets, the rapid mass transfer, an excellent reproducibility and a high monodispersity in size (smaller than 10% in size variation) (Erni et al., 2009; Chung et al., 2012).

For oil encapsulation using (milli)-microfluidic, oil is first injected into a polymer solution forming an O/W emulsion (Figure 8(B)). The emulsion is then injected into an oil phase forming an O/W/O secondary emulsion (Figure 8(B)). Finally, the polymer solution is cross-linked within the capillary tube and oil core-shell capsules are formed (Ren et al., 2010; Chung et al., 2012).

The advantage of (milli)-microfluidic systems consists in the formation of monodispersed capsules with a precise control of their size and composition (oil loading, membrane thickness) (Ren et al., 2010; Datta et al., 2014). The major drawback is the productivity that is quite low (production of several thousand of capsules per second) compared with other techniques of oil encapsulation (Erni et al., 2009). Thus, this technique finds more application in specific areas where

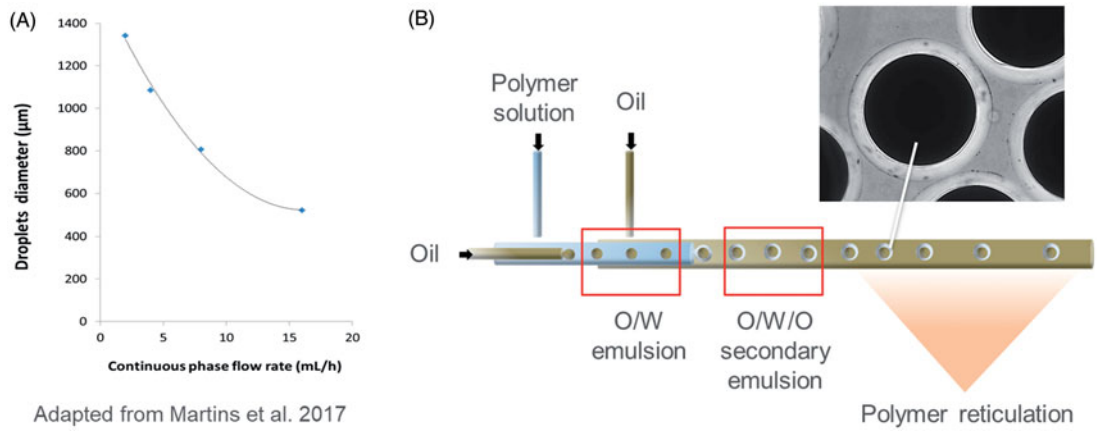


Figure 8. Droplets formation using (milli)-microfluidic devices. (A) Effect of velocity of continuous phase and viscosity on the droplets diameter. (B) Scheme of oil encapsulation using (milli)-microfluidic devices.

precision of size for instance is crucial (e.g. drug delivery systems), than in the industrial applications where the production of the largest volume of material in the shortest amount of time is preferred (Pawlik, 2012).

Remarks about the techniques of oil encapsulation

Among the techniques presented in this review, spray-drying is the most economical and commonly used method to encapsulate oil at large scale (Fuchs et al., 2006). Nonetheless, this technique does not allow high protection of encapsulated oil due the formation of capsules with polynuclear structure. In addition, high temperature (up to 160 °C) is used that improves the oxidation of oils (Kolanowski et al., 2006).

Dispersion methods also allow high capsules production (Table 4); however, despite its efficiency, this technique is expensive and use food-disapproved materials (Abang et al., 2012). (Milli)-microfluidic is a very efficient technique to control the droplets size but the low productivity of this technology still restricts its application for large-scale oil encapsulation (Table 4).

Extrusion-based methods such as simple extrusion-dripping, electrostatic dripping, jet cutting and vibrating jet are simple techniques with easy operation (Table 4). In addition, these methods do not use toxic materials allowing the application of the capsules in food, veterinary, nutritional and pharmaceutical domains. However, these techniques show low-production yields that can also limit their application in oil encapsulation at large scale (Table 4).

As mentioned in Table 4, all techniques of oil encapsulation show drawbacks that, in some cases, restrict their use. Alternative methods are then needed to overcome some of these problems and to expand the availability of existing methods for encapsulating oils for the food, cosmeti, and agriculture industries (Abang et al., 2012).

Alginate

Throughout this review, a wide range of polysaccharides and proteins used as wall material in the capsules were shown (Table 1). However, in this section, special attention will be focus on alginates due to their large use in oil encapsulation and high capacity to form gel at low concentrations. In addition, alginates are biocompatible and non-toxic which makes them favourable for applications in food, cosmetic, veterinary, pharmaceutical and medicinal fields.

Alginates are natural polysaccharides isolated from the cell wall of various species of brown algae. This biopolymer consists of a linear chain of (1–4)-linked residues of β-D-mannuronic acid (M) (M blocks) and α-L-guluronic acid (G) (G blocks) in different proportions and sequential arrangements (Figure 9) (Smidsrød and Haug, 1968; Ouwerx et al., 1998). In the presence of divalent ions, the chains of alginate are cross-linked in three-dimensional networks with high water content (hydrogel). The "egg-box" model was proposed by Grant et al. (1973) to explain how the divalent cations bound in the inter-chain cavities (Ca^{2+} ions are believed to bind solely to G blocks of alginate chains, as the structure of G blocks allows a high degree of coordination of Ca^{2+} ions). By this model, divalent ions interact simultaneously with the hydroxyl and carboxyl groups of the guluronic acid units present along the chains of alginate forming a stable egg-box motif (Figure 9). By increasing the concentration of divalent ions, more polyguluronates sequences are cross-linked forming a porous hydrogel (Figure 9).

However, in case where calcium ions are scarce, more than two carboxylate moieties chelate a single

Table 4. Comparison of the techniques of oil encapsulation based on production and physico-chemical properties of capsules criteria.

CRITERIA	Simple Estrusion dripping	Electrostatic extrusion	Jet cutting	Vibrating jet	Spray-drying	Dispersion	(Milli) microfluidic
Capsules characteristics							
Monodispersed	*	*	*	*	x	X	*
Homogenous and spherical shape	*	*	*	*	x	x	*
Small size[I]	x	*		*	*	*	*
Narrow size distribution[II]	*	*	*	*	x	x	*
Characcteristic of the technique							
Relatively easy set up and simple operation[III]	*	*	*	*	x	*	x
High efficiency[IV]	*	*	x	*	*	*	*
High production rates[V]	x	x	x	x	*	*	x
Ability to use viscous solutions	x	x	*	x	*	*	x
Produce a range of different sized droplets	*	*	*	*	*	*	*

*Conforms to requirements, x does not conform to requirements. I: size smaller than 100 p, m, II: overall deviation lower than ±5% from the mean size, III: does not require experts to repeatedly set up, nor extensive training and supervision to operate the process, IV: no extensive loss of membrane and encapsulated material, V: production capacity of tons/day. Adapted from Whelehan and Marison (2011).

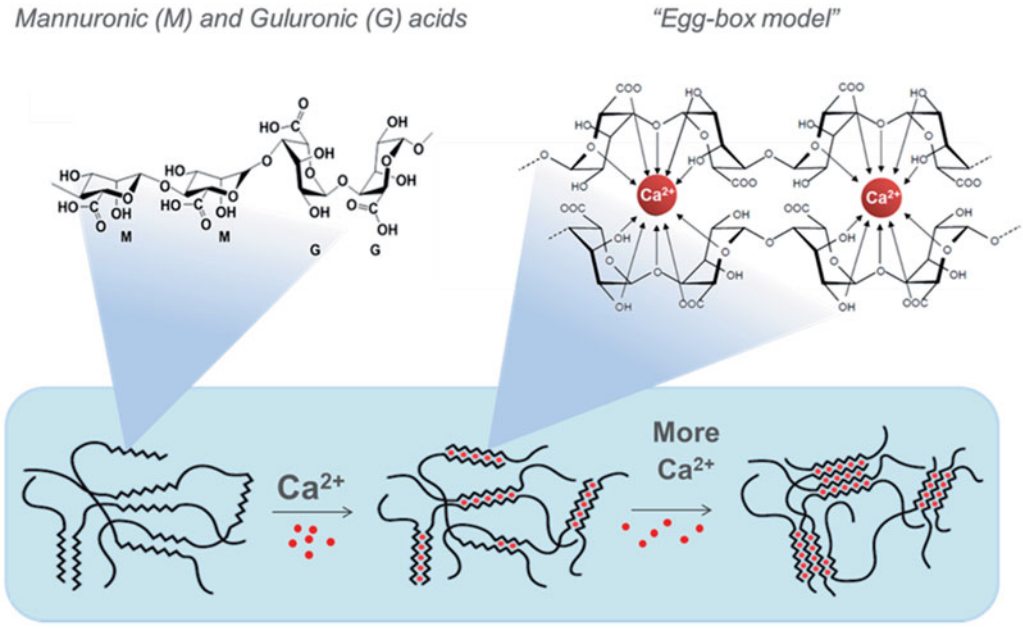


Figure 9. Mechanism of alginate gelation in presence of calcium ions (Ca^{2+}).

ion leading to the formation of metastable structures known as imperfect egg-box motifs (Fu et al., 2014). These motifs can influence the hydrogel properties used for encapsulation (pores size, mechanical resistance and release of actives).

To disrupt a Ca–alginate complex, two energetic barriers, at about 4.4 and 10.2 kcal/mol, need to be sequentially overcome in two steps: (i) from an ideal egg-box structure to an imperfect one, and (ii) from bound to unbound state (Fu et al., 2014). It means that the hydrogels are very stable at room temperature, justifying its wide applications in encapsulation processes.

The divalent ions present different affinities for alginate chains ($Cd^{2+} > Ba^{2+} > Cu^{2+} > Ca^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$) and the type of ion have a direct influence on the mechanical properties of the gel (Smidsrød and Haug, 1968; Ouwerx et al., 1998). More higher is the ion affinity for polyguluronates sequences, more resistant is the hydrogel; however, in most applications, Ca^{2+} is preferentially used due to its low cost and toxicity.

The structure (pores size) and the mechanical resistance of alginate hydrogels can be varied as a function of several factors including the number of guluronic units in the alginate chains, the type of cross-linker agent, the divalent ion concentration, the exposure time of alginate chains to divalent ions and the presence of organic solvent in the cross-linker solution (Smidsrød and Haug, 1968; Ouwerx et al., 1998; Goh

et al., 2012; Fu et al., 2014; Li et al., 2015; Liu et al., 2016).

Liu et al. (2016) verified that in the presence of Ca^{2+} ions, alginate chains associate with fibrils whose diameter and network density increased with the increase of Ca^{2+} ions concentration. According studies performed with electron microscopy revealed that Ca–alginate matrix showed smaller pores with diameters between 5 and 200 nm (Klein et al., 1983; Choi et al., 2002).

Li et al. (2015) demonstrated that alginate films cross-linked in a calcium chloride solution/ethanol had improved visual appearance, thickness, surface homogeneity and mechanical properties. These results were ascribed to the reduced swelling degree of films during crosslinking process in the presence of organic solvent (ethanol).

Beyond the parameters discussed above, Nussinovitch et al. (1996) suggested that the properties of alginate matrix (mechanical strength and release of actives) can also be influenced by addition of other polymers into alginate solution. According to these authors, the addition of polylysine or chitosan in the alginate solution changed the permeability of the alginate membrane resulting in the slowing down of the release of encapsulated proteins. The complexation with other cationic polymers also strengthened the membrane and affected its brittleness.

On the other hand, Lopez et al. (2012) demonstrated that the complete release of encapsulated volatile compound (linalool) in dry Ca–alginate membranes occurred in 24 h. However, by adding glycerol and starch to the alginate, lesser pores were formed in the dry membranes and a slower release of linalool was achieved (>1700 h).

Oil encapsulation in Ca–alginate matrix

In oil encapsulation by alginate as wall material, Ca^{2+} can reach the alginate chains by different routes. Depending on the path taken by Ca^{2+}, three possible mechanisms of gelation can occur: external, internal or inverse gelation.

In a simple set-up of oil encapsulation based on external gelation, an emulsion of oil-in-alginate solution is added dropwise into $CaCl_2$ solution bath (Figure 10(A)). In external gelation, Ca^{2+} ions migrate from the aqueous bath ($CaCl_2$ solution) to the emulsion drop (Martins et al., 2017b). As a result, the alginate chains are progressively cross-linked and polynuclear capsules are obtained (Figure 10(A)). By this method, the Ca^{2+} ions first cross-link the capsule surface leading to a merging of the polymer chains and the formation of a less permeable surface to the diffusion of Ca^{2+}. This resulted in a membrane with a highly cross-linked surface and a less well cross-linked interior.

By external gelation method, it was demonstrated the encapsulation of oils as sunflower oil (Morales et al., 2017), fish oil (Wu et al., 2017), linseed oil (Piornos et al., 2017), Canola oil (Wang et al., 2013), olive oil (Bera et al., 2015), turmeric oil and lemongrass oil (Natrajan et al., 2015), thyme essential oil (Benavides et al., 2016), ethyl acetate (Baimark and Srisuwan, 2014), among others (see Table 1). The capsules can be found applications for pharmaceutical and nutraceutical purposes, human and animal feed, molecular cuisine, controlled release of drugs, cosmetics and antimicrobial activity.

In oil encapsulation based on internal gelation mechanism, oil is emulsified in an alginate solution supplemented with $CaCO_3$, a water insoluble form of calcium. The emulsion is then added dropwise into a bath of oil/acetic acid (Figure 10(B)). H^+ ions, derived from the acid acetic dissociation, diffuse from the oil phase to the emulsion drops decreasing its pH value. The H^+ ions react with $CaCO_3$ that dissociate calcium ions (Johansen and Flink, 1986; Zhang et al., 2007):

$$CaCO_3 + 2H^+ \rightarrow H_2O + CO_2 + Ca^{2+}$$

The released Ca^{2+} ions cross-link the alginate chains resulting in polynuclear capsules formation (Figure 10(B)). In this method, the reaction between the acid and carbonate release CO_2 that leads to the formation of abundant cavities in the Ca–alginate matrix (Chan et al., 2006).

As the capsules are immersed in an oil bath, accurate rinsing steps are necessary which renders the application of this method on a large-scale quite difficult (Li et al., 2015). For this reason, few literature reports have demonstrated the oil encapsulation for industrial purposes. Liu et al. (2013) proposed the soybean oil encapsulation by internal gelation as an alternative to carry actives such as lipophilic drugs, chemicals and nutrients.

The gelation mechanism influences the Ca–alginate matrix structure, which can impact on the mechanical and release properties of the capsules. Chan et al. (2006) demonstrated that Ca-alginate films externally cross-linked showed lower thickness, greater matrix strength, stiffness and permeability than films internally cross-linked. According to the authors, externally cross-linked alginate was more permeable to acetaminophen and showed higher active loading.

In the inverse gelation method, an oil/calcium chloride emulsion is added dropwise into alginate bath

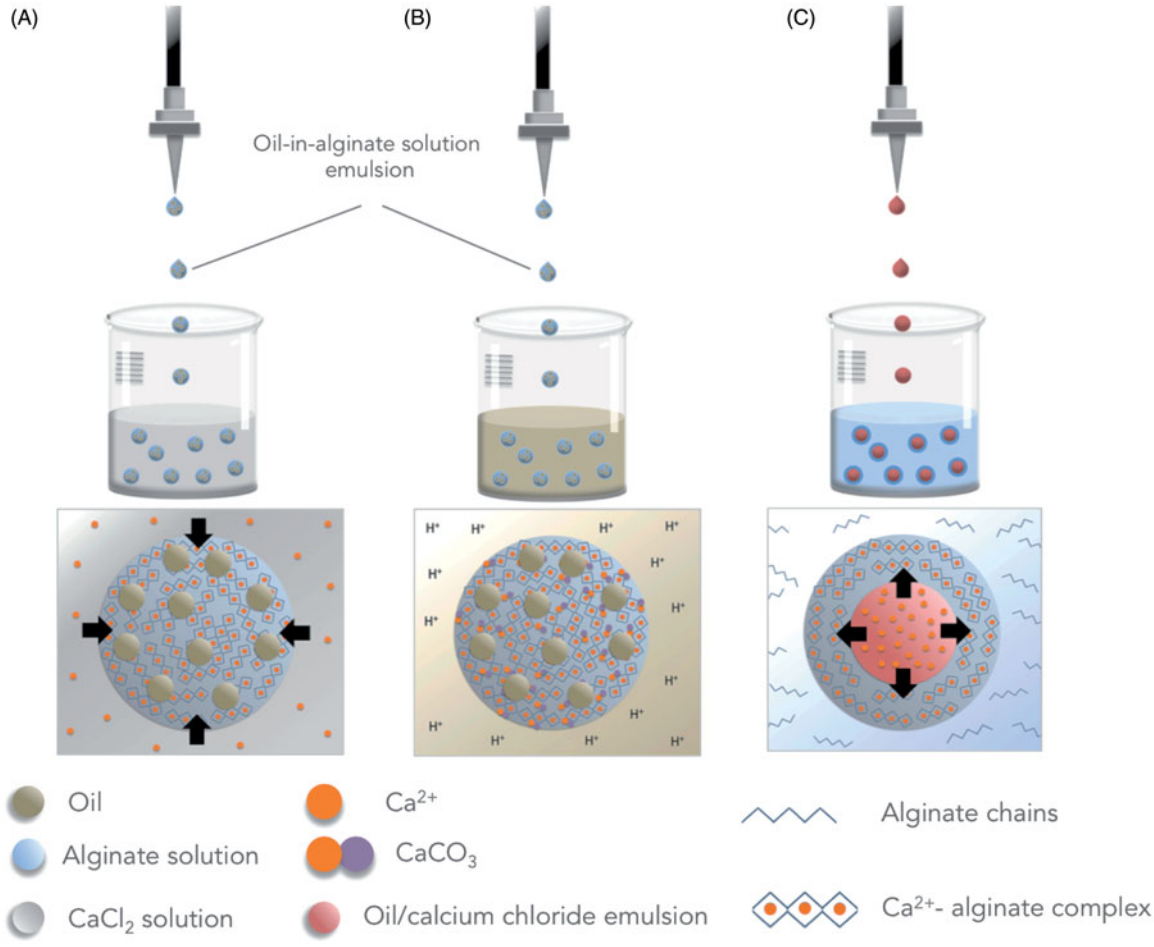


Figure 10. Oil encapsulation by simple extrusion-dripping using external (A), internal (B) or inverse gelation (C) mechanism. Black arrows: direction of migration of Ca^{2+}.

(Figure 10(C)). The Ca^{2+} ions migrate from the emulsion drop to the external polymer solution cross-linking alginate chains (Figure 10(C)). Consequently, a membrane covers all surface of the emulsion drop and a core-shell capsules is obtained (Martins et al., 2017a). Since the Ca^{2+} ions migrate from inside to outside, it is supposed that a matrix with a highly cross-linked internal and a less well cross-linked peripheral surface is created. To improve the cross-linking of the alginate chains at the membrane surface and prevented the sticking of capsules each other, capsules are usually rinsed and suspended in calcium chloride solution (Degen et al., 2015).

The oil encapsulation based on this mechanism is an innovative technique because it allows the production of emulsion core-shell structures by simple extrusion, which cannot be obtained by other mechanism of alginate gelation (Figure 10(C)). Due to the interesting characteristics of these capsules and their promising applications in food, cosmetic and nutritional areas, further details will be given in the next section.

Oil encapsulation by inverse gelation

The application of the mechanism of inverse gelation for active encapsulation was initially proposed by Nussinovitch et al. (1996). Briefly, aqueous-core-shell capsules were produced by dropping a solution of sucrose, calcium chloride and proteins (active) into a bath of alginate solution.

Only 9 years later, Anderson et al. (2005) patented a technique of oil encapsulation by inverse gelation. The method consists basically to produce an emulsion from oil and calcium chloride solution, and added dropwise into stirred alginate bath. When in contact with the alginate solution, Ca^{2+} ions are gradually released from the emulsion core forming the membrane. Alginate stirring is required to facilitate the penetration of the emulsion drops into the gelling bath solution and prevent agglomeration of the capsules (Abang et al., 2012).

In previous studies, Abang et al. (2012) detailed the production of capsules by inverse gelation using simple extrusion-dripping. It was reported that spherical

capsules were only obtained when an ideal distance between the dropping tips and the alginate solution surface (80–100 mm) was respected. For high distance, the emulsion drop broke on impact whereas below 80 mm, the drops did not have sufficient kinetic energy to penetrate the alginate solution surface. In addition, to facilitate the drops penetration, alginate with the lowest viscosity (Algogel 3001, 38 mPa s at 1%) was selected added with surfactant (0.5% v/v Tween 85) to lower its surface tension. It was also demonstrated that the membrane thickness varied in function of calcium concentration and curing time (time of contact between the emulsion drop and the alginate solution). Increasing both calcium chloride concentration and curing time, capsules with thicker membranes were formed (Martins et al., 2015). However, due to the membrane thickness increase, the calcium ions diffusion through the gel network became limiting and the membrane thickening stopped after ≈ 30 min of curing time. After this time, membranes with thicknesses between 0.4 and 0.5 mm for a fixed calcium chloride concentration of 27.7 g/L in the emulsion were formed.

The wet capsules contained 67% v/v of oil loading and had diameters between 2.9 and 3.5 mm (Abang et al., 2012; Lopez et al., 2012). The dried capsules contained up to 90% v/v of oil loading.

The emulsion can be formulated with different oils or include actives as volatile compounds, enzymes or dyes (Anderson et al., 2005). It was also demonstrated, using this technique, the success in the encapsulation of sunflower oil, linalool and lipase (Abang 2011, Lopez et al., 2012). The capsules produced by inverse gelation can be applied in food, home care products (fragrance diffusers, decorative pearls or for crops protection), agriculture and cosmetics (Martins et al., 2017b).

The oil encapsulation by inverse gelation does not necessitate complex equipment or extensive training to produce capsules with high oil loading. In addition, few parameters need to be optimised compared with other techniques, such as vibrating jet or millifluidic for example.

Conclusion

In this review, it was presented the main techniques used for oil encapsulation in alginate matrix as well as their principal advantages and drawbacks. The choice of the technology used for oil encapsulation is based on an intricate balance between productivity, cost, wall material and capsule size.

Disclosure statement

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

References

Abang S. 2011. Immobilisation of porcine pancreatic lipase in liquid-core capsules, PhD Thesis. Ecole Nationale Vétérinaire Agroalimentaire et de l'Alimentation, ONIRIS-Université de Nantes, France.

Abang S, Chan ES, Poncelet D. Effects of process variables on the encapsulation of oil in Ca-alginate capsules using an inverse gelation technique. J Microencapsul, 2012;29(5): 417–28.

ADDIACTIVE. Tendances du monde. Gattefossé France, 2015;1–27. 96.

Anderson PO, Steinberg OG, Leirsund CKL. 2005. Polysaccharide capsules and methods of preparation. U.S. Patent 2005/0106233 A1.

Assis LM, Zavareze ER, Prentice-Hernández C, Souza-Soares LA. Characteristics of nanoparticles and their potential applications in foods. Braz J Food Technol, 2012;15(2): 99–109.

AVEKA. 2015. Available at: http://www.aveka.com/encapsulation-microencapsulation-services.html.

Bae KH, Lee Y, Park TG. Oil-encapsulating PEO-PPO-PEO/PEG shell cross-linked nanocapsules for target-specific delivery of paclitaxel. Biomacromolecules, 2007;8(2):650–6.

Baimark Y, Srisuwan Y. Preparation of alginate microspheres by water-in-oil emulsion method for drug delivery: Effect of Ca2+ post-cross-linking. Adv Powder Technol, 2014;25: 1541–6.

Beindorff CM, Zuidam NJ. 2010. Microencapsulation of fish oil. In: Nicolas Jan Zuidam, Viktor A, eds. Encapsulation technologies for active food ingredients and food processing. Nedovic: Springer, pp. 161–85.

Benavides S, Cortés P, Parada J, Franco W. Development of alginate microspheres containing thyme essential oil using ionic gelation. Food Chem, 2016;204:77–83.

Bera H, Kandukuria SG, Nayak AK, Boddupalli S. Alginate-sterculia gum gel-coated oil-entrapped alginate beads for gastroretentive risperidone delivery. Carbohydr Polym, 2015;120:74–84.

Bremond N, Santanach-Carreras E, Chuab LY, Bibette J. Formation of liquid-core capsules having a thin hydrogel membrane: Liquid pearls. Soft Matter, 2010;6:2484–8.

Brownlie K. 2007. In: Lakkis JM (ed). Marketing perspective of encapsulation technologies in food applications. Asia: Blackwell Publishing.

Bugarski B, Li QL, Goosen MFA, Poncelet D, Neufeld RJ. Vunjak G. Electrostatic droplet generation – Mechanism of polymer droplet formation. Aiche J, 1994;40:1026–31.

CAPSUM. 2015. Available at: <http://www.capsum.net>.

Cárdenas-Bailón F, Osorio-Revilla G, Gallardo-Velázquez T. Microencapsulation techniques to develop formulations of insulin for oral delivery: A review. J Microencapsul, 2014;30(5):409–24.

Carneiro HCF, Tonon RV, Grosso CRF, Hubinger MD. Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different

combinations of wall materials. J Food Eng, 2013;115: 443–51.
Chan ES. Preparation of ca-alginate beads containing high oil content: Influence of process variables on encapsulation efficiency and bead properties. Carbohydr Polym, 2011;84:1267–75.
Chan ES, Lee BB, Ravindra P, Poncelet D. Prediction models for shape and size of ca-alginate macrobeads produced through extrusion-dripping method. J Colloid Interf Sci, 2009;338:63–72.
Chan LW, Lee HY, Heng PWS. Mechanisms of external and internal gelation and their impact on the functions of alginate as a coat and delivery system. Carbohydr Polym, 2006;63:176–87.
Choi BY, Park HJ, Wang SJ, Park JB. Preparation of alginate beads for floating drug delivery system: Effects of CO(2) gas-forming agents. Int J Pharm, 2002;239:81–91.
Chung BG, Lee KH, Khademhosseini A, Lee SH. Microfluidic fabrication of microengineered hydrogels and their application in tissue engineering. Lab Chip, 2012; 12:45–59.
Datta SS, Abbaspourrad A, Amstad E, Fan J, Kim SH, Romanowsky M, Shum HC, Sun B, Utada AS, Windbergs M, et al. 25th Anniversary Article: Double emulsion templated solid microcapsules: Mechanics and controlled release. Adv Mater, 2014;1–14.
de Paula HCB, de Oliveira EF, Abreu FOMS. Esferas (Beads) de Alginato como Agente Encapsulante de Óleo de Croton Zehntneri Pax et Hoffm. Polímeros, 2010;20: 112–20.
Degen P, Zwar E, Schulz I, Rehage H. Magneto-responsive alginate capsules. J Phys Condens Matter, 2015;27:194105.
Erni P, Cramer C, Marti I, Windhab EJ, Fischer P. Continuous flow structuring of anisotropic biopolymer particles. Adv Colloid Interface Sci, 2009;150:16–26.
Ferrari CKB. Lipid oxidation in food and biological systems: General mechanisms and nutritional and pathological implications. Rev Nutr, 1998;(11):3–14.
Fischer P, Erni P. Emulsion drops in external flow fields – The role of liquid interfaces. Curr Opin Colloid Interface Sci, 2007;12:196.
Fu H, Liu Y, Adrià F, Shao X, Cai W, Chipot C. From material science to avant-garde cuisine. The art of shaping liquids into spheres. J Phys Chem B, 2014;118:11747–56.
Fuchs M, Turchiuli C, Bohin M, Cuvelier ME, Ordonnaud C, Peyrat-Maillard MN, Dumoulin E. Encapsulation of oil in powder using spray drying and fluidised bed agglomeration. J Food Eng, 2006;75:27–35.
Gharsallaoui A, Roudaut G, Chambin O, Voilley A, Saurel R. Applications of spray-drying in microencapsulation of food ingredients: An overview. Food Res Int, 2007;40:1107–21.
Goh CH, Paul Heng PWS, Chan LW. Alginates as a useful natural polymer for microencapsulation and therapeutic applications. Carbohydr Polym, 2012;88:1–12.
Gouin S. Microencapsulation: Industrial appraisal of existing technologies and trends. Trends Food Sci Technol, 2004;15:330–47.
Goula AM, Adamopoulos KG. A method for pomegranate seed application in food industries: Seed oil encapsulation. Food Biopro Process, 2012;90:639–52.
Grant G, Morris E, Rees D, Smith P, Thom D. Biological interactions between polysaccharides and divalent cations: The egg-box model. FEBS Lett, 1973;32(1):195–8.
Hernandez EM. 2008. Structured lipids as delivery systems. In: Garti N., ed. Delivery and controlled release of bioactives in foods and nutraceuticals. Boca Raton, Boston, New York, Washington, DC: Elsevier.
Hoad C, Rayment P, Risse V, Cox E, Ciampi E, Pregent S, Marciani L, Butler M, Spiller R, Gowland P. Encapsulation of lipid by alginate beads reduces bio-accessibility: An *in vivo* ^{13}C breath test and MRI study. Food Hydrocolloids, 2011;25:1190–200.
Hosseini SF, Zandi M, Rezaei M, Farahmandghavi F. Two-step method for encapsulation of oregano essential oil in chitosan nanoparticles: Preparation, characterization and *in vitro* release study. Carbohydr Polym, 2013;95:50–6.
Jerobin J, Sureshkumar RS, Anjali CH, Mukherjee A, Chandrasekaran N. Biodegradable polymer based encapsulation of neem oil nanoemulsion for controlled release of Aza-A. Carbohydr Polym, 2012;90:1750–6.
Johansen A, Flink JM. Immobilization of yeast cells by internal gelation of alginate. Enzyme Microb Technol, 1986;8:145–8.
Jyothi NVN, Prasanna PM, Sakarkar SN, Prabha KS, Ramaiah PS, Srawan GY. Microencapsulation techniques, factors influencing encapsulation efficiency. J Microencapsul, 2010;27(3):187–97.
Klein J, Stock J, Vorlop KD. Pore size and properties of spherical Ca–alginate biocatalysts. Eur J Appl Microbiol Biotechnol, 1983;18:86–91.
Kolanowski W, Ziolkowski M, Weiszbrodt J, Kunz B, Laufenberg G. Microencapsulation of fish oil by spray drying – Impact on oxidative stability: Part 1. Eur Food Res Technol, 2006;222:336–42.
Lee SJ, Ying DY. 2008. Encapsulation of fish oils. In: Garti M, ed. Delivery and controlled release of bioactives in foods and nutraceuticals. Boca Raton, Boston, New York, Washington, DC: Elsevier, pp. 370–403.
Lee SJ, Wong M. 2014. In: Kwak HS, ed. Nano- and microencapsulation of phytochemicals, Oxford: Wiley Blackwell.
Li J, He J, Huang Y, Li D, Chen X. Improving surface and mechanical properties of alginate films by using ethanol as a co-solvent during external gelation. Carbohydr Polym, 2015;123:208–2016.
Lidert Z. Microencapsulation: An Overview of the Technology Landscape. In: Delivery System Handbook for Personal Care and Cosmetic Products Technology, Applications, and Formulations. Edited by Meyer R. Rosen Interactive Consulting, Inc. East Norwich, New York Edited by Meyer R, New York 2005, p. 181–90.
Liu L, Wu F, Ju X, Xie R, Wang W, Niu CH, Chuac L. Preparation of monodisperse calcium alginate microcapsules via internal gelation in microfluidic-generated double emulsions. J Colloid Interface Sci, 2013;404:85–90.
Liu S, Li H, Tang B, Bi S, Li L. Scaling law and microstructure of alginate hydrogel. Carbohydr Polym, 2016;135:101–9.
Lopez MD, Maudhuit A, Pascual-Villalobos MJ, Poncelet D. Development of formulations to improve the controlled-release of linalool to be applied as an insecticide. J Agric Food Chem, 2012;60(5):1187–92.
Lord Rayleigh SJW. On the stability of jets. Proc London Math Soc, 1878;10:4–13.

Manojlovic V, Djonlagic J, Obradovic B, Nedovic V, Bugarski B. Immobilization of cells by electrostatic droplet generation: A model system for potential application in medicine. Int J Nanomed, 2006;1:163–71.

MarketsandMarkets. 2012. Global food encapsulation market (2012-2017). Copyright MarketsandMarkets, p: 1–277.

Marques HMC. A review on cyclodextrin encapsulation of essential oils and volatiles. Flavour Fragr J, 2010;25:313–26.

Martins E, Poncelet D, Marquis M, Davy J, Renard D. Monodisperse core-shell alginate (micro)-capsules with oil core generated from droplets millifluidic. Food Hydrocolloids, 2017;63:447–56.

Martins E, Poncelet D, Renard D. A novel method of oil encapsulation in core-shell alginate microcapsules by dispersion-inverse gelation technique. React Funct Polym, 2017a;114:49–57.

Martins E, Renard D, Adiwijaya Z, Karaoglan E, Poncelet D. Oil encapsulation in core-shell alginate capsules by inverse gelation. I: Dripping methodology. J Microencapul, 2017b;34(1):82–90.

Martins E, Renard D, Davy J, Marquis M, Poncelet D. Oil core microcapsules by inverse gelation technique. J Microencapsul, 2015;32(1):86–95.

McNamee BF, White LE, O'Riordan ED, O'Sullivan M. Effect of partial replacement of gum arabic with carbohydrates on its microencapsulation properties. J Agric Food Chem, 2010;49:3385–8.

Morales E, Rubilar M, Burgos-Díaz C, Acevedo F, Penning M, Shene C. Alginate/Shellac beads developed by external gelation as a highly efficient model system for oil encapsulation with intestinal delivery. Food Hydrocolloids, 2017;70:321–8.

Nakagawa K. 2014. In: Kwak H-S, ed. Nano- and microencapsulation of flavour in food systems. Oxford: Wiley Blackwell.

Nakagawa K, Sowasod N, Tanthapanichakoon W, Charinpanitkul T. Hydrogel based oil encapsulation for controlled release of curcumin by using a ternary system of chitosan, kappa-carrageenan, and carboxymethylcellulose sodium salt. LWT – Food Sci Technol, 2013;54:600–5.

Natrajan D, Srinivasan S, Sundar K, Ravindran A. Formulation of essential oil-loaded chitosan–alginate nanocapsules. J Food Drug Anal, 2015;3:560–8.

Nikam VK, Kotade KB, Gaware VM, Dolas RT. Eudragit a versatile polymer: A review. Pharmacol Online, 2011;1:152–64.

Nussinovitch A, Gershon Z, Nussinovitch M. Liquid-core hydrocolloid capsules. Food Hydrocolloids, 1996;10:21–6.

Ouwerx C, Velings N, Mestdagh MM, Axelos MAV. Physicochemical properties and rheology of alginate gel beads formed with various divalent cations. Polym Gels Networks, 1998;6:393–408.

Patel AR, Remijn C, Cabero AIM, Heussen PCM, ten Hoorn JWMS, Velikov KP. Novel all-natural microcapsules from gelatin and shellac for biorelated applications. Adv Funct Mater, 2013;23:4710–18.

Pawlik A. 2012. Duplex emulsions for healthy foods. PhD Thesis. The University of Birmingham, 1–228.

Peng C, Zhao SQ, Zhang J, Huang GY, Chen LY, Zhao FY. Chemical composition, antimicrobial property and microencapsulation of Mustard (Sinapis alba) seed essential oil by complex coacervation. Food Chem, 2014;165:560–8.

Peniche C, Howland I, Carrillo O, Zaldívar C, Argüelles-Monal W. Formation and stability of shark liver oil loaded chitosan/calcium alginate capsules. Food Hydrocolloids, 2004;18(5):865–71.

Perez FS, Bertagnolli SMM, Alves MP, Penna NG. Nanotecnologia: Aplicações na Área de alimentos. Disc Scientia, 2012;13(1):1–14.

Piornos JA, Burgos-Díaz C, Morales E, Rubilar M, Acevedo F. Highly efficient encapsulation of linseed oil into alginate/lupin protein beads: Optimization of the emulsion formulation. Food Hydrocolloids, 2017;63:139–48.

Poncelet D, Lencki R, Beaulieu C, Halle JP, Neufeld JP, Fournier A. Production of alginate beads by emulsification/internal gelation. I. Methodology. Appl Microbiol Biotechnol, 1992;38:39–45.

Prusse U, Vorlop KD. 2004. The Jetcutter technology. In: Nedovic V, Willaert R, eds. Fundamentals of cell immobilisation biotechnology, vol. 8A. Dordrecht: Kluwer Academic Publishers, pp. 295–309.

Reineccius GA. 2001. The spray drying of food ingredients. In: Per Vilstrup, ed. Microencapsulation of food ingredients. England: Leatherhead Publishing, pp. 151–85.

Ren PW, Ju XJ, Xie R, Chu LY. Monodisperse alginate microcapsules with oil core generated from a microfluidic device. J Colloid Interface Sci, 2010;343:392–5.

Risch SJ, Reineccius GAA. 1988. Flavor encapsulation. ACS Symposium Series 370. Washington, DC: American Chemical Society.

Sabliov CM, Astete CE. 2008. Encapsulation and controlled release of antioxidants and vitamins. In: Garti N, ed. Delivery and controlled release of bioactives in foods and nutraceuticals. Boca Raton, Boston, New York, Washington, DC: Elsevier.

Santos GKN, Dutra KA, Lira CS, Lima BN, Napoleão TH, Paiva MGP, Maranhão CA, Brandão SSF, Navarro DMAF. Effects of Croton rhamnifolioides essential oil on Aedes aegypti oviposition, larval toxicity and trypsin activity. Molecules, 2014;19:16573–87.

Schmaltz C, dos Santos JV, Stanisçuaski Guterres SS. Nanocápsulas como uma tendência promissora na área cosmética: A imensa potencialidade deste pequeno grande recurso. Infarma, 2005;16:13–14.

Schmit A, Courbin L, Marquis M, Renard D, Panizza P. A pendant drop method for the production of calibrated double emulsions and emulsion gels. RSC Adv, 2014;4:28504.

Schwinger C, Koch S, Jahnz U, Wittlich P, Rainov N, Kressler J. High throughput encapsulation of murine fibroblasts in alginate using the JetCutter technology. J Microencapsul, 2002;19:273–80.

Smidsrød O, Haug A. Dependence upon uronic acid composition of some ion-exchange properties of alginates. Acta Chem Scand, 1968;22:1989–97.

Sun XT, Liu M, Xu ZR. Microfluidic fabrication of multifunctional particles and their analytical applications. Talanta, 2014;121:163–77.

Tate T. On the magnitude of a drop of liquid formed under different circumstances. Philos Mag, 1864;27:176–80.

Theberge AB, Courtois F, Schaerli Y, Fischlechner M, Abell C, Hollfelder F, Huck WTS. Microdroplets in microfluidics: An evolving platform for discoveries in chemistry and biology. Angew Chem Int Ed Engl, 2010;49:5846–68.

Thies C. 2001. Microencapsulation: What it is and purpose. In: Vilstrup P, ed. Microencapsulation of food ingredients. England: Leatherhead Publishing, pp. 1–30.

Transparency Market Research. 2015. Available in: http://www.transparencymarket research.com/pressrelease/microencapsulation-market.htm.

Umbanhowar P, Prasad V, Weitz DA. Monodisperse emulsion generation via drop break off in a coflowing stream. Langmuir, 2000;16:347.

Vasisht N. 2014. Factors and mechanisms in microencapsulation. In: Gaonkar A, Vasisht N, Khare A, Sobel R, eds. Microencapsulation in the food industry. USA: Academic Press is an imprint of Elsevier, pp. 15–24.

Voncina B, Kreft O, Kokol V, Chen WT. Encapsulation of Rosemary oil in ethylcellulose microcapsules. Textile Polym J, 2009;1(1):1–19.

Weber C. Zum Zerfall eines Flussigkeitsstrahles. Z Angew Math Mech, 1931;11:136–54.

Wang W, Waterhouse GIN, Sun-Waterhouse D. Co-extrusion encapsulation of canola oil with alginate: Effect of quercetin addition to oil core and pectin addition to alginate shell on oil stability. Food Res Int, 2013;54:837–51.

Whelehan M, Marison IW. Microencapsulation by dripping and jet break up. Bioencapsul Innovations, 2011;1:4–10.

Wu Q, Zhang T, Xue Y, Xue C, Wang Y. Preparation of alginate core–shell beads with different M/G ratios to improve the stability of fish oil. LWT-Food Sci Technol, 2017;80:304–10.

Yan C, Wei Zhang W. 2014. Coacervation processes. In: Gaonkar AG, Vasisht N, Khare AR, Sobel R, eds. Microencapsulation in the food industry. USA: Academic Press is an imprint of Elsevier, pp. 125–38.

Zhang H, Tumarkin E, Sullan RMA, Walker GC, Kumacheva E. Exploring microfluidic routes to microgels of biological polymers. Macromol Rapid Commun, 2007;28:527–38.

Ziani K, Fang Y, McClements DJ. Encapsulation of functional lipophilic components in surfactant-based colloidal delivery systems: Vitamin E, vitamin D, and lemon oil. Food Chem, 2012;134:1106–12.

Zuidam NJ, Shimoni E. 2010. Overview of microencapsulation for use in food products or processes and methods to make them. In: Zuidam NJ, Nedovic VA, eds. Encapsulation technologies for active food ingredients and food processing. New York: Springer, pp. 3–30.