Nanoemulsions and nanosized ingredients for food formulations

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6.1 Introduction

Nanoemulsions and nanosized ingredients represent a viable alternative in the development of novel products for including components with specific functions (Abbasi, Samadi, Jafari, Ramezanpour, & Shams-Shargh, 2019; Assadpour & Jafari, 2017; Mohammadi, Jafari, Assadpour, & Faridi Esfanjani, 2016). The ingredients can be incorporated during food processing in order to obtain functional products with adequate organoleptic quality, texture improvement, color homogeneity, and stabilizers, or for the release of active substances during storage, distribution, or consumption. These nanosystems possess a greater surface area, reactivity, solubility, and availability of compounds, and they have the ability to interact with the food components to decrease the physiological and enzymatic reactions, producing new products or contributing to the development of sausages, mayonnaise, or other low-fat products (Quintanilla-Carvajal et al., 2010; Rezaei, Fathi, & Jafari, 2019).

Recently, consumers have exhibited a preference for minimally processed products with the most natural additives and ingredients that represent a health benefit, such as enzymes, prebiotics, probiotics, antioxidants, and antimicrobials that occur naturally as soluble extracts or essential oils obtained generally from plants (Li & Nie, 2016; Tamjidi, Shahedi, Varshosaz, & Nasirpour, 2013). This is where nanotechnology allows improvement of the functionality of various ingredients, modifying their solubility, decreasing the concentration of substances, and potentiating their effectiveness or controlling their release (Jafari & McClements, 2017; Jafari, Fathi, & Mandala, 2015). Moreover, nanosized systems interact with food; thus the components must be selected carefully depending on the food, beverage, drink, sausage, etc., in which they will be used.

The preparation of nanosystems requires several considerations in terms of which the ingredients will be used during the processing, rendering it necessary to request

Handbook of Food Nanotechnology. https://doi.org/10.1016/B978-0-12-815866-1.00006-6

the desired function in the formulation, such as the following: stabilizers of food emulsions (sausages, mayonnaise, functional beverages); improvers of texture (ice cream, cheese, pâtés); homogenization of color; nutrient bioavailability, and enzymatic, oxidative, or respiratory control in minimally processed products. In addition, it remains important to consider the characteristics of the food in which the nanosized systems will be employed and incompatibilities between ingredients. Moreover, physicochemical properties such as pH, water activity, ion charge, fat content, the superficial ionic charge, and composition in general, as well as the desired function that they fulfill during processing, packaging, storage, and consumption should be noted (Oehlke et al., 2014; Weiss, Takhistov, & McClements, 2006).

Preparation of nanostructured systems involves the use of surfactants that allow two immiscible phases to be stabilized for as long as possible; they play an important role in the interactions and these must be taken into account during the formulation of food. The interaction with the food as well as the release of the functional components will depend on its functional groups, hence its surface charge. In this chapter, we will consider that all nanosized systems should be incorporated directly into the food formulation as an ingredient; therefore all of the substances utilized should be generally recognized as safe (GRAS).

Different nanometric size systems are currently applied in food formulation, such as nanoemulsions, polymeric nanoparticles, solid lipid nanoparticles (SLNs), lipid nanocarriers, nanocrystals, nanoliposomes, nanomicelles, noisome, nanofibers, and nanolaminates. Thus the range of possibilities and choices will always depend on the purpose of their use and their relationship with the sensory quality of the products, in that the latter comprises a decisive part in the purchase selection by the consumer.

Nanoemulsions and Pickering nanoemulsions are the systems most studied for their incorporation into food formulations. Due to their characteristics and functionality, these are used for increasing the stability of juices, drinks, sauces, dressings, and ice cream (Oehlke et al., 2014; Thiruvengadam, Rajakumar, & Chung, 2018). The main ingredients used as stabilizers for their preparation are as follows: polyelectrolytic molecules such as amphiphilic proteins; peptides; hydrocolloids such as modified starches (oxidized, acid, alkaline, etc.); chitosan, pectin, and alginate, and/or synthetic stabilizers such as polysorbates, sorbitan esters, and polyoxyethylenes (Hu, Bae, Fleming, Lee, & Luo, 2019; Pérez-Masiá et al., 2015; Zambrano-Zaragoza & Quintanar-Guerrero, 2019). The substances usually desired for incorporation are essential oils with an antioxidant and/or antimicrobial potential effect, vitamins, polyphenols, and enzymes, to mention some. In addition, the solid particles most commonly used in Pickering nanoemulsions for use in food and beverages are silica, while polymeric nanoparticles are the second type of systems used in food formulation and are preferred for the incorporation of functional ingredients for thermal protection during processing and for the controlled release of substances during storage.

6.2 Nanoemulsions in food processing

Nanoemulsions represent one of the systems that have shown the greatest interest for use as ingredients in the food industry, mainly because there are different methods for their preparation, as well as being considered as stable systems for the encapsulation of bioactive substances. Also, their performance as a good release system will depend on the conditions in which they are applied.

6.2.1 Classification of nanoemulsions for food industries

An emulsion is a lyophobic colloidal system composed of two immiscible liquids, in which one of the liquids is dispersed homogeneously in the other liquid in the form of spherical globules (Feng, Chen, Wu, Jafari, & McClements, 2018; Hosseini, Jafari, Mirzaei, Asghari, & Akhavan, 2015). Globule size in emulsions has served as a criterion for classification: macroemulsions are considered when globule sizes are within the range of 1.0–100 μm, while nanoemulsions are systems with globules between 20 and 500 nm, and microemulsions possess droplet sizes between 2 and 100 nm (McClements & Rao, 2011). It can be observed that there is an overlap in globule size; however, there are marked differences in the characteristics of different types of emulsions. For example, macroemulsions and nanoemulsions are thermodynamically unstable, while microemulsions are stable (Mehrnia, Jafari, Makhmal-Zadeh, & Maghsoudlou, 2016, 2017). Another difference exists in terms of their appearance; macroemulsions are turbid or opaque, and nanoemulsions are translucent or opalescent with bluish appearance, due to the Tyndall effect, while microemulsions have a transparent aspect. Table 6.1 describes some other properties of the different types of emulsions.

Emulsions can be classified according to the number of phases and by which phase is dispersed into the other. Binary (double) emulsions are the most commonly

Table 6.1 Characteristics and properties of different types of emulsions.

Emulsion type	Diameter range	Thermodynamic stability	Cremation rate	Surfactant concentration required for stabilization
Macro-emulsion	1.0–100 μm	Unstable	High	Low/medium
Nanoemulsion	20–500 nm	Metastable	Very low or zero	Free to high
Microemulsion	<100 nm	Stable	Zero	High

used in industry applications. Water-in-oil (W/O) and oil-in-water (O/W) are the two types of double emulsions that can be prepared (Faridi Esfanjani, Jafari, & Assadpour, 2017; Gharehbeglou, Jafari, Hamishekar, Homayouni, & Mirzaei, 2019); in fact, multiple emulsions are complex systems in which both W/O and O/W emulsions are present at the same time. Nanoemulsions can also be prepared as binary or multiple systems, and O/W nanoemulsions are those most used in food applications due to their textural and functional properties.

Nanoemulsions in food technology can be classified according to their desired role. In this regard, they can be categorized as follows: (1) encapsulation of active ingredients; (2) delivery of active ingredients; (3) preservation; (4) improvement of nutritional properties; and (5) modification of structural or textural properties.

6.2.2 Preparation methods of nanoemulsions

Nanoemulsions, for their formation, require that energy be supplied to the system. The amount of input energy necessary for the preparation of nanoemulsions is directly related to the increase in surface area due to the creation of the new globules and interfacial tension (McClements & Jafari 2018b; Shamsara, Jafari, & Muhidinov, 2017). In practice, the energy will always be greater than that calculated from the expansion values of the surface area and surface tension because it does not take into consideration the effects of energy dissipation by the dispersing phase (e.g., heat or momentum) or other effects such as coalescence (Gharibzahedi & Jafari, 2018; McClements & Jafari, 2018a). According to the theory of emulsification, dispersion of the droplets in the dispersed phase requires the supply of shear forces (deforming inertial forces) sufficiently large in magnitude to overcome the intrinsic cohesive forces of the fluid to be dispersed (Jafari, He, & Bhandari, 2006, 2007b, 2007c). In the case of nanoemulsions, in addition to the latter, we must consider the effects of curvature, Laplace pressure ΔP (the pressure difference between the inside and outside of the drop), which is responsible for maintaining the spherical shape of the droplet, and, in the case of nanoemulsions, the greater amount of energy (stress) required to deform and break the small drops (Santana, Perrechil, & Cunha, 2013). The preparation methods of nanoemulsions have been classified as high energy and low energy, according to the mechanism of the energy delivery to the system to be emulsified.

6.2.2.1 High-energy methods

In high-energy methods, the fluid is exposed to high shear forces or pressure differences in order to achieve disruption of the droplets. It is common to use mechanical stirrers equipped with suitable propelers, high-speed devices such as rotor-stator systems, high-pressure homogenizers, membrane systems, or ultrasonic devices (Jafari, Assadpoor, He, & Bhandari, 2008). These methods permit a simple industrial scaling up, and it is possible to produce emulsions with globule size with a narrow distribution (Villalobos-Castillejos et al., 2018). The main drawbacks are the use of relatively high concentrations of surfactants and the low efficiency in terms of energy dissipation: only 0.1% is effective for droplet breaking, whereas 99.9% is dissipated as heat during the homogenization process (Tadros, Izquierdo, Esquena, & Solans, 2004).

6.2.2.2 Low-energy methods

These methods are based on the inherent physicochemical properties of the surfactants for the formation of nanoemulsions. The processes unlike those of high-energy methods, occur under laminar flow and are directed by the chemical potential of the system. There are two main methods reported for the preparation of nanoemulsions by low-energy: spontaneous emulsification and phase inversion. In spontaneous emulsification, the latter is performed at the moment of contact of the two phases without the need for external forces (Mehrnia et al., 2016). In this, the physicochemical characteristics of the surfactant play a critical role in the formation of the emulsion. It has been described that the driving force in spontaneous emulsification comprises the rapid diffusion of the surfactant and/or solvent from the dispersed phase to the continuous phase. In some cases, water-miscible solvents (for O/W nanoemulsions) are used to facilitate the diffusion of the solvent and/or surfactant; through this methodology, it is possible to obtain the Ouzo effect (Botet, 2012). The use of partially miscible solvents has also been reported, and adaptations of the emulsification–diffusion method have been proposed that allow obtaining food-grade nanoemulsions and nanocapsules (Mitri et al., 2012; Zambrano-Zaragoza, Mercado-Silva, Gutiérrez-Cortez, Castaño-Tostado, & Quintanar-Guerrero, 2011). On the other hand, in the phase inversion approach, changes in temperature (phase inversion temperature, PIT) or composition (phase inversion composition, PIC) drives the formation of nanoemulsions. In these techniques, change in surfactant curvature is produced as the emulsion switches from negative to positive (to form O/W emulsions) or vice versa (to form W/O emulsions) (Solans & Solé, 2012). As is clear, in the PIT technique, a change in temperature induces spontaneous inversion of the curvature of the surfactant. Only high temperature-sensitive surfactants can be used in this technique, for example, polyoxyethylene-type nonionic surfactants. Finally, in the PIC technique, one of the components (water or oil) is added progressively to an isotropic mixture of the other component (water or oil/surfactant). As in PIT, surfactant spontaneous- curvature changes from negative to zero, lamellar, or bicontinuous structures are formed at zero curvature and when the transition composition exceeds the structures with zero curvature separated into metastable nanosize droplets (Solans & Solé, 2012).

6.2.2.3 Selection of emulsifier or coemulsifier and compatibility of the food processes

Emulsifiers are mandatory for inclusion in the formulation of nanoemulsions. If emulsifiers are not included, the nanoemulsion will rapidly break down due to the high surface area. Stabilizers or emulsifiers during emulsion improve kinetic stability and extend the food shelf life. Selection of the emulsifiers is a crucial step in the design of a nanoemulsion; in addition to contributing stability to the emulsion, the emulsifier also exerts an enormous effect on the functionality, structure, and texture of many foods (Jafari, He, & Bhandari, 2007a; McClements and Jafari, 2018b). Therefore their compatibility should be evaluated. In fact, a goal during the formulation of a nanoemulsion is to reduce the concentration of emulsifiers in order to reduce the cost, not to alter the taste, and not to be worried about safety concerns.

Emulsifiers can be classified as follows: (1) surfactants; (2) protective colloids or hydrocolloids; and (3) finely divided particles. Several factors should be kept in mind to select the appropriate emulsifier type in the formulation of a nanoemulsion. For example, surfactants (small amphiphilic molecules) are sensitive to changes in pH, ionic strength, and temperature. To illustrate this, if a polyoxyethylene nonionic surfactant (Tween or Span) is utilized during the formation of a nanoemulsion, the processing temperature is crucial, due to the phase-inversion temperature behavior; if the temperature is increased, an emulsion with reduced droplet size is expected, and this has implications in stability and texture (Saberi, Fang, & McClements, 2013). Surfactants can be used for both high-energy and low-energy methods; however, in this latter method, very low interfacial tensions are necessary to facilitate the spontaneous emulsification. Under this condition, the surfactant alone is not sufficient to reduce the surface tension; in this case, a cosurfactant is added to the formulation to achieve the reduction. The most common cosurfactants in food-grade nanoemulsions are short- and medium-chain alcohols such as ethanol or cosolvents such as polyols like propylene glycol, glycerol, and sorbitol.

Another aspect to consider is the origin of the emulsifier. Currently, natural emulsifiers are preferred over semisynthetic or synthetic ones. Natural emulsifiers, such as proteins derived from plants or milk, have been employed as effective surfactants during the formulation of nanoemulsions (Assadpour, Maghsoudlou, Jafari, Ghorbani, & Aalami, 2016; Gharehbeglou et al., 2019; Shamsara et al., 2015). Proteins comprise an excellent option because they have a high nutritional value and are GRAS. These proteins include soybean protein isolate, whey protein isolate, β-lactoglobulin (β-lg), and casein.

The formulator should take into account that nanoemulsions require a high percentage of emulsifiers in the formulation; consequently, the emulsifier can modify the sensorial and textural properties of the food. For example, protective colloids or hydrocolloids are lyophilic macromolecules that can act as stabilizer or emulsifiers; in food technology, those most utilized are gums such as Arabic, guar, or xanthan, modified starches, modified celluloses, some types of pectin, and some galactomannans (Yousefi & Jafari, 2019). Protective colloids are good stabilizers to a greater degree than good emulsifiers (Dickinson, 2009). Their use in the stabilization of O/W nanoemulsions is based on the steric repulsion effect at the interface and to the thickening of the aqueous phase, reducing the velocity of creaming. The use of protective colloids for stabilization is intrinsically bound to the modification of the textural properties of the food due to the protective colloids also acting as structuring/thickening/gelling agents.

6.2.3 Applications of nanoemulsions and their effect on food

Food nanoemulsions represent one of the most commonly used colloidal systems as ingredients in food formulation during food processing. These are used in beverages, juices, dressings, sauces, and ice cream, among many others, and they possess great stability, in addition to being clear and facilitating the incorporation of water-insoluble ingredients such as vitamin, essential oils, colorants, and flavors (Maswal & Dar, 2014). As mentioned in Section 6.2.1, nanoemulsions are used in foods to improve the performance of the formulations ingredients. This includes some functionalities that are described here.

6.2.3.1 Encapsulation of active ingredients

The encapsulation of substances into nanoemulsions can adhere to the protection or solubilization of actives (Akhavan, Assadpour, Katouzian, & Jafari, 2018; Rafiee & Jafari, 2018). For example, in liquid foods such as beverages, it is common to use encapsulated food components such as oil-soluble flavors, vitamins, colorants, preservatives, and other bioactives in order to protect the active ingredients against degradation derived from external factors such as oxygen, light, or others (Joung et al., 2016; Kim, Ha, Choi, & Ko, 2014; Qian, Decker, Xiao, & McClements, 2012a). In line with the same example, in beverages, sometimes flavors or functional active ingredients can affect their clarity. Nanoemulsions are very attractive because they can solubilize and produce products with high stability and clarity. Other applications of encapsulation include masking the unpleasant taste or smell of some substances, increasing the bioavailability of some active ingredients or decreasing the evaporation of food aroma (Salem & Ezzat, 2018). More details have been provided in Chapter 8, Nanoencapsulation of Bioactive Food Ingredients.

6.2.3.2 Delivery of active ingredients

Nanoemulsions are excellent carriers of both lipophilic/hydrophilic active compounds in food (Faridi Esfanjani, Assadpour, & Jafari, 2018; Rostamabadi, Falsafi, & Jafari, 2019a). Nanoemulsions are well tolerated orally and can deliver the active ingredients in a controlled manner, improving the nutritional value of some active substances in food. As in pharmaceutical products, nanoemulsions can improve the absorption of highly nutritional compounds, controlling the active release profile (RP) (Jafari, Paximada, Mandala, Assadpour, & Mehrnia, 2017b). The full details are discussed in Chapter 9, Enhancing the Bioavailability of Nutrients by Nanodelivery Systems.

6.2.3.3 Preservation

Nanoemulsions are used for surface treatment in minimally processed foods. At present, many ingredients are of natural origin, such as essentials oils with antioxidant and antimicrobial properties. Considering the minimal sensory changes, the concentrations required are low, with the same or better effectiveness than the substance alone. This is because the interactions are increased, reaching the specific sites or interacting better with the food or with its structures and tissues (Zambrano-Zaragoza et al., 2018). Another point to take into account is the fact that essential oils contain terpenes, terpenoids, phenols, esters, and oxides, among other compounds. Also noteworthy is that they are, in addition, antiseptic or known for their antioxidant effects, resulting in interactions with food. Therefore the sensory perception will be modified. These components interact with cellular structures in foods such as meat, cereals, fruits, and vegetables. Together with the surfactant used in the stabilization of nanoemulsions, these promote modifications in the ionic charge and pH, which in turn will destabilize the nanoemulsions, thereby inducing the content to come in contact with the food and contributing to preservation (Prakash, Baskaran, Paramasivam, & Vadivel, 2018; Rezaei et al., 2019; Roy & Guha, 2018).

Another field of application for nanoemulsions is as an edible coating for food preservation (Prakash et al., 2018). Nanoemulsions based on antimicrobial compounds such as essential oils have recently been explored as systems of preservation (Jamali, Assadpour, & Jafari, 2019; Yousefi, Ehsani, & Jafari, 2019); nanoemulsions have proven to be more effective against bacteria than conventional emulsions due to their reduced droplet size, providing an extensive covering area on the surface of the food (Acevedo-Fani, Soliva-Fortuny, & Martín-Belloso, 2017). Additionally, antimicrobial substances formulated in nanoemulsions can have a long lifetime due to the reduced degradation, increasing their bactericidal effect. To cite an example, Sessa, Ferrari, and Donsì (2015) tested the functionality of different essential oil-loaded nanoemulsions (lemon, mandarin, oregano, or clove essential oils) incorporated into a chitosan matrix as preservation systems in leafy vegetables, specifically rucola leaf; the edible nanoemulsions provided a 3- to 7-day increase in the shelf life in comparison to that of the untreated leaf. Another example is the application of an α-tocopherol nanoemulsion as a coating in a nopal mucilage matrix, applied on the surface of a fresh-cut apple. It was found that this system increased the storage time up to 21 days, decreasing the loss of texture and inhibiting the enzymatic browning. This was attributed to the antioxidant action of α-tocopherol, which diminishes polyphenol oxidase and pectin methylesterase activity. Also, the mucilage matrix may contribute to decreasing the oxygen absorption rate in the tissue and interacts with pectic substances, favoring the maintenance of texture (Zambrano-Zaragoza, Gutiérrez-Cortez, et al., 2014a; Zambrano-Zaragoza, Mercado-Silv et al., 2014b).

6.2.3.4 Improvement of nutritional properties

Nanoemulsions are suitable for improving the digestibility and bioavailability of nutrients. One example of the model molecules is the carotenoids; they exhibit poor water-solubility and low bioavailability, and their incorporation into many foods is a challenge at present (Rostamabadi et al., 2019a). The impact of the carrier oil and droplet size on the in vitro bioaccessibility of β-carotene nanoemulsions has been studied by Qian, Decker, Xiao, and McClements (2012b) and Salvia-Trujillo, Qian, Martín-Belloso, and McClements (2013). The reduction in the size of droplets leads to the increase in bioaccessibility, whereas the carrier oil also plays an important role in the bioaccessibility, formation, and size of mixed micelles (salt bile, free fatty acids). The latter are related to the composition of the carrier oil that makes up the nanoemulsions, illustrating the importance of starting materials. In another type of compound, the ability of nanoemulsions to increase bioaccessibility has been demonstrated; for example, vitamins, minerals, plant extracts, polyphenols, omega-3 fatty acids, phytosterols, and tocopherols. Some concerns with respect to the increase in toxicity due to the formulations of nutrients in nanoemulsions are also involved in the debate, and the increase in absorption and repeated intake according to some research could be a risk for the consumers (Addepalli et al., 2017).

6.2.3.5 Modifying structural or textural properties

Nanoemulsions can be used as texture modulators. Depending on oil composition, internal-phase proportion, type and concentration of the stabilizer, and droplet size, nanoemulsions can exhibit different rheological behaviors from those of viscous liquids in viscoelastic solids (Dasgupta & Ranjan, 2018). For example, nanoemulsions have been employed to formulate low-fat foods such as mayonnaise and ice cream without sacrificing their texture, but offering a healthier option to consumers (Silva, Cerqueira, & Vicente, 2012). Low-fat nanoemulsions represent a formulation challenge because, due to their reduced oil content, they should be structured with emulsifiers or binders/fillers to increase viscosity. Pickering emulsions have been an excellent option for formulating highly stable low-fat nanoemulsions because the solid particles used for stabilization can act as thickening agents.

Nanoemulsions are also utilized as ingredients in foods that are spreads, such as pâtés, sausages, dips, and other low-fat products. It has been shown that these help to avoid protein instability, due mainly to oxidation of polyunsaturated fatty acids, and in maintaining or improving the texture and sensorial quality of products, such as quercetin nanoemulsions (0.3 g/L) prepared by inversion of phases, in which Tween 80 or Brij 30 were used as surfactants, revealing that nanoemulsions prepared with Tween 80 as surfactant had a 63% inhibition of lipooxidation. It has also been highlighted that sensory changes with the use of nanoemulsions are minimal, while the use of free quercetin demonstrated evident changes in the flavor of the pâté (de Carli, Moraes-Lovison, & Pinho, 2018). Another area where nanoemulsions are considered is in the conservation of margarines, creams, and in the formulation of beverages and juices, where it is important to consider the manufacture of functional foods.

Table 6.2 presents some examples of nanoemulsion applications in food and beverage formulation. The main effect in food processing or storage is mentioned, highlighting the emulsifier type that, due to this, plays an important role for incorporation of nanoingredients. In some cases, the use of a natural surfactant is preferred; however, in others, the use of synthetic surfactants manages to maintain

Table 6.2 **Effect of nanoemulsions as ingredients in food processing and shelf life.**

Food ingredient in nanoemulsions	Surfactant	Potential use/ application in food formulation	Function	Effect on food preservation
Quercetin (0.3 g/L)	Tween 80 Brij 30	Inhibition of lipid oxidation in spreadable pâté	Modified rheological behavior and stability of pâté	Maintenance of texture and sensorial quality de Carli et al. (2018)
Astaxanthin (2%) more antioxidant potential of β-carotene	Gypensides natural stabilizer (1%) Tween 20	Gypensides had lower fat digestion than Tween 20	Low fat sausages, dressings and other emulsified foods	Thermal treatment and protection of astaxanthin, controls release of anti-oxidant Chen et al. (2018)
ϒ-oryzanol (0.1%) in 3% fish oil	Tween 80 and Span 20 (10%)	Incorporated into yogurt as stabilizer	Modifying viscosity	ϒ-oryzanol/fish oil increasing the water- holding capacity and stabilizes the yogurt Zhong, Yang, Cao, Liu, and Qin (2018)
Oregano essential oil	Soy lecithin and medium-chain triglycerides (1:1)	Ingredient (0.05/100 g) of nanoemulsion in hake hamburger	Increasing shelf life	Decreasing the bacterial growth rate with incorporation of nanoemulsion and minimal sensorial changes Asensio, Quiroga, Huang, Nepote, and Grosso (2019)

Table 6.2 (Continued)

Food ingredient in nanoemulsions	Surfactant	Potential use/ application in food formulation	Function	Effect on food preservation
Curcumin/sunflower oil	Poly-sorbate 80 oil phase and glycerol aqueous phase	Ice cream	Stability and sensorial acceptance	Viscosity modifier. Good acceptability at 50% of nanoemulsion and higher stability Borrin, Georges, Brito-Oliveira, Moraes, and Pinho (2018)
Lycopene (0.015–0.085 mg/mL)	Tween 20 (0.3–0.7 mg/mL)	Beverages	Lycopene concentration optimization	Beverage stability, between 17 and 39 days depend of lycopene concentration Kim et al. (2014)

charges and can achieve the absorption of lipid compounds more easily (Chen et al., 2018).

6.2.4 *Pickering nanoemulsions and stabilization of emulsified foods*

Pickering emulsions are stabilized by solid particles (nanosizes), and they have garnered increasing interest in recent years in food technology due to their high stability and because their use is possible as food-compatible emulsifiers such as nanosize GRAS substances as stabilizers, rather than as surfactants (Shaddel, Akbari-Alavijeh, & Jafari, 2019). The main challenge during the formulation of Pickering emulsions is to find or synthesize the solid particles with the appropriate wetting behavior.

Similar to the rule of Bancroft, the rule of Finkle determines what type of emulsion (O/W or W/O) will result, depending on the wetting angle of the solid particle: if the wetting angle of the particle is >90 degrees, the particle has preference for the aqueous phase and curves the interphase into the formation of O/W emulsions, whereas if the wetting angle is <90 degrees, W/O emulsions are formed. However, if particles possess wetting angles of <30 degrees or >150 degrees, from the energy point of view, these particles would not create stable emulsions (Binks & Clint, 2002; Hunter, Pugh, Franks, & Jameson, 2008)

There are various classes of particles that can be employed as Pickering emulsion stabilizers in food applications, including minerals, polysaccharides, fat crystals, synthetic polymers, and proteins (Linke & Drusch, 2018; Xiao, Li, & Huang, 2016). Some of the most used Pickering stabilizers in food emulsions and foams are starch granules (native or with chemical modification) (Rostamabadi, Falsafi, & Jafari, 2019b). Starch is considered a GRAS ingredient, it is biodegradable, thus sustainable, and it is inexpensive. Several examples have been developed from different starch sources: rice, maize, wheat, amaranth, and quinoa (Leal-Castañeda et al., 2018; Li, Li, Sun, & Yang, 2013; Rayner, Timgren, Sjöö, & Dejmek, 2012; Song et al., 2015; Tan et al., 2012; Timgren, Rayner, Sjöö, & Dejmek, 2011). Despite the great advances in the development of food-grade Pickering emulsions, there are very limited examples of nanoemulsions: the main limitation is the particle size of the stabilizer, which should be considerably smaller than the droplet size to cover the surface. For example, if the nanoemulsion has a droplet size of 100 nm, the size of the stabilizer particles should be <10 nm in order to contribute enough particles at the interphase. Efforts in the development of Pickering nanoemulsions should be concentrated onto synthesized GRAS nanoparticles of less than 100 nm, and food-grade minerals, lipids, and polymeric nanocrystals profile themselves as promising candidates.

6.3 Polymeric nanoparticles in food processing

6.3.1 Definitions and classification of polymeric nanoparticles

Over the last decade, research on nanomaterials for food processing and packaging applications has increased significantly. Thus nanoencapsulation can solve key food challenges, such as the following: (1) masking flavors; (2) preventing degradation (e.g., oxidation) due to processing conditions such as mechanical stresses, heat, pressure, or chemical changes; (3) improving stability (thermodynamic and kinetic) of different compounds, facilitating their application; (4) increasing solubility and enhancing bioavailability due to the higher surface area; (5) controlling the release of active ingredients (e.g., micronutrients, antimicrobial compounds, antioxidants, vitamins, phytosterols); and (6) potentiating spatial ubication in specific food targets, etc.

Although there is not a universal nanoencapsulation system, polymeric nanoparticles represent the most studied and promising model of a nanomaterial in the food field (Brandelli, Brum, & dos Santos, 2017; dos Santos, Andrade, de, Flôres, & Rios, 2018; Sarkar, Irshaan, Sivapratha, & Choudhary, 2016; Squillaro, Cimini, Peluso, Giordano, & Melone, 2018). These systems have attracted the interest of the food sector as emerging applications that could provide innovative solutions for the challenges previously mentioned (Abaee, Mohammadian, & Jafari, 2017; Katouzian & Jafari, 2019; Taheri & Jafari, 2019). For example, it is possible to produce active edible coatings when active molecules are encapsulated in polymeric nanoparticles. In these formulations, the compound may be delivered or have its delivery extended or controlled, to create an on-demand microenvironment that improves the properties of foods (e.g., increasing shelf life or nutrimental value). Edible coatings are packing systems that are highly predisposed to incorporate polymeric nanoparticles, due to the chemical compatibility of the nanoparticle matrix or shell and the composition of edible coating support. This ensures that the compounds will be well-dispersed over the surface of treated food (Sarkar et al., 2016; Zambrano-Zaragoza and Quintanar-guerrero, 2019).

Polymeric nanoparticles are spherical colloidal structures containing bioactive molecules and macromolecular materials that measure between 10 and 1000 nm, typically 100–600 nm in diameter. Two types of polymeric nanoparticles can be described in terms of morphology and architecture: nanospheres and nanocapsules (Faridi Esfanjani & Jafari, 2016). Nanospheres are formed by a solid polymeric matrix, while nanocapsules are composed of an oil core surrounded by a polymeric membrane (Fig. 6.1A and B). In the case of nanospheres, the food-active molecule to be trapped can be adsorbed onto the surface or molecularly dispersed within the matrix. With nanocapsules, in contrast, the bioactive ingredient can be retained in an aqueous or oily core surrounded by a single thin polymeric wall (Galindo-Pérez, Quintanar-Guerrero, Cornejo-Villegas, & Zambrano-Zaragoza, 2018; Mendoza-Munoz, Quintanar-Guerrero, & Allemann, 2012; Zambrano-Zaragoza et al., 2018).

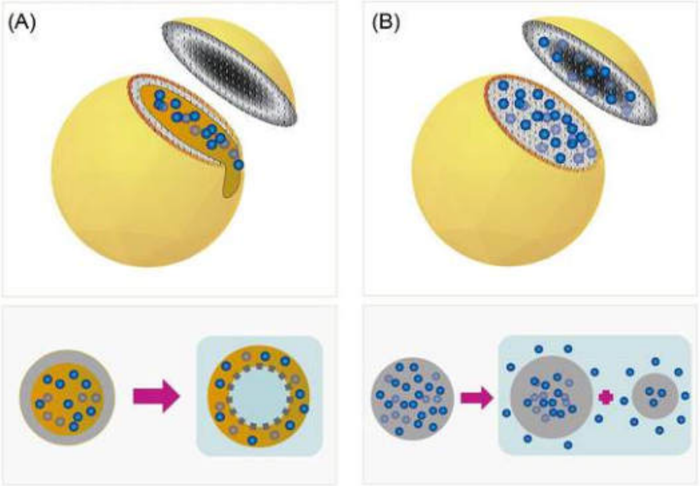

Figure 6.1

Currently, polymeric nanocapsules comprise the nanostructures most utilized in food development, due to their stability during storage, high efficiency in encapsulating active molecules, their central cavity avoiding direct contact of the active molecule with the external environment, and/or chemical reactions reducing toxicity. They also have easy, large-scale preparation, and allow controlled release and/or localization of the active molecules in specific regions of the food system, enhancing optimal bioactivity (dos Santos et al., 2018; Zambrano-Zaragoza & Quintanar-Guerrero, 2019).

6.3.2 Preparation methods of polymeric nanoparticles

In general, "milling" techniques are useful for preparing nanocrystals or other food pure nanomaterials of a material block, but not for submicronic systems with active delivery properties. Several techniques starting from "solutions" have been described in patents and research papers, beginning in the 1980s. These are reported as more suitable for obtaining polymeric nanoparticles for food purposes (Quintanar-Guerrero, De La, Zambrano-Zaragoza, Gutiérrez-Cortez, & Mendoza-Muñoz, 2012). They can be classified into the following: (1) in situ polymerization of dispersed monomers (for example, interfacial polymerization), and (2) dispersion of preformed polymers. Typically, methods based on preformed polymers are preferred due to their ease of implementation and lower potential toxicity. Thus polymeric nanoparticles prepared by polymerization can contain by-products that are not completely biocompatible, residues such as remaining monomers, oligomers, and catalysts that can be toxic, and the unlikelihood of cross-reactions with the bioactive ingredient.

Five methods with their modalities are reported to obtain polymeric nanoparticles from preformed polymers with food applications: (1) solvent displacement or nanoprecipitation; (2) coacervation including ionic gelation; (3) solvent evaporation including double emulsion; (4) emulsification diffusion and emulsification diffusion by direct solvent displacement, and (5) salting-out (Hu et al., 2019). Fig. 6.2 summarizes the processing steps of each method. Except for coacervation, all of these techniques are similar in that they involve an organic solution (typically the solvent phase), containing the nanoparticle components, and an aqueous solution (typically the nonsolvent phase), containing stabilizers that will constitute the

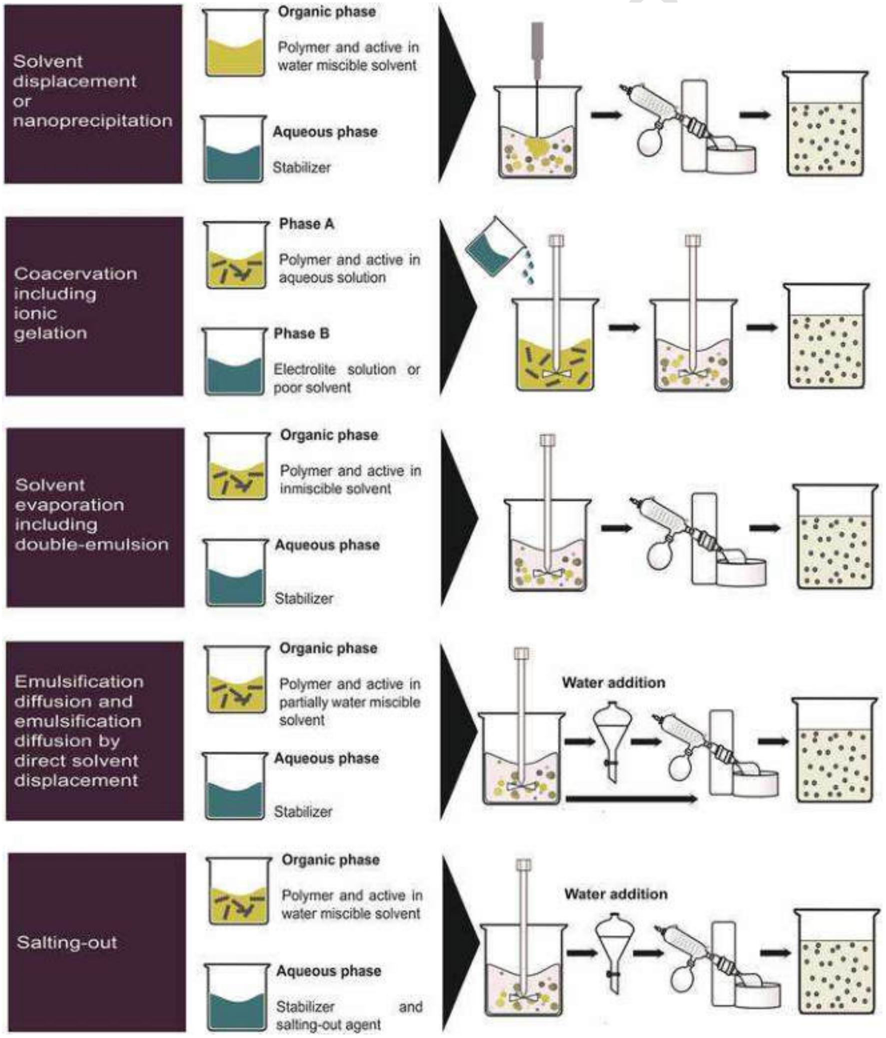

Figure 6.2

dispersion medium. These form an emulsion as a prior step to the formation of nanoparticle dispersion. Also, these methods require purification (e.g., reduced pressure, ultracentrifugation, dialysis, or cross-flow filtration) and drying operations (e.g., spray drying or freeze drying) to obtain a powder amenable to administration. One of the main problems with these techniques is the poor encapsulation of water-soluble materials, which separate from the organic phase into a continuous aqueous phase. A double emulsion (water/oil/water) technique can be employed to overcome this drawback (Mendoza-Munoz et al., 2012; Piñón-Segundo, Mendoza-Muñoz, & Quintanar-Guerrero, 2012).

Coacervation is a conventional chemical method used to form food microparticles, and at present, to prepare nanoparticles. Polymer solutions tend toward dehydration and phase separation by means of changes in conditions, such as the addition of an electrolyte (ionic gelation), pH, temperature, the addition of a nonsolvent, etc., producing polymer droplets in suspension. If this system is left to undergo separation, two liquid phases are observed: one concentrated colloidal phase, and another highly diluted phase. However, if the process is performed including a bioactive molecule and the particles are recovered before coacervation occurs, nanoparticles are obtained. A modality of coacervation is when two or more macromolecules opposite in charge are present. Coacervation is driven by electrostatic interactive forces (anion–cation interactions), this is referred to as complex coacervation, as shown in Fig. 6.3 (Brandelli et al., 2017; Zambrano-Zaragoza & Quintanar-guerrero, 2019).

Nano spray drying is a recent mechanical technique also used to prepare polymeric nanoparticles for food purposes (Arpagaus, Collenberg, Rütti, Assadpour, & Jafari, 2018). Spray drying is the transformation of feed from a fluid state into a dried particulate form by spraying the feed into a hot, drying medium. To obtain nanoscale particle modifications in the conventional spray dryer, the equipment

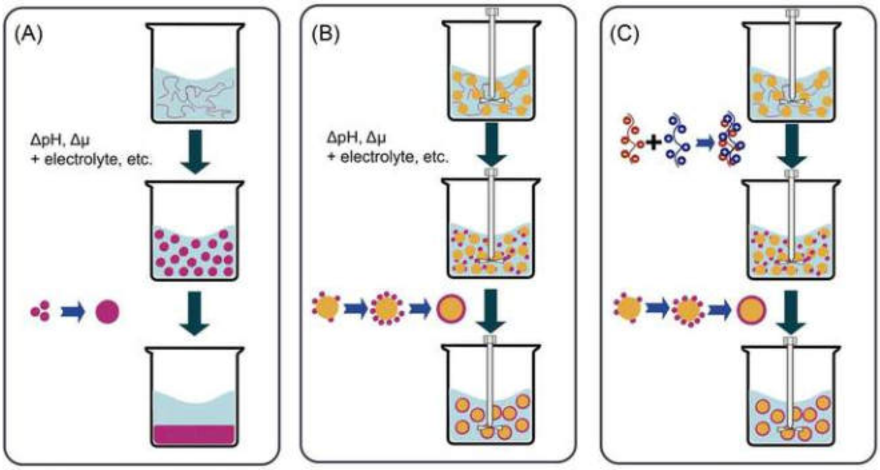

Figure 6.3

requires the following modifications (Assadpour & Jafari, 2019): (1) the atomizer (a piezoelectric-driven vibrating mesh atomizer is mounted to produce nanosize feed droplets); (2) the spray chamber (with vertical configuration to provide laminar air flow); and (3) product collection (by an electrostatic precipitator), depicted in Fig. 6.4. For this method, smooth-spherical particle morphology with particle diameters within the nanoscale range and homogeneous size distribution (SD) are obtained (Pérez-Masiá et al., 2015; Prasad Reddy, Padma Ishwarya, & Anandharamakrishnan, 2019).

The selection of a preparation technique needs to consider several aspects, such as the type of food application, the physicochemical characteristics of the bioactive to be encapsulated, food regulatory restrictions, and the desired physicochemical and morphological parameters of the polymeric nanoparticles (size, surface charge, hydrophilicity, controlled release time, etc.) (Mendoza-Munoz et al., 2012). Nonbiodegradable as well as biodegradable polymers from synthetic or natural sources have been widely investigated for different food applications, including coating, encapsulation, and packing. Their selection plays a key role in the most significant characteristics of the polymeric nanoparticles related to the active compound, for example, in the entrapment/encapsulation efficiency (EE) of active compound, release rate, degradation process, and protective ability, to name just a few. Because of their biocompatibility, biodegradable polymers are preferred for food applications, because they can be degraded into acceptable biocompatible products by chemical or enzymatic processes, they are free of immunogenicity, and their physicochemical properties are predictable and reproducible.

The most common biodegradable polymers are poly(alpha-hydroxy acids), poly(anhydrides), poly(ortho esters), poly(amino acids), chitosan, and alginates (Barbosa, Costa Lima, & Reis, 2019; dos Santos et al., 2018; Quintanar-Guerrero et al., 2012). It is noteworthy that all of the materials involved in a nanoencapsulation process need to be GRAS. Choice of the coating material depends on the physical properties and functionality of the encapsulated material. Probably of greatest importance in this regard is the selection of solvents with minimal toxicity and food

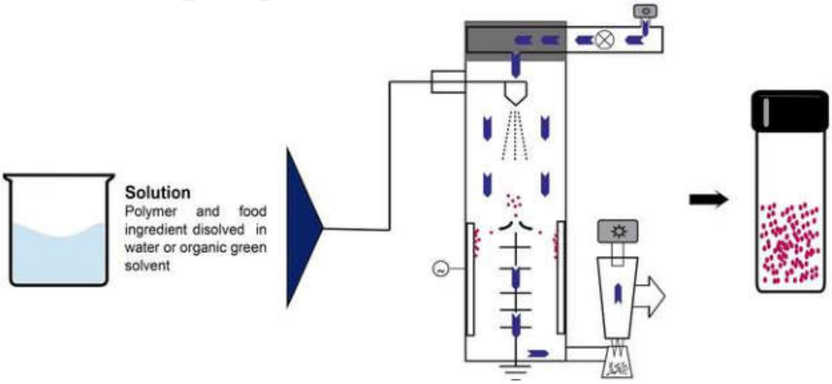

Figure 6.4

acceptability. This is an important issue in terms of considering a potential risk for human health and undesirable adverse effects on organoleptic food properties. Regardless of the polymeric nanoparticles drying process, the residual solvent needs to fall within acceptable food limits (Mendoza-Muñoz, Alcalá-Alcalá, & Quintanar-Guerrero, 2016; Piñón-Segundo et al., 2012; Zambrano-Zaragoza & Quintanar-Guerrero, 2019).

6.3.3 Characterization of polymeric nanoparticles

Polymeric nanoparticles can be used as dispersion or dry powder. In general, their characterization can include all types of conventionally measured properties such as organoleptic and textural characteristics, composition, rheology, densities, pH, water content, etc. Other techniques such as Fourier-transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), Raman spectroscopy (RS), and X-rays are performed to confirm a possible formation mechanism (e.g., ionic gelation), surface modification, or chemical cross-linking among functional groups (Fernández, González, & Parada, 2018; Hu et al., 2019). However, these properties are not sufficient to obtain real information of nanosystem behavior (e.g., stability and release behavior) and to acquire a better overall understanding of the relationship between food structures and polymeric nanoparticles (e.g., food application and product formulation). Thus more informative techniques based on nanometric analysis are required to define polymeric nanoparticle properties (Jafari & Esfanjani, 2017). Some common specific properties to be characterized are as follows:

1. MD, SD, and polydispersity index (PDI). These are the first properties evaluated in a polymeric nanoparticle after preparation to confirm submicronic size, dispersion homogeneity, and surface area. Particle-size parameters allow the selection of an adequate preparation method and are tools to optimize the preparative variables. During storage, an increase in particle size suggests physical instability (e.g., particle aggregation or bioactive crystallization). A narrow SD corresponds to particle uniformity in suspension. In contrast, PDI values higher than 0.5 indicate broad distribution and a distribution between 0.1 and 0.25 demonstrates a narrow SD. The PDI is estimated considering the particle mean size, the refractive index of the solvent, the measurement angle, and the variance of the distribution. Various commercial equipment based on different principles is available to determine mean diameter (MD) and SD, such as laser diffraction (LD), Dynamic light scattering (DLS) or quasielastic light scattering (QELS), surface area analysis (Bruneaur–Emmett–Teller, BET), and X-ray diffraction peak broadening. The most used among these is DLS or QELS, which permits the description of mean size, particle-SD, and polydispersity in a simple and rapid manner. The method consists of particle interaction with light (e.g., laser beam), generally at an observation angle of 90 degrees, and the calculation model is generally based on the equivalent sphere principle (dos Santos et al., 2018).
2. Zeta potential (Ψ_z). Ψ_z is the method most frequently utilized to determine the surface charge of particles in dispersion. Ψ_z is a criterion to predict particle stability in suspension. This parameter is influenced by nanoparticle composition (e.g., polymer type) and the materials (e.g., stabilizers and electrolytes) in the dispersion medium. Ψ_z may also be

applied to investigate whether a food bioactive ingredient is trapped in the polymeric nanoparticle or only adsorbed on its surface, and whether the components of the food substrate affect the surface charge. The actual technique to evaluate Ψ_z is based on the electrophoretic mobility that corresponds to the boundary of the surrounding liquid layer attached to the moving particles in the medium. Values higher than 30 mV (in absolute value) promote high stability and prevent particle aggregation (dos Santos et al., 2018).

3. Morphology. Direct visualization of polymeric nanoparticles enables the confirmation of particle size and statistical distribution, and also can show the form, architecture, surface characteristics, porosity, etc. Observation of nanostructures requires the use of techniques based on wavelengths (e.g., electron beams and lasers) much smaller than those of the photons (optical microscopy). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) are the techniques-of-choice to analyze the morphology of polymeric nanoparticles. SEM shows their surface in three dimensions after coating the sample with a metal (e.g., gold), whereas TEM reveals ultrastructure as well as wall thickness for nanocapsules and polymer porosity for nanospheres (Jafari, Esfanjani, Katouzian, & Assadpour, 2017). TEM analysis of nanoparticles is generally performed after the freeze-fracture of nanoparticles (Hu et al., 2019).
4. Loading capacity (LC), EE, and RP. The main purpose of a polymeric nanoparticle is to function as a platform that contains the bioactive in sufficient quantities to render it in effective amounts on the food substrate, while LC, EE, and RP are the parameters to evaluate this function. LC is the amount of the active ingredient loaded per unit weight of nanosized system indicating the mass percentage of the nanoparticle that is due to the encapsulated active ingredient [%LC=(Entrapped active/nanoparticle weight)×100]. EE is the percentage of active ingredient that is successfully entrapped within the nanoparticles [%EE=(bioactive added − bioactive unentrapped)/bioactive added×100]. Both are variable parameters dependent upon the physicochemical properties of the bioactive ingredient, fabrication process, and type of polymer and stabilizers used. Specifically, for nanocapsules, entrapment within the core is related to the solubility of active ingredient in the oily phase. If, during optimization, LC and EE are high, the quantity of active in nanoparticles required for a specific effect on a food can be reduced. LC and EE can be measured after preparation and separation of polymeric nanoparticles from the continuous phase. Some typical separation techniques include ultracentrifugation, size exclusion chromatography, ultrafiltration, or tangential filtration and dialysis. The quantification technique is linked to the chemical structure of active ingredient and UV-visible spectrometry, HPLC, and U-HPLC are frequently used (dos Santos et al., 2018; Uskokovic & Stevanovic, 2009).

   The RP provides critical information concerning the polymeric nanoparticles used to assess product safety and efficacy (Ganje, Jafari, Tamadon, Niakosari, & Maghsoudlou, 2019). This parameter also provides details on the release mechanism and kinetics, enabling a rational and scientific approach to product development. Release studies on food can be performed under different conditions (temperature, pH of the dissolution medium, stirring, containers, etc.) depending on the food properties, the process involved, and storage temperatures (dos Santos et al., 2018). The RP of polymeric nanoparticles is currently evaluated employing methods such as sample and separate (SS), continuous flow (CF), and dialysis membrane (DM), and novel techniques such as voltammetry and turbidimetry. Currently, the method most used is dialysis, which consists of the formation of a dialysis bag with a clip through which nanoparticles are added with release media and the bag is subsequently sealed. This sack is placed in a vessel containing sufficient release media to maintain sink conditions and agitated to minimize unstirred water-layer effects. Samples are taken with a replacement of fresh media at periodic intervals and the active ingredient is quantified by an analytical method to build the slope's released amount (M_t) versus time (t) (Pereira, Soares, Monteiro, Gomes, & Pintado, 2018).

5. Stability of polymeric nanoparticles. The stability can be performed determining the mean size and/or visible organoleptic changes under different conditions and time intervals. Recently, different equipment (e.g., Turbiscan) based on multiple light scattering (MLS) has been proposed to detect the destabilization phenomena of diluted and concentrated dispersions at a very early stage (González-Reza, Quintanar-Guerrero, Del Real-López, Piñon-Segundo, & Zambrano-Zaragoza, 2018b). MLS equipment detects the intensity of both transmitted and backscattered light over the whole cell height. These intensities permit direct monitoring of local physical heterogeneities with vertical resolution down to 20 μm. Thus nascent destabilization phenomena can be detected and monitored over time at different intervals (Formulation Smart Scientific Analysis, n.d.).

6.3.4 Mechanism of active delivery by polymeric nanoparticles

One important tool for designing a food-active formulation and as an experimental verification of a release mechanism is to predict the release of active ingredient as a function of time using mathematical models (Assadpour, Jafari, & Maghsoudlou, 2017; dos Santos et al., 2018). Thus to identify a particular release mechanism, it is necessary to obtain experimental data of statistical significance and to find the mathematical model with best correlation on considering the physical characteristics of the system and the properties of the release system; in this case of the food environment and the characteristics of nanoparticles (Siepmann & Peppas, 2011). In the food field, there are few studies that address this issue. Release models are generally based on diffusion equations. Diffusion is highly dependent on the properties of the material that constitutes the release platform and the morphology and architecture of the system. In the case of encapsulated active molecules in biodegradable polymers, release depends on polymer type, structure (nanosphers or nancapsules), quantity of active loading, and loading method. Considering the large specific area of polymeric nanoparticles, it is expected that the release rate will be more rapid than that of other food-release systems (e.g., microparticles or coatings). Thus polymeric nanoparticles are not recommended for long active-RPs.

Although the architecture of nanospheres and nanocapsules can correspond to matrix and capsular systems, respectively (Fig. 6.1A and B), their release mechanism does not correlate with these models. In general, when the active ingredient is absorbed on the surface of nanoparticles, release is practically immediate when the system comes into contact with the food media by a simple partitioning process. When the active ingredient is encapsulated within the nanosphere matrix, diffusion into the surrounding food environment prevails. When the nanosphere is formed by a biodegradable polymer, diffusion and erosion will be involved (Sarkar et al., 2017) (see Fig. 6.1B, box below). Korsmeyer–Peppas semiempirical model can be employed to determine the release mechanism (Fickian or non-Fickian) and release type (time dependence, t^n):

$$M_t/M_\infty = k \times t^n \tag{6.1}$$

where M_t/M_∞ is the fraction of bioactive released at time t, k is the kinetic rate constant, and n is the release exponent characterizing the different release mechanisms. In their logarithmic form:

$$\log\left(M_t/M_\infty\right)\infty = n \log t + \log k \tag{6.2}$$

The exponential n can be obtained from the slope of the graphics of log (M_t/M_∞) versus log t. Then, when n=0.5, release kinetics follow Fickian diffusion. The Higuchi equation can be applied in this case, suggesting matrix-like behavior. For n<0.5, the release mechanism is non-Fickian, meaning that both diffusion and degradation occurred together. For 0.5<n>1.0 refers to an anomalous transport mechanism. Finally, a value of n=1.0 correlates with zero-order kinetics (Biswal & Saha, 2019).

In contrast, the release of active ingredient from nanocapsules with an oily core is related to instantaneous partition processes found within immiscible phases if the food is rich in water, or dissolution if the food is of a lipophilic nature. The membrane wall of nanocapsules practically does not control the release; thus zero-order kinetics are not observed (see Fig. 6.1A, box below). Our group has found that nanocapsules incorporated into coatings fit better to the Higuchi model (Zambrano-Zaragoza, Quintanar-Guerrero, Del Real, Piñon-Segundo, & Zambrano-Zaragoza, 2017). The Higuchi equation was utilized to quantify active release from thin ointment films, containing a finely dispersed active ingredient into perfect sink conditions. Based on a pseudo-steady approach, direct proportionality between the cumulative amount of the active ingredient released and the square root of time (M_t=$K_H t^{1/2}$) can be demonstrated in a physically realistic meaning. Thus when the nanocapsules are dispersed in a coating film, the release behavior is explained as a matrix system similar to that obtained with the Higuchi model (Siepmann & Peppas, 2011).

Bioactive leakage from nanocapsules has been reduced by additional coatings (e.g., PEG, phospholipids). Recently, polymer nanocomposites, hybrid nanoparticles, and stimuli-response polymeric nanoparticles have been proposed for new functional food applications (e.g., antibacterial packaging and oral bioactive delivery) (González, Olmos, Lorente, Vélaz, & González-Benito, 2018; Wang, Bae, Lee, & Luo, 2018).

6.3.5 Application of polymeric nanoparticles in food processing

Polymeric nanoparticles possess many advantages in relation to other nanosized systems. Using polymers makes it possible to achieve higher efficiency of encapsulation, LC, and the controlled release of functional ingredients. In addition, thermolabile, light, and oxygen-sensitive substances can be used during processing, the selection of polymers used, being important in the preparation of these nanoparticles. It is possible to have polymers with high glass transition temperatures, as in the case of polysaccharide matrices, which allow the achievement of stable ingredients during thermal processing, and subsequently, the release of substances during storage because of the modification of structural polymers by mechanisms of erosion, degradation, or solubilization due to moisture content, pH, and ionic charge. These exert beneficial effects that promote the increased shelf life of food products (Ubbink, 2016). It is also possible that, at the time of application in the food matrix, polymeric nanoparticles decrease their ionic charge, destabilizing the system and modifying the Ψ_z, thus releasing the total content. Therefore it is important to consider the superficial charges for better control of release in the functional ingredient (Cano-Sarmiento et al., 2018).

Another important aspect to consider in nanoparticle preparation for use as an ingredient in food processing is the pH and ionic strength, since modification of the latter results in structural changes in the components of food or of the phase separation, in yogurts, beverages, and fruit concentrates. In addition, kinetics of release are dependent on pH, soluble solids, and temperature (González-Reza et al., 2018b). Some studies consider the preparation of nanoparticles using anionic and cationic polysaccharides in the release kinetics of curcumin, using fucoidan as an anionic polysaccharide and chitosan as a cationic polysaccharide, observing variations in Ψ_z due to the fucoidan:chitosan ratio and showing that Ψ_z was negative at pH=7 and 7.4, with values of −18 and −14 mV, respectively, while at pH=6, zeta potential was minimal and negative equal to −4 mV. This was due to the deionization of ammonium ions, which gives rise to a rapid disintegration of the biopolymer and rapid release of curcumin, while at pH=4 and 7, there was a slower release of curcumin in comparison with nonencapsulated systems, being useful in release control in the digestive tract and in food with different pH values (Barbosa et al., 2019). However, according to the pH of foods, it would also be important to take this into account for the release of substances during storage or the release of flavors or aromas during consumption of the product. Many hydrocolloids are employed as natural polymers to prepare nanocapsules, because their nanometric size increases their capacity to absorb water, serving as texture modifiers, thickeners, and gelling agents, among others (Li & Nie, 2016). Other major possibilities that demonstrate polymeric nanoparticles as ingredients for food formulation include greater thermal resistance; inorganic materials can be utilized, such as nanoclays. In addition, these materials also allow for better release control due to the increase of nanostructure tortuosity (Aliofkhazraei, 2015).

Lipophilic antioxidant encapsulation is also important to decrease the oxidation of oils; the latter would quickly lose their antioxidant capacity because, in general, they are sensitive to oxygen, light, pressure, temperature, and other processing conditions, such as the use of biodegradable natural polymers or synthetic polymers for trapping or encapsulating ingredients in nanosize, limiting the loss of active ingredients during processing. In addition, it is possible to have controlled release during storage. Thus in the preparation of ethyl cellulose nanoparticles with

ϒ-oryzanol (a mixture of sterols and ferulic acid) stabilized with polyvinyl alcohol, an increase was found in load capacity, and greater thermal resistance and better control release were also achieved. Therefore on being more stable, it is possible to use this in beverages and oil stabilization, even when the oils are heated for frying and the oil remains at high temperatures (Ghaderi, Ghanbarzadeh, Mohammadhassani, & Hamishehkar, 2014).

Epigallocatechin gallate, a powerful antioxidant, was nanoencapsulated in a mixture of zein/chitosan to achieve controlled release in food systems, showing that electrostatic interactions and hydrogen bonds are responsible for nanoparticle formation; the interaction of nanoparticles among nanosystems improved EE (65%–80%), with Ψ_z positive from 21.2 at 34.9 mV, an important consideration in the release of antioxidant substances into food products. Therefore epigallocatechin gallate nanoencapsulated in zein/chitosan can be used for the protection of foods rich in fats, such as ice cream and margarines (Liang et al., 2017).

Polymeric nanoparticles are important in encapsulation of colorants since, at present, natural colorants are preferred by the consumer (Mahdavee Khazaei, Jafari, Ghorbani, & Hemmati Kakhki, 2014; Mahdavi, Jafari, Ghorbani, & Assadpoor, 2014). These are sensitive to light, oxygen, temperature, pH, and ionic strength. The use of polymers and the nanosize structure entertains great advantages in the preparation of systems loaded with coloring substances, such as carotenoids, flavonoids, anthocyanins, and other natural pigments. Polymeric nanoparticles represent an option for protecting colorants during processing, reconstituting the natural color lost during processing and, especially, for the development of attractive products (Almeida et al., 2018; González-Reza et al., 2018). Encapsulation of colorants also has the objective of increasing solubility and facilitating incorporation into food matrices. Colorant nanoencapsulation increases the solubility of these and facilitates their incorporation into food matrices. Among the colors that have been most nanoencapsulated in polymeric structures, we find the carotenoids, in that these are widely employed in the dairy industry, in the preparation of functional beverages, and in the development of products with health benefits (González-Reza et al., 2018b; Rao & McClements, 2012; Rostamabadi et al., 2019a).

6.3.6 Effect of polymeric nanoparticles on physicochemical properties of food during storage

Polymeric nanoparticles are preferred in the development of new products in which stability, easy incorporation, and compatibility are important, because these encapsulation processes also allow obtaining ingredients in powder form, which facilitates the formulation and processing of foods and beverages. Polymeric nanoparticles possess important characteristics that define the compatibility between the foods and components of nanosize systems. Thus the Ψ_z and pH effects, as well as the surface composition of the food, must be taken into account in order to allow for adhesion and chemical compatibility with polymeric nanoparticles and the release of active ingredient (Liang et al., 2017; Weiss et al., 2006). Food products are developed at different pH values, solid content, and water activity; therefore a large number of polymeric nanoparticles can respond to the pH, surface charge, osmolarity, and water content. For example, in the nanoencapsulation of epigallocatechin gallate with zein/chitosan utilized to release this antioxidant into food, changes in antioxidant capacity in relation to zein concentration (72–288 mg) were evaluated, revealing that a high concentration had a positive Ψ_z between 21 and 35 mV. However, this has a limit, since, at a concentration of 288 mg, Ψ_z decreased slightly, finding that Ψ_z is also influenced by the concentration of epigallocatechin gallate; when increased to 8 mg, the Ψ_z decreased, in turn decreasing the rate of release of the active ingredient into the food. Therefore physicochemical analysis suggested that electrostatic interaction was the main factor in nanoparticle preparation, and this will be a relevant factor when it is incorporated into a food (Liang et al., 2017).

Polymeric nanoparticles have a potential use in beverage and semisolid foods, in which a homogeneous distribution of antioxidant and natural colorants is necessary, considering a sensorial balance in the nucleus of the food. The main physical properties of polymeric nanoparticles include modification of viscosity, density, and light dispersion, permitting the development of stable and attractive products for the consumer. However, the physicochemical properties of the food and beverages formulated with nanoparticles as ingredients can vary considerably during storage, depending on the polymer used in the preparation of nanostructures and the composition in terms of pH, soluble solids, proteins, lipids, and water content of the food. For example, when poly-ε-caprolactone, a biodegradable synthetic polymer, was employed, a slight acidification of the product was observed, due to polymer degradation, which in turn can contribute to the modification of other components in the food, producing color degradation (González-Reza et al., 2018b).

The physicochemical properties of beverages and other functional foods are affected by the type of polymer used in the preparation of nanoparticles, such as polysaccharides, proteins, and their modified structures, as well as synthetic biodegradable polymers. When proteins are utilized, it is necessary to consider different parameters, which will exert an influence on the stability of nanostructures, therefore on the matrix of food that is applied. In this way, the factors to be considered include functional groups, molecular mass, pH, dissolution grade, and cross-linking of food, as well as sensitivity to the temperature during storage time, since these properties will exert an influence on the strength of nanoparticles and the release of functional ingredients in such a way that beneficial changes in the food are produced for maintaining viscosity, color, and general food stability (Saxena, Sachin, Bohidar, & Verma, 2005). Modifications associated with proteins such as casein, gelatin and zein, are widely used in nanoparticles, such as in the shell or matrix during nanoencapsulation of food ingredients, that interact with lipids, proteins, carbohydrates, and other components of foods, producing stability only for some time. This is because the stabilization of these systems are functions of the hydrogen and amino bridges, which are clearly modified by the effect of pH, temperature, and water content. Therefore the physicochemical changes expected during storage will comprise the phase precipitation and separation, syneresis, color changes, and the loss of sensorial quality. The majority of studies carried out have focused on the simulated stabilization of polymeric nanoparticles. Thus it will be necessary to conduct studies on potential nanoparticle–food interactions in relation to final application and function during storage.

Polysaccharides represent other polymers that are employed in the preparation of nanoparticles. The most likely interactions with food will be hydrogen bonds, with the hydroxyl group (Kilburn, Claude, Schweizer, Alam, & Ubbink, 2005), the factor that will exert the greatest effect on the behavior of incorporated nanoparticles, as ingredients in the nuclei of food. Water will cause changes in viscosity, and thus in the rheological behavior of the food, increasing the release of substances during the storage step.

6.4 Nanofibers, nanolaminates, and nanocrystals

6.4.1 Preparation methods

6.4.1.1 Nanofibers

Nanofibers are traditionally produced by electrospinning, a technique used since 1934 for the manufacture of continuous fibers [mainly of polymers, but also with ceramic compounds (Dai, 2016)] with a diameter of nano- to micrometers. A controlled mesh deriving from the nanosize usually offers better mechanical properties, and the high surface area allows the adhesion or release of active ingredients with unique properties (Torres-Giner, 2011). Electrospinning for nanofibers is based on an electrical charge for drawing fibers from a conductive liquid (Rezaei, Nasirpour, & Fathi, 2015). The voltage is gradually increased and, when a sufficient electric charge is achieved on the tip of the syringe and the conductive liquid, the force of electrostatic repulsion exceeds the force of surface tension (Dai, 2016). Then, the droplet is stretched, with a critical point reached where the repulsion force exceeds the surface tension, and a liquid propulsion is released from the surface, creating a conical shape: the Taylor cone. The jet tip is directed toward the opposite electrode where the collector is located. The jet dries during the propulsion (Rezaei et al., 2015). There is a strong relationship among the parameters of the electric field, physical and chemical conditions of the polymer, and the conductive liquid. Fig. 6.5 shows the electrospinning process used to obtain nanofibers.

It is possible to obtain different diameters, lengths, morphologies, and framework types. Some of the polymers widely used in food include poly-ε-caprolactone, poly(L-lactic acid), polyvinyl pyrrolidone, cellulose acetate, casein, soy protein, chitosan, and collagen (Rostami, Yousefi, Khezerlou, Aman Mohammadi, & Jafari, 2019). The main applications in the food area are the packaging and encapsulation of active ingredients. In packaging materials, applications consist of the release of antimicrobial compounds, in some cases for antioxidant applications (Torres-Giner, 2011), and the use nanofibers for enzyme immobilization for a reaction surface with

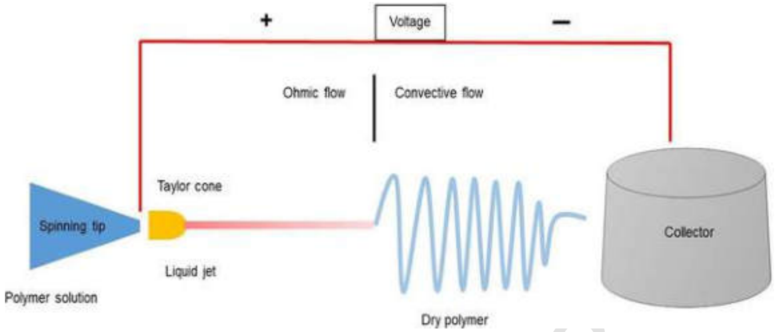

Figure 6.5

food ingredients. This method permits increased stability and higher activity. At present, there are instruments for industrial production of nanofibers that permit obtaining fibers with a length of up to 1.6 m and a capacity of 40 million square meters of coated material annually in a single production line (Tekmen & Engineering, 2014).

6.4.1.2 Nanolaminates

Nanolaminates for food applications are usually produced as thin polymer films formed by the alternating physisorption of polyanions and polycations, by means of the layer-by-layer (LbL) technique. The incorporation of nanolaminates allows nearly precise control of the thickness of the multilayer (nm), which is easily moldable to any food surface, and one of its greatest attractions is the incorporation of active ingredients (Arnon-Rips & Poverenov, 2018). Nanolaminates fabricated by means of the LbL technique require an electrically charged surface and involve immersion in different polyelectrolyte solutions, followed by a wash after each deposition. For this reason, the multilayer formation of nanolaminates by LbL is driven by electrostatic interactions, which are the main driving forces (Klitzing, 2006). This sequential follow-up has been commonly observed in several reports on food physisorption and where the Ψ_z changes sign and magnitude. Inversion of the electric charge in some substrates is not necessary, and slight changes in the Ψ_z may be sufficient for the formation of the multilayer (Klitzing, 2006). The formation of each layer will depend on the interaction of two polyelectrolytes. In consecutive layers, the substrate layer in turn will depend on the previous interaction. For example, in a nanolaminate LbL comprising alginate–chitosan–alginate–chitosan–alginate, the interaction of first and second alginate layer will entertain a different potential. A classic method of nanolaminate deposition on a fruit is that followed by Medeiros et al. in the edible coating of pectin/chitosan mangoes. The mango was washed with water and left to dry. After this, the mango was immersed in pectin solution (pH=7.0) for 15 minutes, rinsed with distilled water with pH=7, and dried with a nitrogen flow. Afterward, the same mango was immersed in the chitosan solution at pH=3 for 15 minutes, rinsed with distilled water with pH=3, and dried with nitrogen flow (Bartolomeu, Pinheiro, Carneiro-Da-Cunha, & Vicente, 2012). Generally, the number of nanolaminates deposited is five.

6.4.1.3 Nanocrystals

Nanocrystals are nanosize active ingredient particles that are stabilized by surfactants, polymers, or a mixture of both (Lin, Huang, & Dufresne, 2012). This concept implies a dispersed system of crystalline or partially crystalline particles (Habibi, Lucia, & Rojas, 2010). When there is a change from a crystalline into an amorphous state, the final formulation, these are denominated amorphous nanoparticles. Sometimes the change into the amorphous and the nanosize state can be combined to favor the process of dissolving active ingredients (Patel, Sharma, & Mehta, 2018). The nanocrystal concept also refers to a system with high bioactive loading (nearly 100%), unlike other nanoencapsulated systems in which the active ingredient depends on the composition of the main matrix. Another advantage of nanocrystals is the increase in apparent saturation solubility, a property dependent on size. Nanocrystals, like other colloidal systems, have a high Gibb's free energy; therefore the addition of stabilizers that possess a charge repulsion mechanism or steric phenomena is necessary (Patel et al., 2018). Nanocrystals can be produced in two ways; bottom-up and top-down. The bottom-up method is based on particles obtained from a molecular solution into nanoparticle size; taking advantage of the classical precipitation process, the active ingredient dissolved in a solvent is added to a nonsolvent (Malamatari, Taylor, Malamataris, Douroumis, & Kachrimanis, 2018). Some variants of the classical method may include sonication, ultrasound, multiinlet vortex, supercritical fluids, and evaporative precipitation. Some of the main parameters studied are type of solvent, type of nonsolvent, proportion of both solutions, proportion of the bioactive, type and concentration of stabilizer, type and speed of agitation, and reactor, among others. With the bottom-up method, there is greater control in the size of nanocrystals and in particle-SD, while with top-down methods, the process starts with large-size crystals that decrease to a small size. The most common methods include wet-milling, microfluidization, and high-pressure homogenization (Malamatari et al., 2018). In the latter two, a stabilizing agent is used to maintain the size of the nanocrystals. Energy consumption is greater by means of this modality, and less control is observed in the size and distribution, however, high bioactive loading is obtained.

6.4.2 Use of nanolaminates in edible coating materials

Edible coatings are intended to maximize sensorial parameters and shelf life by control of moisture transfer, gas exchange, or oxidation processes (Dhall, 2013). Edible coatings have a long history in food with the participation of wax coatings to control the transpiration of water in lemons and oranges. Edible coatings must withstand the internal changes of the food and maintain resistance against various environmental parameters such as temperature and humidity. One of the most attractive applications of edible coatings is the possible incorporation of various active ingredients into the coating (Vahedikia et al., 2019). Some examples can be antimicrobials, antioxidants, nutraceuticals, antibrowning agents, colorants, and flavors (Dhall, 2013). Edible coatings are traditionally made up of polysaccharides (cellulose, starch, gums, and chitosan), proteins (casein, whey protein, collagen, gelatin, keratin, wheat gluten, soy protein, peanut protein, corn-zein, and cotton seed protein), lipids (waxes, oils, fatty acids, monoglycerides, resins, and preparations with emulsions), or combinations of these or derivatized products (Dhall, 2013). Lipid composition is the most attractive of these due to the hydrophobic nature of lipids and their greater ability to regulate water loss. Edible coatings are usually applied to some fresh fruits and vegetables, while for meat, these are generally in the packaging material.

Edible coatings are also represented as edible nanolaminates, constructed as very thin coatings of food-grade materials such as polysaccharides, proteins, or combinations with lipids. Nanolaminates used as edible coatings are generally prepared by means of LbL procedures, as described in the previous section. The addition of multiple layers is controlled by opposing electrical charges from a defined substrate, and with different repetitions of the immersion of substrate into coating solutions. The LbL procedure is also referred to as an electrodeposition technique (Fig. 6.6) that allows for adequate adhesion onto hydrophilic surfaces, offering minimal processing of fruits and vegetables.

As noted for edible coatings, it is possible to incorporate active ingredients into the thin layers (Shit & Shah, 2014), even combining different active ingredients into each layer. For example, in an ideal case, among the multilayers, proceeding from the center to the outside, we would first find an antibrowning layer, and after this, the antioxidant, antimicrobial, colorant, and flavoring layers. Acevedo-Fani, Soliva-Fortuny, and Martín-Belloso (2018) prepared LbL folic acid-loaded nanolaminated films from an alginate/chitosan composition. These authors used PET sheets and positively charged quartz slides. After this, LbL buildup was performed by

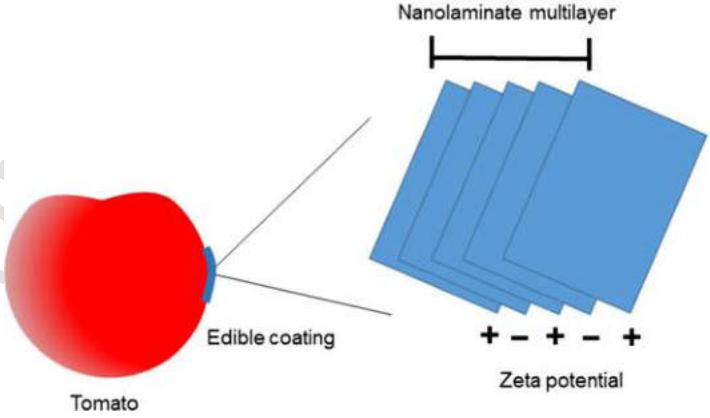

Figure 6.6

immersion in an anionic alginate solution. The washes were required for better adhesion of the next thin layer; subsequently, formation of the nanolaminate was continued by immersion in cationic chitosan solutions. A total of 20 layers were deposited on the initial substrate. Some critical factors included wash times, immersion times, and concentrations of the anionic and cationic solutions. In this study, the authors added hydrophilic active ingredients through the postdiffusion method. It is expected that, by means of this procedure, the folic acid is loaded within the nanolaminates by diffusion and immobilization in the binding sites inside the structure. The authors demonstrated an incorporation of 70 μg folic acid for each cm^2. With this procedure, folic acid maintained its adequate stability under exposure to UV light exposure.

In another study, Brasil, Gomes, Puerta-Gomez, Castell-Perez, and Moreira (2012) prepared an edible nanolaminate coating of chitosan/pectin with trans-cinnamaldehyde as an antimicrobial encapsulated in β-cyclodextrin. The preparation was applied onto fresh-cut papaya. Prepared in this fashion, papaya accrued greater acceptance by the food-tasting panelists and was characterized by maintaining its color and texture. Edible coatings by means of nanolaminating extended the shelf life of fresh-cut papaya up to 15 days at 4°C; without the coating, the shelf life was <7 days. Interestingly, the authors mention the influence of fruit packaging on the functionality of edible nanolaminate coating. While nanolamination confers adequate protection, traditional robust packaging is always a guarantee of additional protection; in this study, it was demonstrated by the use of Ziploc packaging (Brasil et al., 2012). On the other hand, Medeiros et al. (2014) prepared an edible nanolaminated coating of alginate/lysozyme on “Coalho” cheese shelf life. The nanolaminate was obtained by LbL methodology, and five alternate layers of alginate and lysozyme were deposited onto the “Coalho” cheese. To monitor the mechanism of basic formation of nanolaminates by the attraction of electrical charges, control of the pH was an important factor in the procedure. The authors confirmed deposition of nanolaminates by UV-vis spectroscopy, contact angle, morphology by SEM, and gas barrier properties. The shelf life of cheese was prolonged by the combined factors of gas barrier and antibacterial action (Medeiros et al., 2014).

In the same manner, Chiou et al. (2018) prepared edible nanolaminate coatings by means of an LbL technique of chitosan/alginate applied to fruit bars enriched with ascorbic acid. The fruit conserved a high content of ascorbic acid, antioxidant capacity, firmness, and fungal-growth prevention for 6 additional days, and high shelf life. Nanolamination did not prevent the browning phenomenon. Interestingly, the authors evaluated the performance of two types of chitosan according to their sources of origin: animal and vegetable. The results revealed that there were no important differences according to the chitosan type in the performance of nanolaminate. On the other hand, Bartolomeu et al. (2012) obtained pectin/chitosan nanolaminates by means of LbL for application on “Tommy Atkins” mangoes. The authors noted that a basic tool for determining the formation of the nanomultilayer was the change in contact angle. The novel edible coating produced conservation of up to 45 days with adequate sensory properties. As in other studies, the authors of this research employed the in vitro method of nanolaminate deposition onto a transparent PET film that was first aminolyzed/charged to evaluate water vapor, oxygen, and carbon dioxide permeabilities. Afterward, the aminolyzed PET was positively charged with HCl to attach pectin, then washed, and chitosan was subsequently applied. A total of five nanolaminates were deposited. In general, the nanolaminate reduced gas flow, mass loss, and total soluble solids, and presented higher titratable acidity (Bartolomeu et al., 2012). In a similar manner, Salas-Méndez et al. (2019) prepared edible nanolaminate coatings with antimicrobial applications by means of *Flourensia cernua* extract loaded to extend the shelf life of tomato. The authors applied five alternating films of alginate/chitosan nanolaminates. Formation of the coating was also demonstrated by the changes in contact angle. In general, the tomato controlled gas exchange, reduced weight loss, and extended shelf life (Salas-Méndez et al., 2019).

6.4.3 Physicochemical, textural, and color changes in nanocoated foods

Due to the increase in the demand for minimally processed foods and preferably those with health benefits, in recent years there has been a great interest in the development of edible coatings. The functionality of these coatings has clearly been improved when nanolaminated coatings are utilized in order to preserve the microbiological, physicochemical, and sensory quality of fresh foods such as fruits, vegetables, and ready-to-eat products, as well as meat and fish. Generally, nanocoating considers the use of lipophilics or hydrophilics of natural origin with a function as antimicrobials and antioxidants, which depends on the nanocoating-food interaction to fulfill the function of efficient food preservation. The functionality of these nanostructures incorporated into the polysaccharide or the protein matrix is attributable to their homogeneous distribution on the food surface, regulating gas exchange, and the release of compounds trapped inside the matrix. This has been shown in nanocoatings prepared with SLNs supported by xanthan gum, demonstrating that these contribute to reducing physiological weight loss as well as to textural changes by decreasing the activity of pectin methylesterases. In addition, they exerted an effect on phenol metabolism, in that they clearly modified the maturation process. Another effect of nanocoatings is their distribution in the pericarp, similar to the distribution of natural waxes in the fresh product, demonstrating the functionality of these when used in the nanometric size (García-Betanzos et al., 2017).

It is important to highlight that for the physicochemical modifications to the food, the use of the nanosize systems used for coatings must take into consideration the following: (1) type of oil and interaction with the product; (2) amount of oil used in the nanostructured system; (3) type of surfactant used; (4) oil used as dissolvent of active substance; (5) pH at which it will be applied; (6) antimicrobial activity of coating including all components; and (7) degree of processing. All of these are associated with physicochemical, textural, and color changes. Next, a brief summary will be presented on the effect of edible nanocoatings applied as functional ingredients during minimal treatments carried out on fruits, meats, and cheeses, with the purpose of highlighting their effectiveness in the increase of shelf life. We will describe the effect of nanosize systems on the physicochemical, textural, and color parameters in these foods.

6.4.3.1 Effect of nanocoatings on the physicochemical properties of food

Nanocoatings have the purpose of maintaining the physicochemical composition of minimally processed products as long as possible without significant variations. Changes in composition, such as humidity, protein and fat content, pH, and acidity index, are important in products of animal origin, while in the case of vegetable products, there will be important changes in pH, weight loss, leakage loss, titratable acidity, and soluble solids. There are currently some studies that consider the use of different types of coatings incorporated into nanosize systems, where it has been shown that their use considerably reduces physicochemical variations and that changes in pH and ionic strength are associated with the polymer type.

Nanoemulsions are the systems most used in the preparation of edible coatings. The apple has been one of the models used to evaluate these coatings, and it has been found that apples manage to significantly reduce cellular oxidative stress, contributing to the maintenance of its physicochemical characteristics (Salvia-Trujillo, Soliva-Fortuny, Rojas-Graü, McClements, & Martín-Belloso, 2017; Zambrano-Zaragoza, Gutiérrez-Cortez, et al., 2014a; Zambrano-Zaragoza, Mercado-Silv et al., 2014b). Nanoemulsions have been used in chicken, meat, and cheese preservation as edible coatings, considering the antioxidant capacity of essential oils and the possibility of decreasing the concentration of these when used as nanoingredients and increases in superficial area. The latter reveals that the type of stabilizer, superficial charge, or the film-forming dispersion are important factors to take into account (Abdou, Galhoum, & Mohamed, 2018; Zambrano-Zaragoza et al., 2018).

Other nanosize systems that have been used in the preparation of coatings include SLNs, which have exhibited a different effect on the physicochemical properties, depending on their concentration in the coating. In the conservation of fresh-cut guava, SLNs prepared with candeuba wax were employed, demonstrating that, at 50 g/L of nanoparticle dispersion, there is a control in the changes of pH and °Bx (González-Reza, Pérez-Olivier, Miranda-Linares, & Zambrano-Zaragoza, 2018a). SLNs have been utilized in the conservation of tomatoes to decrease their ripening rate and to increase their shelf life for 26 days at 12°C, which clearly reduced the changes in pH, °Bx, and weight loss (Miranda-Linares, Escamilla-Rendón, Del Real-López, González-Reza, & Zambrano-Zaragoza, 2018).

Polymeric nanoparticles have also been used in edible coatings for the conservation of fresh-cut fruits and vegetables, fish, meat, and other minimally processed foods. The natural polymers that have been employed are mainly chitosan, alginate, and synthetic polymers such as ethyl cellulose and poly-ε-caprolactone. Their effects on physicochemical properties depend on particle size, composition, and antimicrobial and antioxidant capacity. For example, in coatings based on chitosan nanoparticles, analyzing the effect of particle sizes between 400 and 800 nm on tomatoes stored under refrigeration determined that weight loss was lower in emulsified chitosan than in the chitosan nanoparticulate edible coating. However, there were no statistically significant differences in the trend or behavior (Mustafa, Ali, & Manickam, 2013).

6.4.3.2 Effect of nanocoatings on textural changes

Many changes associated with the quality of foods are related to textural changes, including enzymatic, microbial, and respiratory activity and/or oxygen absorption, which produce drastic changes in palatability, firmness, shear, and compression resistance. An alternative that aids in preserving textural parameters for as long as possible are edible coatings. Many polysaccharides and proteins have been tested as a base for coatings, demonstrating that these are effective as ingredients of film-forming dispersion to preserve the texture of foods (Shit & Shah, 2014; Yilmaz et al., 2016). However, in recent years, nanosize systems have been an alternative sought to add active substances with an antioxidant and antimicrobial capacity for foods with a positive effect on texture. Control of texture during storage is dependent on polymers used in nanoparticle coating formation since these have different action modes in the function of tissue and origin of food. Chitosan can be polymerized by endogenous enzymes that could include the participation of hydrophobic interactions, hydrogen bonding, and electrostatic interactions (Wang et al., 2015). Table 6.3 summarizes some applications of nanosize systems in foods and the effect on texture of products.

6.4.3.3 Effect of nanocoatings on color changes associated with shelf life

Color represents one of the most important factors for the acceptance of a food. It is for this reason that the effect of nanosize systems has been studied in terms of color changes during the storage of different foods. With regard to nanoemulsions and nanocapsules incorporated into polymeric matrices, one of the first studies with nanoemulsions applied to the conservation of fresh-cut fruits was the application of α-tocopherol nanoemulsions incorporated into nopal mucilage matrix. In this study, the effect of lipophilic antioxidant on inhibition of browning index was investigated in relation to the polyphenol oxidase activity in the fresh-cut apple. It revealed that this treatment was effective in the inhibition of browning, increasing the apple shelf life by 21 days at 4°C. In this case, particle size exerted a significant effect, which was attributable to interaction with cellular components being more effective at a smaller particle size (Zambrano-Zaragoza, Gutiérrez-Cortez, et al., 2014a; Zambrano-Zaragoza, Mercado-Silv et al., 2014b). In another study carried out on fresh-cut "Fuji" apple, the use of lemongrass essential oil in the emulsion and nanoemulsion within the sodium alginate matrix showed that luminosity decreased during refrigerated storage. This did not occur with apples coated only with sodium alginate, which was attributed to the fact that phenolic compounds of the essential oil are substrates for the polyphenol oxidase activity. In addition, it was considered that there is an increase in the permeability of the cell membrane due to the presence of

Table 6.3 **Effect of nanosize systems on color, textural properties, and shelf life of foods.**

Nanosize system	Polymer used/ active	Food application	Textural effect	Color effect	Shelf life increasing
Nanoemulsion	–	Leaf vegetable	Nanocoating diminish the firmness loss at	No significant effect	Increase from 3 at 7 day with nanocoating rucola leaf Sessa et al. (2015)
Nanolaminate coating	*Flourencia cernua* extract	Tomato fruit	Minor firmness loss with extract in nanolaminate (35 % vs 57% without coating)	More stable redness	Nanolaminate with extract treatment, extend shelf life for 15 days at 0°C Salas-Méndez et al. (2019)
Nanoparticles	Chitosan	Whiteleg shrimp	Minimal hardness decrease (235–205 g) when nanoparticles are used compared with control (239–105 g)	–	10 days of storage at 4°C Wang et al. (2015)

Table 6.3 (Continued)

Nanosize system	Polymer used/ active	Food application	Textural effect	Color effect	Shelf life increasing
Nanocapsules	Poly-ε-caprolactone/α-tocopherol	Fresh-cut “Red delicious” apple	–	Nanocapsules and nanocapsules/xanthan gum shown best color control with ΔE<5	From 12 days without coating to 21 days of storage at 4°C Galindo-Pérez, Quintanar-Guerrero, Mercado-Silva, Real-Sandoval, and Zambrano-Zaragoza (2015), Zambrano-Zaragoza, Gutiérrez-Cortez, et al. (2014a), Zambrano-Zaragoza, Mercado-Silv et al. (2014b)
Nanoparticles	Alginate/ag-montmorillonite	Fresh-cut carrot	–	–	Shelf life prediction of 69.9 days respect fresh-cut carrot without edible coating Costa, Conte, Buonocore, Lavorgna, and Del Nobile (2012)
Nanolaminate	Alginate/lysozyme	“Coalho” Cheese	Increase of storage time with less weight loss	Changes in transmittance minor in coating cheese	20 days with less growth of mesophilic and psychotropic microbial counts and best visual aspect Medeiros et al. (2014)

Table 6.3 (Continued)

Nanosize system	**Polymer used/ active**	**Food application**	**Textural effect**	**Color effect**	**Shelf life increasing**
Nanocrystals	Cellulose	Shelled walnuts	–	Best color retention for coated walnuts	Accelerated shelf life test. 30 days of storage at 40°C Fotie, Limbo, and Piergiovanni (2018)
Nanocapsules	β-carotene/poly-ε-caprolactone	Fresh-cut melon	The application of nanocoating helped conserve firmness (only 9.9% decrease)	The best retention of color was from the fresh-cut melon with nanocapsules/ xanthan gum with intensity (4.03%).	21 days of storage at 4°C Zambrano-Zaragoza et al. (2017)
Solid lipid nanoparticles (SLNs)	Carnauba wax/ xanthan gum	Fresh-cut guava	Less firmness loss with 5 g/L of SLNs (35 %)	Browning index reduction with 5 g/L of SLN	18 days of storage at 4°C González-Reza et al. (2018a)

volatile compounds in the essential oil that promote modification in the cell cytoplasm, allowing the interaction of phenols and enzymes (Yilmaz et al., 2016). It is noteworthy that there are many studies to be carried out in order to ascertain the minimal inhibitory concentration for limiting browning and color changes in fruits due to the effect of polyphenols and enzymes, as well as the effect of polymer type employed as matrix or as a coating in nanoemulsions.

6.4.4 Effect of nanocrystals and other nanosize systems on color and sensorial aspects

In recent years, there has been a growing interest in the use of nanocrystals and other nanosize systems as ingredients in food processing, mainly those in which their rheological behavior is important or in which their spreadable properties play a relevant role in the sensorial acceptance of the product (Lin et al., 2012). Nanocrystals prepared from hydrocolloids that possess a great capacity for absorbing water have been used in the stabilization of Pickering emulsions; however, it is necessary to consider the changes in the crystallinity of starch depending on the pH, ionic strength, and nanocrystal concentration. In a study in which nanocrystals were prepared with a waxy starch, it was shown that an increase in the nanocrystal concentration was favorable for the formation of stable and gel-like Pickering emulsions, with stronger stiffness at a pH between 5 and 10, these being more susceptible to the concentration of NaCl, although not achieving stable emulsions (Yang et al., 2018).

Nanocrystals have been useful in the development of low-fat products, where the sensory effect depends both on taste and textural perception at the moment of product consumption; these physical properties are in turn related with the viscosity associated with fluidity and smoothness. It is then possible to mention that hydrocolloids can replace some fat in mayonnaise, dips, and dressings, being dependent on the molecular characteristics and their influence on bulk physicochemical properties such as thickening, gelling, dilution grade, and light transmission (Dickinson, 2009; Li & Nie, 2016).

Cellulose and native starch or their modification are abundant, biocompatible, biodegradable, and nontoxic. Nanocrystals are prepared from starch or cellulose and these have the ability to increase the viscosity of aqueous dispersion; however, it is necessary to take into account the content of fat in the food formulation, since its presence modifies the water-retention capacity of starch, modifies the form of the hydrated molecules, and forms a gel (Choi & Kerr, 2003). The proportion of nanocrystals employed as ingredients in the replacement of fat and the origin of starch or cellulosic materials are factors that are important to study. It has been shown that the concentration of nanocrystals used to reduce fat between 25% and 75% using concentrations of 10%, 12%, and 14% of corn starch nanocrystals decreased the particle size in relation to the concentration. This is attributable to the water present binding to the surface of nanocrystals with Ψ_z between −18, −4, and 31.9 mV to form the hydrogen bonds, and a higher nanocrystal concentration improving the food–emulsion stability, and thus no creaming. In addition, based on the rheological properties, the addition of corn starch nanocrystals formed a gel-like network that trapped the oil droplets, revealing an electrostatic repulsion that produced stability during 6 months (Javidi, Razavi, & Mohammad Amini, 2019).

6.5 Toxicological and normative regulatory issues of nanoparticles in food processing

Nanoparticles as ingredients for food can exhibit different chemical or physical properties, or biological effects compared with larger-scale counterparts. The high surface area exposed increases the reactivity of functional groups, which is associated with a high degree of particle interpenetration into tissues. Dimension-dependent properties in food are usually reflected as more protective food-packaging materials (Thiruvengadam et al., 2018) and improved delivery of a functional ingredient or a nutrient in food (FDA, 2014). For a considerable time period, regulatory entities such as the FDA have paid more attention to nanomaterials within the range of 1–100 nm. However, there is sufficient evidence in various areas of science that properties dependent on aggregation size are not restricted to the 100-nm limit. Therefore the new recommendations found in FDA documents explore the "possibility" of novel and different material properties depending on an aggregation size of up to 1000 nm. Even more so, some statements from the FDA's "Guide to Industry" suggest a better understanding of the interaction of physical and chemical characteristics with biological effects.

When toxicological aspects are addressed in the food area, a greatest risk associated with nanomaterials derives from the possibility that they are ingested with food (Wani, Masoodi, Jafari, & McClements, 2018). Consequently, after nanomaterials enter the human body, they could exert some adverse effects. Of course, it is true that a fraction of new materials will enter the human body and that they depend on their proximity with food, even in the case of packaging materials. The next sentence. described in "Guidance for Industry, Considering Whether an FDA-Regulated Product Involves the Application of Nanotechnology" (FDA, 2014), draws attention to the flexible and nonspecific nature of the following statement: "The use of the word *should* in Agency guidance documents means that something is suggested or recommended, but not required" (FDA, 2014). Therefore all the assertions on the requirements are subject to each particular case. At present, there is no specific establishment of limits in the concentration of nanomaterials, types of permitted nanomaterials, and the function of surface phenomena in the types of nanomaterials present in foods, interaction of nanomaterials with food components, biodistribution, biotransformation, and bioelimination. This advance in official regulations is limited by the progress in the knowledge of basic science and by the economic regulatory policies of the food market.

The presence of nanoparticles in a food can comprise intentional alterations, deriving from food-handling processes, food components, or contaminants (Bajpai et al., 2018). It is evident that the manipulation of ingredients toward nanoparticles will "result in new properties not seen in traditionally manufactured food substances." Essential considerations for the manufacturer should consist at least of particle size, particle SD (PDI value), Ψ_z, batch-to-batch reproducibility, estimation of surfactant residues on the surface of nanoparticles if applicable, interactions among materials, and interactions with proteins, biodegradation, and possible accumulation in tissues. The first point of interaction of nanoparticles with the biological systems is, naturally, the surface. There are multiple conformations of the surface: the matrix of nanomaterial; surfactants for stabilization; a mixture of both; a surface with one or more layers of organic or inorganic waste (Jain, Ranjan, Dasgupta, & Ramalingam, 2018); or a protein corona. Interaction can even take place with accumulated nanomaterials to reduce surface free energy. Formation of the corona, deposition of one or more layers of proteins on the surface of nanomaterial, is nearly unpredictable because it depends on the biological composition of the food and physiological state of the person.

One of the main mechanisms of nanomaterial cytotoxicity is through the induction of reactive oxygen species (ROS). The presence of ROS is related to possible inflammatory responses due to the presence of a xenobiotic, generation via peroxisomes, or to by-products of the mitochondrial electron transport chain. Pairs of highly reactive electrons on the surface can also favor the production of ROS (Jain et al., 2018). There are different models in vitro, ex vivo, and in vivo to know the possible reactions of nanomaterials that are present or in contact with food. The in vitro models include simulations and predictions of surface reactivity in terms of energy, ROS evaluation, inflammatory processes, viability, and cell proliferation in different cell lines. Ex vivo models include permeation pathways and kinetics in tissues such as skin, lung, liver, kidney, and brain, while in vivo models comprise those of biodistribution and biotransformation. A correlation of different models at different levels usually provides useful information.

6.6 Conclusions and future trends

There are many important aspects to consider in the development and application of nanoemulsions and nanosize systems, being necessary to consider the method of preparation as well as the materials and conditions required. There are important factors related to the type and concentration of surfactants employed, such as the amount of compound, the superficial charge that stabilizes the colloidal system, and compatibility with the food in which it will be used as an ingredient, in addition to monitoring the need for and stages at which it must be released to enhance the expected effect in relation to the product characteristics. It is also necessary to take into account the preservation of food during storage, or its bioavailability at the moment of being consumed. The superficial charge of the nanosize system and the way that these remain stable once prepared, as well as the food composition and the potential interactions are some other significant parameters. When nanosystems are incorporated as ingredients into foods and beverages, the Ψ_z with absolute values of >30 mV is preferred; other factors that must be considered are the degree of dilution to be carried out, the way that it is incorporated, and the viscosity, pH, ionic strength, thermal resistance, and interaction with food components.

The use of nanosize systems as ingredients is also important in order to analyze the function that is desired. Thus nanoemulsions are preferred in the formulation of beverages, juices, fruit pulp, sauces, and ice cream, while polymeric nanoparticles are preferred in thermal processes in order to confer thermal resistance to components such as flavorings, colorants, vitamins, essential oils, and other thermolabile substances utilized as ingredients in food processing. Nanocoatings provide protection against O_2, light, temperature, and humidity, being possible to employ the LbL technique, polymeric nanoparticles, nanoemulsions, and other geometries. In all cases, it is necessary to consider the surface treatment or the composition of minimally processed food. Finally, nanocrystals have been employed for the stabilization of Pickering emulsions and have demonstrated a positive effect on the control of rheological behavior of emulsified foods and in spreads such as pâtés, margarines, and dips, modifying the sensorial effect with beneficial results.

According to the analyses, the nanosize systems have been used as ingredients in food processing and preservation, as antioxidant and antimicrobial natural substances, and as essential oils, colorants, and vitamins. This shows that they interact with the cell metabolism of fresh-cut fruit and vegetables, as well as controlling lipid oxidation reactions in meats and their products. This thereby reduces the action of enzymes and microorganisms present, such as polyphenol oxidases and pectin methylesterases in vegetables, and causes the decrease of microorganisms and enzymes responsible for color changes in meat and their products. In meats, the principal essential oils utilized are rosemary, oregano, thyme, clove, and cinnamon, which decrease tissue degradation due to microbial growth, and for their antioxidant capacity, which decrease the diffusion of oxygen. With the use of nanosize systems, it has been shown that the amount of active ingredients utilized in food formulation and processing is lower, due to minor losses of the volatilization of aromatic components. The latter, in turn, is beneficial, since there is a minimal sensory change in the products. In addition, there has been good progress in the development of novel products with sensory characteristics that appear on chewing the product.

Some studies have been conducted on the release kinetics of different components such as essential oils, polyphenols, and other plant extracts with antioxidant and antimicrobial effects. However, due to the monitoring of volatile residuals during product storage, it remains necessary to investigate the effect of interaction of nanosize food systems and the factors that contribute to maintaining the stability of these for as long as possible. The selection of the correct polymer in the formation of polymeric nanoparticles is another important point to consider in the preparation of nanosize systems for use as an ingredient in food processing and preservation, as well as the matrix polymer in the nanocoating and its function on the surface of products. Cellular internalization analyzes the mechanisms that promote its conservative effect and the changes in signaling that give rise to the expression of enzymes and the degradation of components in food. In addition, there must be a continuation of investigation into the potential uses of multilayer and multicomponent nanostructured systems that contribute to strengthening the efficiency of controlled release for different types of food in response to changes in pH, ionic strength, and even tissue modification during the diffusion process, which promote the functionality of nanoingredients.

Nanoemulsions and nanosize systems as ingredients in the extension of shelf life of food and beverages and in the development of novel functional products will be useful tools that will potentially permit their use to reduce costs in relation to thermolabile components and their reconstitution due to processing, and in addition, on considering the effective protector of the substances and therefore their protection during storage and consumption, thereby maintaining the effectiveness of the nanoingredient incorporated into the food or beverages.

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