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Review

Versatile Emulsion-Based Encapsulation System Production Processes: A Review

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Abstract: Encapsulation is defined as the entrapment of active agents within another substance, which can be either solid or liquid. These substances need to be protected in order to preserve their functional and physicochemical properties, to enhance their stability, and to extend their shelf-life. Among all the existing methodologies, emulsion-based techniques are selected to be investigated in this review. Emulsion-based techniques are versatile and adaptable to different applications and different substances. In fact, these methods use the emulsion structure to protect the compounds of interest. Emulsions can be used as standalone systems or as a template for the production of polymeric particles. This review provides a comprehensive overview of emulsion-based techniques, with a particular focus on production processes. The emulsions have been described in terms of classification, composition, and characterization. The main production processes are examined in detail, with the main advantages and disadvantages of each methodology highlighted to provide a comprehensive overview of the topic.

Keywords: emulsion; polymeric particles; active agents; encapsulation; emulsion production methods

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1. Introduction

Encapsulation is defined as the entrapment of active agents within an immiscible substance, which can be either liquid or solid. The encapsulated compound is referred to as the core or internal phase, while the carrier is defined as the wall material, shell, or external phase. The encapsulation is an extremely versatile technique, and it can be applied in various industries, including pharmaceutical, cosmetic, food, agricultural, and medical industries [1,2]. Polyphenols, vitamins, natural extracts, microorganisms, probiotics, prebiotics, and drugs are some of the encapsulated compounds in these sectors [3,4]. The main objective of encapsulation is to incorporate active compounds into excipients, thereby preserving their functional and physicochemical properties. This process can enhance their bioactivity, stability, and shelf-life. Additionally, the carrier system may mask undesirable tastes and provide protective barriers against environmental factors such as light, temperature, moisture, and oxygen. Finally, encapsulation allows for the modulation of release profiles, adapting them to specific administration types [3,5,6].

There are several techniques for the encapsulation process, and no one technique is suitable for all compounds that need to be encapsulated. In fact, the active agents to be encapsulated are diverse and differ both in chemical characteristics and in the purpose of encapsulation. Therefore, in the beginning, it is necessary to decide what kind of encapsulation system is suitable for the encapsulation of specific substances in terms of encapsulating materials, encapsulation techniques, and final product characteristics in function of size, formulation, and application [2,7,8]. Depending on the different needs, the more suitable encapsulation techniques can be selected for each specific case. The most used techniques are emulsification-based techniques, spray drying, liposome entrapment, lyophilization, extrusion, nanoprecipitation, and coacervation [8,9].

The encapsulation process can be divided into three main categories depending on the resulting product size: nano-, micro-, and macroencapsulation. In the case of macroencapsulation, the products obtained have a size greater than 1000 µm, while, for microencapsulation, a range between 1 and 1000 µm is obtained. Nanoencapsulation is characterized by a product size of less than 1 µm. Except for some specific applications, micro- and nanoencapsulation are mainly used for the stabilization of sensitive compounds [1,10,11].

Moreover, encapsulation strategies are generally classified into two main approaches: bottom-up and top-down. The bottom-up approach exploits atom-by-atom or molecule-by-molecule techniques using several interactions, such as ionic, hydrophobic, and van der Waals interactions. Techniques like nanoprecipitation and coacervation are in this category. The top-down approach, on the other hand, relies on physical processing of the coating and core materials by applying energy for the size reduction. Emulsification-based techniques, extrusion, and spray drying are representative of this approach [1,12].

Among the various techniques, there are the emulsification-based techniques, which exploit the emulsion structure to protect the active agents. In fact, emulsions are liquid dispersions composed of two immiscible liquids, where one phase is dispersed in the second phase as small spherical droplets. Therefore, the sensitive compounds can be entrapped in the dispersed phase droplets, while the outer phase provides a protective barrier for the loaded dispersed droplets [8,13,14]. Emulsion-based techniques are versatile and adaptable to different applications and different substances. In fact, emulsions can be used as a standalone encapsulation system, where the internal phase consists of the compounds to be protected. In this case, the final product is a liquid formulation. Beyond this role, emulsification can also be the first step in the production of micro- and nanoparticles via further processing, such as polymerization reaction of monomers and dispersion of preformed polymers [15,16]. In this case, polymeric micro- and nanoparticles are obtained and they contain the active ingredient homogeneously dispersed in the polymer matrix or confined in a central core and enclosed by the polymer matrix. In both cases, the product size depends on the selected emulsion production methods and on the process operating conditions. Thus, emulsification-based techniques can be used to produce micro- or nanocarriers [17,18]. Some examples of applications for emulsion-based techniques for encapsulation of active agents are reported in Table 1, highlighting the high applicability and versatility of these methodologies.

The objective of the present review is to provide a comprehensive overview of emulsion-based processes employed in the development of encapsulation systems for active agents. The main aim is to guide researchers in identifying the most suitable process within the broad category of emulsion-based encapsulation techniques, which include both emulsions and polymeric particles. This review begins with a detailed overview of emulsions, describing the fundamentals of emulsions in terms of definitions, classification, composition, instability, properties, and characterization. Successively, production techniques for both liquid emulsions and polymeric particles are deeply examined, including the production processes, as well as their respective advantages and limitations. This review serves as a practical guide for selecting the most appropriate encapsulation techniques for specific applications.

Table 1. Examples of applications for emulsion-based encapsulating techniques.

Sector of Application	Active Agents	Carrier Agent	Encapsulating System	Size	Ref.
Food	Curcumin	Medium chain triglyceride, canola oil or linseed oil	Emulsion	400–800 nm	[19]
	Lactobacillus reuteri	Medium chain triglyceride oil	Emulsion	13–15 µm	[20]
	Lactobacillus acidophilus	Sunflower oil	Emulsion	5 µm	[21]
	Vitamin E	Corn oil	Emulsion	0.1–0.5 µm	[22]
	Omega-3 fatty acid	Sunflower oil	Emulsion	150 nm	[23]
	Arthrospira platensis polyphenolic extracts	Polycaprolactone	Polymeric particles	140–800 nm	[24]
	Vitamin E	Polycaprolactone	Polymeric particles	60–150 nm	[25]
	Propolis	Poly(lactide co-glycolides) (PLGA), ethyl cellulose or polycaprolactone	Polymeric particles	2–5 µm	[26]
	β-carotene	Polycaprolactone and xanthan gum	Polymeric particles	122–220 nm	[27]
Cosmetic	Resveratrol	Rose oil, jasmine oil or lemon oil,	Emulsion	10–70 nm	[28]
	Quercitin	Capric triglyceride	Emulsion	–	[29]
	Tocopheryl acetate	Medium chain triglyceride	Emulsion	120 nm	[30]
	Retinol	Eudragit RS 100	Polymeric particles	180–300 nm	[31]
	Vitamine E	Sodium polystyrene sulfonate	Polymeric particles	1–1.3 µm	[32]
Pharmaceutical	Insulin	Medium chain triglyceride oil	Emulsion	10–30 µm	[33]
	Malaria vaccine adjuvant	Squalene	Emulsion	2.8–18 µm	[34]
	Insulin	Poly(lactide co-glycolides) (PLGA)	Polymeric particles	1.8–16.9 µm	[35]
	Ketoprofen	Poly(lactide co-glycolides) (PLGA)	Polymeric particles	100–200 nm	[36]
	Ibuprofen	Chitosan	Polymeric particles	200–280 nm	[37]
	Curcumin	Poly(lactide co-glycolides) (PLGA)	Polymeric particles	250–500 nm	[38]
	Peptide	poly(ethylene glycol)-block-polycaprolactone	Polymeric particles	100–200 nm	[39]
Agriculture	*Sinorhizobium meliloti*	Canola oil	Emulsion	–	[40]
	Pseudomonas simiae and *Azospirillum brasilense*	Isopropyl palmitate	Emulsion	80–150 µm	[41]
	Bacillus thuringiensis	Mineral oil	Emulsion	5–8 µm	[42]
	Two bacteria, a yeast, and two saprophytic fungi	Soybean oil	Emulsion	5 µm	[43]
	Pseudomonas putida	Sodium alginate and bentonite	Polymeric particles	25–100 µm	[44]
	Atrazine	Poly(epsilon-caprolactone)	Polymeric particles	408–483 nm	[45]
	Carbendazim and tebuconazole	Polycaprolactone	Polymeric particles	520–540 nm	[46]

2. Emulsions

2.1. Definitions and Classification

Emulsions are dispersions made up of two immiscible liquid phases, such as oil and water, which are mixed using mechanical shear and surfactant [47]. In an emulsion, one phase is dispersed in the other as small spherical droplets. Emulsions can be conveniently classified according to the relative spatial distribution of the liquid phases [48]. The simplest emulsions are single emulsions, which are divided into oil-in-water or o/w emulsions and water-in-oil or w/o emulsions. The first one is a system in which oil droplets are dispersed in an aqueous phase and are used for the distribution of hydrophobic substances. In contrast, the other type consists of water droplets dispersed in an oil phase and is used for the delivery of hydrophilic substances. The liquid phase forming the droplets is referred to as the dispersed, discontinuous, or internal phase, while the surrounding liquid is known as the continuous or external phase [49,50]. More complex emulsions, such as double or multiple emulsions, also exist, where droplets of the dispersed phase contain smaller droplets with a composition similar to the continuous phase. The two most common types of double emulsions are water-in-oil-in-water (w/o/w), where the inner water phase (w_1) and the outer water phase (w_2) are separated by the oil phase, and oil-in-water-in-oil (o/w/o), where a water phase separates the internal (o_1) and the external (o_2) oil phase [51–53]. The different emulsion structures allow both hydrophobic and hydrophilic compounds to be encapsulated in the emulsion, changing only the relative spatial distribution of the emulsion. In addition, multiple emulsions have several advantages over simple emulsions; in fact, double emulsions have emerged as an innovative technique for several applications. In particular, this complex emulsion holds significant promise for the encapsulation of molecules due to its unique multi-compartmentalized structure. Moreover, droplet size homogeneity and physicochemical properties can be better controlled [50,54–56].

Recently, innovative structural designs have been developed to obtain emulsions with improved properties. Among the multiple emulsions, which are also included among the innovative configurations, two other emulsion types have been developed: high internal phase emulsions (HIPEs) and Pickering emulsions [57]. The High Internal Phase Emulsions (HIPEs) have a semi-solid consistency and remarkable capacity to encapsulate and protect high amounts of sensitive compounds, making them an efficient delivery system. In fact, they are characterized by an internal phase volume fraction exceeding the theoretical close-packing limit, that is typically more than 74%. Due to the high droplet concentration, droplets may deform into polygonal shapes, giving unique rheological properties to the emulsion. Moreover, the HIPEs can be both of oil-in-water or water-in-oil type, resulting in a very adaptable system as a function of the specific application [57,58]. On the other hand, another innovative emulsion system is represented by Pickering emulsions. They are defined as emulsions that are stabilized by solid particles. In fact, the oil–water interface is stabilized by the presence of solid particles that can be of different origins. The main advantages are higher physical stability, lower toxicity, and reduced production costs. As for the other systems, all the types of emulsions can be stabilized by solid particles, generating a Pickering emulsion. Moreover, the solid particles can be customized, allowing high versatility [59–61].

Another classification is based on emulsion droplet diameter and thermodynamic and kinetic stability. The two phases that compose the emulsion are immiscible, and their contact is thermodynamically unfavorable, making emulsions inherently thermodynamically unstable. However, by using stabilizers, it is possible to create emulsions that are kinetically stable. They are known to be metastable, and they are characterized by a stability from a few days to months or even years. A stabilizer is a substance used to improve the kinetic stability of an emulsion, and its classification depends on its mode of action, which can include being an emulsifier, weighting agent, texture modifier, or ripening inhibitor [62]. So, it is possible to introduce another classification, in which emulsions are categorized based on their droplet diameter, thermodynamic, and kinetic stability as macroemulsions, nanoemulsions, and microemulsions. Macroemulsions, also called conventional emulsions, are characterized by a droplet size greater than 500 nm. Nanoemulsions are characterized by a droplet size between 20 nm and 500 nm, while microemulsions have a droplet size smaller than 100 nm [63,64]. Both macroemulsions and nanoemulsions are thermodynamically unstable and kinetically stable (metastable), meaning that they tend to break down over time due to a variety of destabilization mechanisms, such as gravitational separation, coalescence, flocculation, and Ostwald ripening [65,66]. Due to the smaller droplet size, nanoemulsions are typically more stable against gravitational separation and droplet aggregation than macroemulsions. In fact, the thermodynamic and kinetic stability of the emulsions is related to the droplet size and, in particular, the stability of the emulsion increases as the droplet diameter decreases [65,67,68]. Microemulsions, like nanoemulsions, are small in size, which gives them good stability against gravitational separation and results in systems that are optically clear. Unlike nanoemulsions, microemulsions are thermodynamically stable systems [65,69,70].

2.2. Components

As mentioned above, emulsions are composed of immiscible liquid phases that are distributed in different ways depending on the type of emulsion. Considering the simplest case of an o/w or w/o emulsion, two immiscible liquid phases make up the emulsion, and the composition of each phase is a function of the application and the desired product type. Therefore, liquid emulsions and polymeric particles can be produced as a function of phase composition.

In the case of liquid emulsions, the two phases are composed as follows:

- Oil phase: lipids, in particular oils, which are components that are soluble in organic solvents but immiscible or poorly miscible with water. The specific type of oil is selected based on the intended application. For instance, edible oils derived from plants or seeds are employed in food applications.
- Water phase: usually consists of water [71,72].

For the purpose of encapsulation, the compound that need to be protected is dispersed in the oil or water phase, depending on its solubility, and the phase that contains the compound will become the inner phase of the emulsion, while the other phase will serve as the external phase, allowing for the production of either an o/w or w/o emulsion [14,73].

Moving on to the case of polymeric particles, an o/w emulsion is used as a template for particle production. In this case, the composition of the oil phase, also called the organic phase, is modified due to the polymer. Therefore, the polymer is completely dissolved in an organic solvent, forming a polymeric solution that is used as the oil phase. There are a number of general principles that should be considered when selecting a polymer and solvent combination. The selection of the polymer depends on the intended application. Focusing on pharmaceutical, nutraceutical, and food applications, the polymers should be non-toxic, biodegradable, or/and biocompatible. Polymers can be classified as natural, semi-synthetic, or synthetic. Examples of natural polymers include gelatin, casein, chitosan, gum acacia, whey protein, xanthan gum, or sodium alginate [15,74]. The most commonly utilized semi-synthetic polymers are ethyl cellulose and carboxymethyl cellulose. Among the synthetic polymers, polylactides (PLAs), polyglycolides (PGAs), poly(lactide co-glycolides) (PLGAs), polycaprolactone, and polyglycolide are the most commonly utilized. Moreover, the polymer must be completely insoluble in water to facilitate the production of an o/w emulsion. The selection of polymer is also based on the physical properties required for the specific application [75–78]. Regarding the solvent, its selection is typically based on the chosen polymer. Some of the selection criteria are the ability to dissolve the polymer, immiscibility or poor miscibility with the external phase, and high volatility. Moreover, the physicochemical properties of the solvent must be considered, as properties like surface tension, viscosity, density, and solubility influence particle size. The most used organic solvents are chloroform, dichloromethane, and ethyl acetate [76,79,80].

Both for liquid emulsion and polymeric particles, beyond the compounds described above, ionic liquids and deep eutectic solvents can be used. These solvents offer numerous advantages, making them emerging candidates for emulsion production. The ionic liquids are salts with a melting point lower than 100 °C, allowing them to be liquid at room temperature. Moreover, they are often referred to as designer solvents due to their tunable properties, which can be precisely adjusted by varying the combinations of cations and anions. In fact, depending on the cation–anion combination, they can be hydrophilic or hydrophobic. This capacity gives the possibility to use ionic liquid both as an oil and a water phase, in the function on the desired application [81–83]. Deep eutectic solvents are of even greater interest than ionic liquids. They are defined as a combination of two or more solid compounds that, when mixed in a precise molar ratio, result in a liquid at room temperature. They are usually identified as a subclass of ionic liquids. In fact, these solvents can be both hydrophilic and hydrophobic, like ionic liquids, but they result in less toxicity because they can be derived from natural sources, making them appealing for emulsions. Moreover, they are safe and economic [84–86]. The appropriate deep eutectic solvent can be used to produce liquid emulsions and also to produce polymeric particles starting from emulsion systems [85,87,88].

Finally, in the case of double emulsions, three phases are present, and the internal phase has similar physical properties to the external phase. For the w/o/w emulsion, which is more interesting for this study, the three phases are composed as follows:

- Internal water phase: aqueous phase containing active agents;
- Oil phase: oil or polymer solution, depending on the desired product;
- External water phase: water.

Other fundamental components of the emulsion are the stabilizers, which play an important role in the correct formation of the emulsion and in its stability [79,89].

Stabilizers

Stabilizers are fundamental for the creation and stabilization of emulsions. The classification of stabilizers is based on the mode of action and can be divided into the following categories:

- Emulsifier: surface-active molecules that adsorb to the surface of freshly formed droplets during homogenization, forming a protective layer that prevents the droplets from aggregation.
- Texture modifiers are divided into thickening agents and gelling agents, depending on their mode of operation and the rheological characteristics of their solutions. Both thickening agents and gelling agents act on the continuous phase of the emulsion, either by increasing its viscosity or by forming a gel, respectively. As a result, texture modifiers enhance emulsion stability by slowing the movement of the droplets.
- Weighting agent: a substance added to the dispersed phase to reduce the density difference between the droplets and the surrounding liquid, thereby slowing down gravitational separation.
- Ripening inhibitors are highly non-polar substances, with very low water solubility, that are added to the oil phase to inhibit Ostwald ripening through an entropy of mixing effect.

In the development of an emulsion-based product, the identification of the most appropriate stabilizer or combination of them is fundamental [58,90–92].

Focusing on the emulsifier, emulsifiers are amphiphilic molecules, with a hydrophobic tail and a hydrophilic head, and they are capable of adsorbing to an oil–water interface and protecting emulsion droplets from aggregation, such as flocculation and coalescence. The emulsifier is rapidly adsorbed to the oil–water interface during emulsion formation, generating an interfacial tension reduction and preventing droplet coalescence during homogenization. In addition, it is usually important that the emulsifier forms an interfacial layer that prevents droplet aggregation during manufacture, transport, storage, and utilization. The most commonly used emulsifiers are small-molecule surfactants, amphiphilic biopolymers, phospholipids, and certain types of particulate matter [67,93–98].

The head of the surfactant molecule can be non-ionic, anionic, cationic, or zwittertonic, while the tail part usually consists of one or more hydrocarbon chains with between 10 and 20 carbon atoms. Surfactants are classified according to their electrical characteristics, which are related to the charge of the head group:

- Ionic surfactants: there are two types of ionic surfactants, that is, anionic, in which the head part is negatively charged, such as fatty acid salts, stearoyl lactylate salts, diacetyl tartatric acid esters of monoglycerides, and citric acid esters of monoglycerides, and cationic, in which the head part is positively charged, such as lauric arginate.
- Non-ionic surfactants: the head part contains no charge. The most common are monoglycerides, acetic acid esters of monoglycerides, lactic acid esters of monoglycerides, Tweens, and Spans. Some polymers are also used as non-ionic surfactants, such as Pluronic F-127, also known as Poloxamer 407, and Polyvinyl alcohol (PVA).
- Zwitterionic surfactants: the head part contains both charges, such as lecithin.

There are numerous surfactants that can be used to produce emulsions, and each emulsifier has specific properties that depend on the type of head and tail group. It is, therefore, essential to select the most appropriate surfactant for the specific emulsion. In order to facilitate the choice of the correct surfactant, several classification schemes have been developed based on different properties, including the solubility of the surfactant in oil and/or water, the ratio of hydrophilic to lipophilic groups, the relative affinity for oil and water phases, and the molecular geometry [93,99–101].

One of the most common classifications is based on the ratio of hydrophilic to lipophilic groups, and it is called the Hydrophile–Lipophile Balance (HLB). This balance is described by a number that depends on the molecular properties of the surfactant and gives an indication of its relative affinity for the oil and water phases. Hence, each surfactant is assigned an HLB number according to its chemical structure: a molecule with a high HLB number has a high ratio of hydrophilic groups to lipophilic groups, and vice versa. This number can be calculated in a number of ways, including semi-empirical methods, experimental measurements, or by knowing the number and type of hydrophilic and lipophilic groups present in the emulsifier. The HLB number of a surfactant gives a useful indication of its solubility in either the oil and/or water phase and can be used to predict the type of emulsion that will be formed by a surfactant. The typical ranges of HLB number and solubility are as follows:

- A surfactant with a low HLB number (3–6) is predominantly hydrophobic, meaning it dissolves preferentially in oil and is typically used to stabilize water-in-oil emulsions.
- A surfactant with a high HLB number (10–18) is predominantly hydrophilic, so it dissolves preferentially in water and stabilizes oil-in-water emulsions.
- A surfactant with an intermediate HLB number (7–9) shows no strong affinity for either phase and is classified as a “wetting agent”.

- Molecules with HLB numbers below 3 (very hydrophobic) and above 18 (very hydrophilic) tend to accumulate in the bulk oil or water phases rather than at the oil–water interface, without having surface activity.

These surfactants are, therefore, absorbed at the interface between the two phases and are arranged with a hydrophobic non-polar tail, which prefers to be in contact with non-polar liquids such as oil, and a hydropolar head, which prefers to be in liquids such as water [100,102–106].

2.3. Mechanisms of Emulsion Instability

Due to thermodynamic instability, emulsion droplets tend to increase in size, which reduces their interfacial area and lowers their total free energy. Various physical mechanisms contribute to the break-up and instability of emulsions, such as gravitational separation, flocculation, coalescence, Ostwald ripening, and phase inversion (Figure 1).

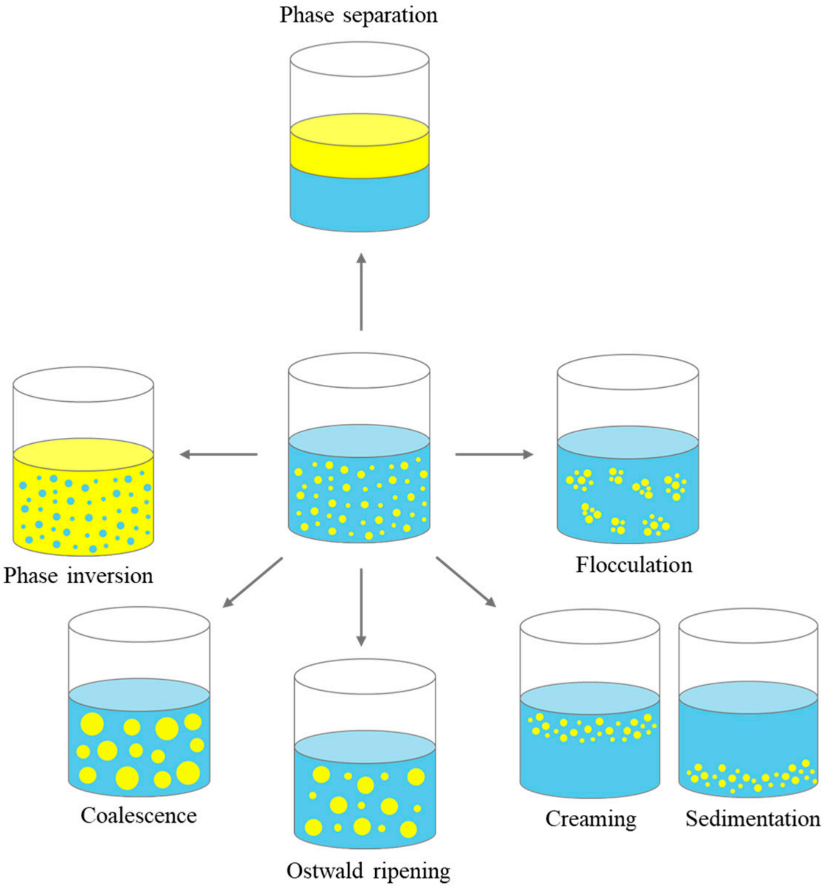

Figure 1. Mechanisms of emulsion instability.

The study of these mechanisms and the factors that influence them is crucial for developing effective strategies to control emulsion stability. The instability mechanisms are the same for single and double emulsions, however, the double emulsions tend to exhibit greater instability due to their increased structural complexity [48,96,105,107–109].

2.3.1. Gravitational Separation

Due to the disparity in density between the dispersed and continuous phases, droplets are able to move in either an upward or downward direction in response to gravity. Specifically, creaming occurs when the dispersed phase has a lower density than the continuous phase, causing the droplets to rise and form a cream layer at the top of the emulsion. On the other hand, sedimentation happens when the dispersed phase has a higher density than the continuous one, causing the formation of a sediment layer at the bottom of the emulsion. Gravitational separation can be quantified by measuring the separation velocity of the emulsion.

This velocity depends on the density difference between the two phases, the viscosity of the continuous phase, and the droplet size. There are several strategies to reduce gravitational separation: using two phases of similar density, reducing the droplet diameter by increasing the amount of emulsifier and enhancing the energy during homogenization, or increasing the viscosity of the continuous phase [62,108,110].

2.3.2. Flocculation

Flocculation is the process by which droplets are attracted to each other while remaining separated by a thin film of continuous phase. In this case, aggregates of flocculates are formed. This phenomenon occurs when the attractive forces, such as van der Waals forces and electrostatic forces, between the droplets become greater than the repulsive forces. Flocculation is a relatively weak and reversible process. To reduce flocculation, the frequency of collisions between droplets must be reduced. One potential approach is to enhance the viscosity of the continuous phase through the addition of thickening agents. Furthermore, flocculation can enhance the gravitational separation process by forming larger droplets that move faster [96,111,112].

2.3.3. Coalescence

Coalescence is defined as the union of two droplets in close contact and occurs when the thin film between the droplets is broken. It occurs when two droplets collide, and, the longer the droplets remain in contact, the greater the probability of coalescence. In fact, coalescence takes place after creaming and flocculation and can lead to complete phase separation.

In order to reduce this phenomenon, it is essential to act on the contact area and the thickness of the interfacial film. In general, an increase in the thickness of the interfacial film results in an enhancement of its strength, which, in turn, leads to an intensification of the repulsive forces and a reduction in the probability of rupture. Consequently, the addition of a greater quantity of emulsifier may serve to augment the thickness of the interfacial film. Furthermore, by reducing the contact area by reducing the droplet diameter, it is possible to reduce the probability of coalescence. Another crucial parameter is the viscoelastic property of the interfacial film, as it determines whether or not the globule will collapse. Raising the surfactant concentration increases viscoelasticity and the strength of the interfacial film, thereby reducing the probability of coalescence [96,106,107].

2.3.4. Ostwald Ripening and Phase Inversion

Ostwald ripening is the process in which components of the dispersed phase diffuse through the continuous phase from smaller to larger droplets. It is a common phenomenon in emulsions with polydisperse droplets and occurs more frequently in w/o emulsions than in o/w emulsions. This process is driven by diffusion, where the continuous phase acts as a transfer medium. Therefore, it is necessary that the dispersed phase is soluble in the continuous phase. To reduce this mechanism, it is necessary to reduce the solubility of the dispersed phase in the continuous phase. Ostwald ripening is a gradual mechanism that results in the eventual disappearance of small droplets. Furthermore, Ostwald ripening should lead to the integration of all droplets into a single drop, a process called phase inversion. Phase inversion happens when the phases undergo a spontaneous exchange, with the dispersed phase transforming into the continuous phase, and vice versa. Following phase inversion, an o/w emulsion becomes a w/o emulsion or vice versa [14,113,114].

2.4. Properties and Characterization of Emulsions

It is essential to study the chemical and physical properties of emulsions as they influence the properties of the final product. Characterization of emulsions includes a variety of methods to determine their properties, such as composition, texture, rheological and thermal properties, electrical conductivity, droplet size, size distribution, concentration, surface charge, and others. The most important properties to be considered are droplet morphology, droplet size distribution, optical properties, rheological properties, and droplet charge [108,109,115].

2.4.1. Droplet Morphology

Analysis of droplet morphology is essential to have information on the size, shape, and distribution of the emulsion produced. Furthermore, by analyzing the morphology over time, the stability of the emulsion can be evaluated. Microscopic analysis is usually employed to determine morphology. Optical microscopy and electron microscopy are usually the most used methods [116].

Optical microscopy is a simple and accessible method for initial estimations, providing qualitative information on droplet size and distribution. This instrument contains a series of lenses that direct light through the sample and magnify the resulting image. However, its limited resolution often necessitates the use of more advanced techniques for obtaining a more detailed analysis. In fact, the theoretical limit of resolution is about 0.2 µm, but it is already difficult below 1 µm [109,115,117].

Electron microscopy exploits electron beams, instead of light, to analyze the sample. The direction of these beams is achieved through the utilization of a series of magnetic fields, rather than optical lenses. Thanks to these electron beams, the resolution is about 0.2 nm. Electron microscopy is divided into scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM is based on sample surface scanning with a beam of electrons under high voltage. Thanks to the interaction between electrons and the sample, two electron signals are generated, in particular, backscattered electrons and secondary electrons. Backscattered electrons are generated from the deeper parts of the sample, and they give information about the composition. Secondary electrons are generated from the surface parts of the sample, providing topographic information about the surface. All these signals are collected and used for generating a three-dimensional image. In TEM, the electron beam is partially absorbed or scattered by the sample, while the rest is transmitted. The beam of transmitted electrons is magnified by a magnetic lens and then projected onto a screen to create the sample image. The sample must be very thin to allow the electron beam to pass through the sample. The images generated by TEM are usually in the form of a two-dimensional image.

One of the principal limitations of electron microscopy is the complex sample preparation required before observation, which typically includes steps like dilution, spreading, freezing, or drying. Additionally, electron beams can damage delicate structures, leading to images that may not accurately replicate the sample's natural state in liquid form. However, recent advancements in electron microscope design and sample preparation techniques are addressing many of these challenges. Particularly, the development of environmental SEMs has made it possible to observe emulsions in their natural state, eliminating the extensive sample preparation [109,115,118,119].

2.4.2. Droplet Size Distribution

Droplet size can influence many properties of emulsions, such as appearance, shelf-life, and stability, and monitoring droplet size allows the stability of emulsions to be studied and their behavior under storage conditions to be understood. Therefore, the average droplet size, droplet size distribution, and polydispersity index are fundamental for studying the homogeneity of the emulsion. The classification of emulsions as monodisperse or polydisperse is dependent upon the degree of uniformity observed in their droplet size.

Emulsions consisting of droplets that are all the same size are referred to as monodisperse, while emulsions with a variety of droplet sizes are called polydisperse. Most emulsions are polydisperse. In such cases, the droplet size is described by its size distribution. Additionally, it is important to determine the mean droplet size and the standard deviation, which indicates the spread or width of the distribution.

The emulsion droplet size distribution is typically measured by static or dynamic light scattering, ultrasonic spectrometry, small-angle X-ray scattering, or electrical pulse counting techniques. Among all these techniques, light scattering devices are the most used thanks to their simplicity of utilization and their speed of analysis. Droplet size analysis of emulsions is typically performed using automated light scattering instruments. There are two main categories of commercial instruments: dynamic light scattering (DLS) and static light scattering (SLS) [116,120,121].

In DLS measurements, the emulsion is illuminated by a monochromatic light beam, and the variations in intensity of the scattered light are measured as a function of time. Smaller droplets, which exhibit faster Brownian motion, induce higher rates of intensity fluctuation, while larger droplets move slowly, generating slow variations in intensity. These fluctuations, which depend on the droplet size, are analyzed by an autocorrelation function, allowing for the mathematical conversion of intensity variations into droplet size, droplet size distribution, concentration, and polydispersity index. This technique is suitable for particle dimensions from 3 nm to 5 µm [115,122,123].

The SLS technique is based on the principle that droplets illuminated by a laser beam scatter light at an angle related to their size. As the droplet size decreases, the observed scattering angle increases logarithmically. The scattering intensity also depends on the droplet size and decreases with the cross-sectional area of the droplet. Thus, large droplets scatter light at narrow angles and high intensity, while small droplets scatter at wider angles and low intensity. Droplet size distributions are calculated by comparing the scattering produced by a sample with an appropriate optical model and using a mathematical inversion process. Two different models are widely used: the Fraunhofer approximation and the Mie theory. This technique is suitable to measure droplet size from 100 nm to 1000 µm [108,123,124].

2.4.3. Optical Properties

Another fundamental parameter for emulsions is their optical properties; in particular, opacity and color are the most important properties to be evaluated. They are the result of interactions between emulsion and light waves. These properties can be described quantitatively using tristimulus color coordinates, such as the $L^*a^*b^*$ system, which is the CIELAB system established by the Commission International de l'Eclairage (CIE). These coordinates allow the standardization of the evaluation of these properties and the complete description of these properties using only mathematical coordinates. In this system, the lightness is represented by L^*, while a^* and b^* represent the color coordinates. In detail, negative a^* indicates green, positive a^* indicates red, negative b^* indicates blue, and positive b^* indicates yellow. Low L^* indicates dark, while high L^* indicates light. Using this system, the opacity is characterized by the lightness (L^*), while the color intensity is characterized by the chroma, defined as $C = (a^{*2} + b^{*2})^{1/2}$. These optical properties are principally determined by the characteristics of the emulsion, such as refractive index, size, and concentration of droplets. In particular, the lightness of an emulsion tends to increase with increasing refractive index contrast, increasing droplet concentration, and decreasing droplet size. The inverse relationship is observed with regard to the color intensity. Consequently, as the diameter and concentration of the drops decrease, the emulsion will tend to appear clearer and more transparent, while, with larger drops, it will have an opaque appearance [125–127].

Nowadays, colorimeters are used for the automatic evaluation of the tristimulus coordinates. Colorimeters can be classified into two categories based on their operating principles: spectrophotometric and trichromatic colorimeters. Spectrophotometric colorimeters determine emulsion color using UV–visible spectrophotometers that measure the transmission and reflection of light from objects at different wavelengths in the visible region. The transmittance and reflectance spectra obtained are used to characterize the relative absorption and scattering of light by an emulsion across different wavelengths. Alternatively, the spectra can be analyzed using an appropriate mathematical transformation function in order to obtain directly the trichromatic coordinates. Trichromatic colorimeters are designed to evaluate the color of materials in the same way as the human eye sees objects. The device uses detectors to measure the intensity of the red, green, and blue light components, from which the tristimulus coordinates are determined [127–129].

2.4.4. Rheological Properties

The rheological properties provide information on the material's response to applied forces, allowing for the study of the mechanical behavior, stability, and structure of emulsions for understanding their performance for different applications. In addition, characterization of the rheological properties is fundamental for predicting the emulsion response to external conditions usually imposed during production. Emulsions can vary significantly in terms of rheological properties, from low-viscosity Newtonian fluids to non-Newtonian liquids. The main parameters measured are viscoelastic properties and viscosity [108,109].

Viscoelastic properties are measured through the evaluation of the shear modulus. The shear modulus measures the capacity to resist deformation under shear stress. For emulsions, the shear modulus is related to the intensity of the interactions between the phases and to the interfacial properties of the droplets. The shear-rheological properties are measured using instruments that apply oscillatory frequency-sweep or strain-sweep and measure the stress [108,109,130].

Another fundamental parameter is viscosity. In emulsion, viscosity is affected by both the continuous phase and the dispersed phase. A low viscosity typically suggests an oil-in-water (o/w) emulsion, whereas a high viscosity is more characteristic of a water-in-oil (w/o) emulsion. The continuous phase viscosity affects the droplet movement and consequently the physical stability. A higher viscosity of the continuous phase reduces the droplet movement, reducing instability phenomena, such as creaming, sedimentation, and coalescence. The viscosity can be measured using the viscometers. Several types of viscometers exist, and they can be divided into various categories, including spindle, parallel plate (plate-plate), cone–cone, cone–plate, concentric cylinder, and spindle apparatuses, as a function of the geometry of the measurement cell [121,131,132].

Finally, the properties of the interface are particularly important for emulsions. Despite its small size, the interface is a very important region that determines the emulsion stability. The elasticity and viscosity of the interface are crucial for studying stability. A more elastic interfacial layer prevents the aggregation and coalescence of the droplets, allowing long-term stability. On the contrary, a less elastic interface can enhance droplet coalescence [48,113,133].

2.4.5. Droplet Charge

The droplets in an emulsion hold an electrical charge, which results from the adsorption of the emulsifier at the interface. This charge plays a crucial role in influencing the emulsion's aggregation stability, chemical stability, and surface interactions. The magnitude and sign of this electrical charge are dependent on the type and concentration of adsorbed emulsifier at the interface. In fact, the emulsifier can have a positive, negative, or neutral charge. There are numerous methods for quantifying this electrical charge, such as the electrical surface potential, the surface charge density, and the zeta potential. The zeta potential is the most used method for determining the droplet charge [62,109,134,135].

In emulsions, the continuous phase may contain ions, some of which are strongly attached to the droplet surface, forming the stern layer, while others are weakly bound, creating the diffuse layer. This results in the formation of an electrical double layer around each droplet. The boundary that defines this double layer is referred to as the slipping plane. As a droplet moves within the continuous phase, it takes the ions within this boundary with it, while those outside remain with the bulk dispersant. The potential measured at this boundary is the zeta potential. The charge on a droplet is crucial as it controls its interactions with other charged species. Typically, all droplets in an emulsion are coated with the same emulsifier, resulting in a uniform electrical charge across the droplets. If this charge is sufficiently high, the droplets will not aggregate because the repulsive forces exceed the attractive forces [55,136–138]. The significance of zeta potential is that its value can be related to the short- and long-term stability of emulsions. Emulsions with high zeta potential (negative or positive) are electrically stabilized and are, therefore, stable systems, whereas emulsions with low zeta potential tend to coagulate or flocculate [120,139].

Zeta potential can be measured using micro-electrophoretic analyzers, which assess it by evaluating the electrophoretic mobility of emulsion droplets under an electric field. The direction of droplet movement indicates the sign of the electrical charge, while the velocity of the droplets reveals the magnitude of the charge on the droplet surface [138,140].

3. Emulsion Production Processes

The emulsion production process involves homogenization, which provides the necessary energy input. Two immiscible liquids prefer to stay in their thermodynamically stable state, which is characterized by the smallest possible contact area. Providing sufficient energy through homogenization, one of the two phases can break into droplets to form the emulsion. The energy input, combined with the presence of the surfactant, allows a kinetically stable emulsion to be produced for a reasonable period of time. In fact, the absence of the surfactant causes the complete separation of the two phases, which is driven by the thermodynamic nature of the system of minimum contact area. In fact, as mentioned above, the surfactant is fundamental for emulsion formation and emulsion stability.

During formation, it is quickly adsorbed onto the droplet surface, lowering interfacial tension and creating a protective layer that prevents coalescence. This protective effect continues during emulsion storage, minimizing droplet aggregation and enhancing emulsion stability [13,141].

There are numerous methods for producing emulsions that involve the use of equipment that provides the energy needed for emulsion formation. These methods are classified according to the energy required into the following (Figure 2):

- High energy, which uses conventional emulsification devices such as rotor–stators, high-pressure homogenizers, and ultrasound homogenizers, and provides high shear rates and energy input per unit of volume. They are widely used in industrial applications and for large-scale production.

- Intermediate energy, which uses membrane homogenizers and microfluidic systems and provides intermediate shearing rates and energy inputs per unit volume. They are used in both industrial and laboratory-scale applications.
- Low energy, which uses the energy stored in the system to form emulsions. They have some industrial applications, but they are less common than high-energy methods [142,143].

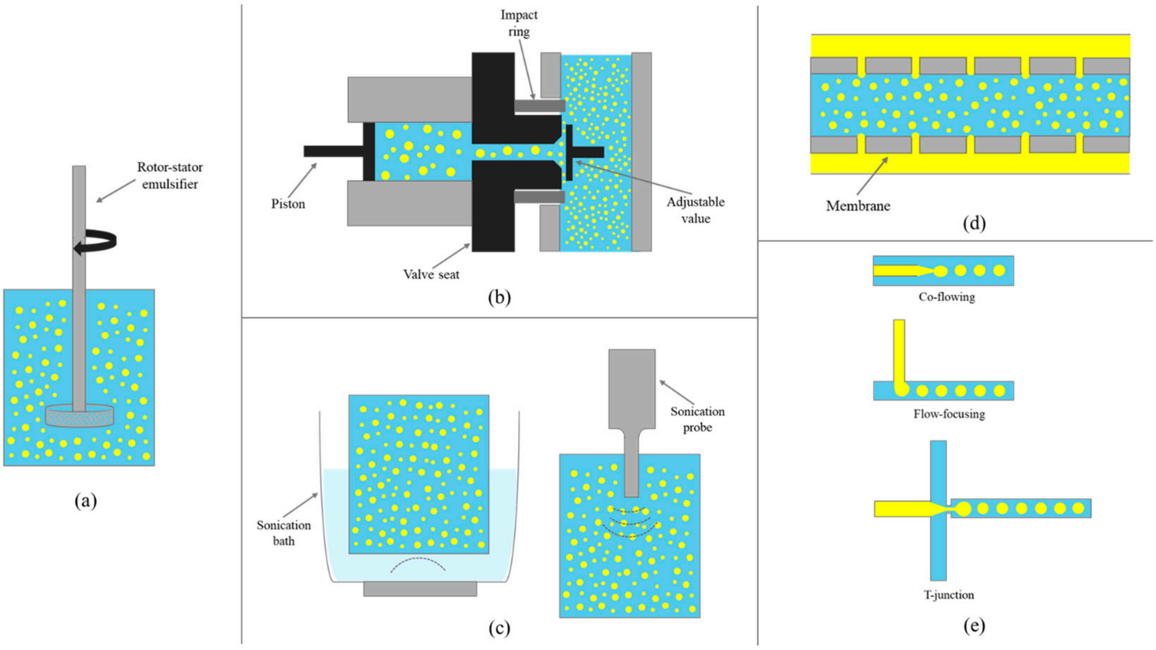

Figure 2. Emulsion production methods: (**a**) rotor–stator emulsifier; (**b**) high-pressure homogenizer; (**c**) ultrasound homogenizer; (**d**) membrane homogenizer; (**e**) microfluidic emulsification.

3.1. Rotor–Stator Emulsifier

Rotor–stator emulsifiers, also called high shear homogenizers, are composed of a rotating shaft (rotor) inside a stationary tube (stator), with the tip of the stator designed with slots or holes to facilitate droplet formation (Figure 2a). The rotation of the rotor, typically at speeds of 3000–12,000 rpm, creates a suction effect that draws the sample into the space between the rotor and stator. In this confined space, the sample experiences high shear forces due to the extreme velocity variation and mechanical impact forces against the instrument walls, resulting from the fluid acceleration. The centrifugal forces then push the material through the holes in the stator, and the rapid fluid movement, caused by the rotor–stator configuration, ensures that the process is repeated as the liquid and sample pass through repeatedly. Rotor–stator devices require significant energy consumption because of the centrifugal forces generated by the movement of the rotor and stator. There are various mixing head designs available, each tailored to generate more intense and evenly distributed shear forces, which help produce smaller droplets, reduce homogenization times, and ensure more uniform mixing [123,144,145].

The rotor–stators emulsifier is available in both batch and continuous configurations. In the batch configurations, the rotor–stator unit is placed in a tank. Baffles can be fixed in the inside walls tanks to achieve better homogenization, thanks to the uniform liquid distribution throughout the vessel. In the continuous configuration, the rotor–stator head, which is usually the same one used for the batch configuration, is placed in a process line with an inlet and an outlet allowing a single pass operation [141,146].

The intensity and residence time of the droplets within the shearing field represent the primary parameters for controlling the droplet size of the emulsion. Additional factors influencing the device's performance include the viscosity of the two liquids, the presence of surfactants, the rotor/stator design, and the volume and volume ratio of the two phases. In comparison with other techniques, these systems have the following advantages: easy installation and operation, low investment costs, relatively high throughput, compatibility with viscous systems, and large volume emulsion preparation. Therefore, they are widely used for emulsion production both at laboratory and industrial scales. However, the emulsions produced by rotor–stators have a wide droplet size distribution, which may not be desirable in some applications. Additionally, they have limitations in achieving very small droplet sizes, particularly droplet sizes below 0.5 µm [59,147–149].

3.2. High-Pressure Homogenizer

High-pressure homogenizers exploit high pressure to force the liquid through a valve or nozzle with very narrow slits to homogenize the sample. The main components of the high-pressure homogenizers are a high-pressure pump, a valve, and a chamber for homogenization and interaction (Figure 2b). The high pressure (100–2000 bar) generated by the pump forces the fluid to pass through small holes. At this point, the turbulence, shear stresses, pressure drop, and cavitation break the coarse emulsion into smaller drops (up to 0.1 µm in diameter), which are immediately stabilized in the interaction chamber by the surfactant. The specific flow regime that allows droplet formation depends on several parameters, such as the physicochemical properties of the liquid phase, the size, and the design of the valve. With this equipment, the liquids must be pre-emulsified to form a coarse emulsion that can be further homogenized to a fine emulsion. In addition, high-pressure homogenization requires large amounts of energy [102,141,150].

The mean droplet size and particle distributions are influenced by three key parameters: homogenization pressure, fluid flow rate, and number of cycles. The main advantage of this device is the possibility to produce nanoemulsions, with droplet diameters smaller than 1.0 µm. It is also used on a laboratory and industrial scale. On the other hand, emulsions produced by high-pressure homogenizers have a broad droplet size distribution. Additionally, the device is unsuitable for producing emulsions comprising sensitive compounds that can be destroyed by high pressure, resulting in an increase in temperature [142,151].

3.3. Ultrasound Homogenizer

Ultrasonic homogenizers exploit high-intensity ultrasound waves to generate the droplets. Ultrasound in the range 16–100 kHz has the capacity to generate physical changes to liquids thanks to the cavitation phenomenon. In order to create emulsions with nanosized droplets, sonication greater than 20 kHz is required. In general, these devices consist of three main components: a power generator that provides and regulated the power, a transducer (also known as a converter) containing piezoelectric crystals capable of converting electrical energy into high-frequency mechanical motion, and a titanium probe that rapidly vibrates in a longitudinal direction, transmitting ultrasonic energy to the sample. These ultrasound waves produce mechanical vibrations and acoustic cavitation, which allow the bubbles to break. The collapse of these bubbles generates strong shockwaves, which create significant shear stresses and localized turbulence, resulting in the collapse of droplets and emulsion formation. Ultrasound emulsification can produce droplet sizes as small as 0.1 µm in diameter [143,152–155].

There are two sonication techniques (Figure 2c):

- Direct: a probe sonicator is used, in which an ultrasonic horn or sonotrode is immersed in the liquid, transmitting high-intensity ultrasonic waves directly through the sonotrode;
- Indirect: ultrasonic waves are transmitted through the vessel and into the liquid via a water bath.

The operative parameters that affect the emulsion formation are ultrasound frequency, power, temperature, device parameters, such as sonotrode diameter, and surface tension or viscosity of the medium [143,156]. These production techniques have some advantages, such as ease of operation, low cost, ease of maintenance, and excellent cleanliness. Moreover, reduced energy consumption is required; in fact, this apparatus is more energy efficient. The main drawbacks associated with this equipment are the increase in temperature and the consequent damage to heat-sensitive components. In addition, ultrasound homogenization is principally used to form a small amount of emulsion; therefore, it is used at a laboratory scale [143,157].

3.4. Membrane Homogenizer

Membrane emulsification involves the use of a membrane with microscopic holes through which the dispersed phase is forced to pass. In this process, a transmembrane pressure is used to force the dispersed phase to pass through the membrane. Small droplets are generated at the outlet and are subsequently carried away by the continuous phase flowing over the membrane surface (Figure 2d). Two different types of membrane emulsification technology can be distinguished. Direct Membrane Emulsification (DME) and Premix Membrane Emulsification (PME). In the case of DME, the dispersed phase is driven through the pores of the membrane at controlled injection rates and shear conditions, resulting in the reproducible droplet formation on the downstream side of the membrane, which is in contact with the cross-flow or agitated continuous phase. Conversely, in PME, a coarse emulsion or premix is extruded through the membrane to produce a fine emulsion by breaking up droplets within a porous structure [158–162].

Membrane homogenization can be conducted in either a batch or continuous process. In the case of a batch process, the dispersed phase is forced through a membrane that is immersed in the continuous phase. For the continuous process, the dispersed phase is forced through a membrane that is located in a tube through which flows the continuous phase.

The membrane properties are fundamental to the control of the droplet size. In particular, the membrane pore size and shape influence droplet size and polydispersity. The membrane polarity determines the type of emulsions that can be formed: hydrophobic membranes are capable of producing w/o emulsions, while hydrophilic membranes are necessary for creating o/w emulsions. In addition to these parameters, transmembrane pressure, wall shear stress, and phase parameters (e.g., interfacial tension, viscosity, and density of continuous and disperse phases) affect the emulsion formation. This process is highly energy efficient and can produce emulsions with a narrow droplet size distribution, achieving droplet sizes down to 0.3 μm in diameter, but is typically used to produce larger droplets [159,163,164]. The principal advantages of membrane emulsification are the production of uniform particles, control of droplet size by appropriate choice of membrane pore size, reduced shear stress, reduced energy requirements, high versatility, gentle working conditions, and precise, selective, and flexible production. The main critical aspect observed is related to the fouling phenomenon, which can affect the membrane, especially in the case of protein surfactants. Moreover, the low dispersed phase flux is another drawback of this technology, which mainly limits its application to the laboratory level [159,163].

3.5. Microfluidic Emulsification

Microfluidic emulsification allows the emulsion formation through the manipulation of two immiscible phases within a microchannel. These apparatuses are composed of a pumping device and a microfluidic chip. The pump allows the liquids to flow inside the microfluidic chip, which is composed of a channel and a junction for the interaction of the two fluids. The formation of droplets is enabled by the junction.

The fundamental component of these devices is the microfluidic chip, and there are several configurations for producing emulsion. The most diffused configurations are co-flowing devices, flow-focusing devices, and cross-flowing devices, most commonly called T-shaped junction or T-junction (Figure 2e). In each configuration, different geometries and different fluid interactions are used for emulsion formation [165–171].

The simplest method used is the co-flowing device, which is based on the principle of concentric microchannels. The dispersed phase is injected into a central capillary channel, which is placed in the middle of another channel of larger dimensions. Droplet break-up occurs at the end of the capillary channel due to its instability. Two different formation regimes can be observed: the dripping regime and the jetting regime. These regimes differ in the position of the droplet break-up. In the dripping regime, the break-up occurs immediately after the junction, while, in the jetting regime, it occurs further downstream from the junction. In the dripping regime, the droplet formation is related to the competition between interfacial forces and viscous forces. In particular, the interfacial force tends to pull back the forming droplets to the junction, so droplet formation occurs when the viscous forces overcome the pinning force created by the interfacial tension. In the jetting regime, the two immiscible fluids flow together in the main channel, and droplet break-up takes place after the junction. A jet is formed, and the break-up happens at the end of the jet. The transition from dripping to jetting is a function of the increasing velocity of the continuous phase; in particular, it occurs at a certain critical velocity [162,172,173].

In the T-junction device, the continuous phase flows through a channel, while the dispersed phase comes through a perpendicular channel, and they meet in the junction area. The droplet break-up occurs at the junction, and various formation regimes can be observed. Three potential regimes have been identified: dripping, squeezing, and jetting. In the squeezing regime, the dispersed phase tends to block the main channel, thereby reducing the channel pressure. When the pressure drops across the dispersed phase becomes too great, a droplet is produced. In the dripping regime, the dispersed phase breaks up immediately after the junction. Finally, in the jetting regime, a jet is formed after the junction, and droplets are formed from the jet [174–176].

Finally, in the flow-focusing device, the continuous phase flows into two side channels, and the dispersed phase is injected into a central one. The two streams of continuous phase surround the dispersed phase and force droplet formation. Again, three different regimes can occur, which are the same as the T-junction device. This configuration is the most commonly used for droplet production because it allows better control and stable droplet production with respect to the T-junction, due to the symmetric flow used in the flow focusing device [174,177,178].

Several parameters influence the droplet formation. First, the fluid properties, such as interfacial tension and viscosity of both phases, are fundamental for the correct formation. In addition, the geometry of the intersection where the two phases meet and the flow rates have to be considered to determine the local stresses that deform the interface and lead to droplet production. Finally, the chip material influences the formation of the desired emulsion type. The most used materials are polydimethylsiloxane (PDMS), poly(methyl methacrylate) (PMMA), and glass. Each material shows a hydrophilic or hydrophobic nature, and they are more suitable for the production of the different emulsion types.

However, surface modification can be applied to the materials to change their surface properties and to obtain the desired one. For example, PDMS is hydrophobic in nature, but, through surface treatment, it is possible to make it hydrophilic to produce o/w or w/o/w emulsion, for which it is necessary to ensure wetting of the water phase and to avoid the oil phase adhering to the channel wall [176,179–182].

This technique offers numerous advantages over conventional techniques, including precise emulsification, homogeneity of droplet sizes, and precise control of physicochemical conditions. This high degree of control is a very important aspect at both the research and industrial levels. Moreover, microfluidic devices are highly versatile, as evidenced by the ability to customize microfluidic chips in terms of geometry and materials. In fact, all the desired droplet sizes can be produced, in particular, up to 100 nm. The main drawbacks are related to the facility of clogging, which compromises the precision of the manufacturing process, and the complexity of scaling up, which presents a challenge for industrial production [170,179].

As demonstrated in the previous chapter, several apparatuses can be used for emulsion production. There is no one perfect method for emulsion production, and the selection of an optimal device depends on several factors, such as the desired droplet size, the process volume, the acceptable energy consumption, and the physicochemical properties of the two involved fluids. Once the emulsifier has been selected, it is essential to optimize the operating parameters to achieve the desired characteristics of the final product. The following Table 2 provides a summary of the potential sizes, advantages, and disadvantages of the techniques illustrated. These are the initial criteria for selecting the most appropriate emulsifier [102,143].

Table 2. Droplet size, advantages, disadvantages, and scale of emulsion production processes.

Process	Droplet Size	Advantages	Disadvantages	Scale Up
Rotor–stator emulsifier	>1 µm	Ease to install, user friendly, low investment cost, high throughput, compatible with viscous systems, large volume production	Wide droplet size distribution, nanoemulsions cannot be produced	Laboratory and industrial scale
High-pressure homogenizer	>0.1 µm	Possibility to produce nanoemulsion	Wide droplet size distribution, not suitable for sensitive compounds	Laboratory and industrial scale
Ultrasound homogenizer	>0.1 µm	Ease of operation, low cost, ease of maintenance, excellent cleanliness, reduced energy consumption	High increase in temperature, not suitable for sensitive compounds, small product volume	Laboratory scale
Membrane homogenizer	>0.3 µm	Highly energy efficient, narrow particle size distribution, reduced shear stress, low energy requirements, high versatility	Fouling phenomenon, low dispersed phase flux	Laboratory scale
Microfluidic emulsification	>0.1 µm	Precise emulsification, high homogeneity of droplet size, highly versatility, ability of customize microfluidic chip	Facility of clogging, complexity of scale up	Laboratory scale

4. Polymeric Particles Production Processes Based on Emulsions

The synthesis methods of polymeric particles are generally classified into two main categories: the direct polymerization of monomers and the dispersion of preformed polymers. Within each of these two wide categories, there are several techniques for producing polymeric particles. This section will focus on emulsion-based techniques that utilize preformed polymers. This category has been selected among all the techniques proposed in the literature due to its flexibility, efficiency, and ability to encapsulate both hydrophilic and hydrophobic compounds with a good control over the particle dimensions. Moreover, the emulsion-based techniques have the advantage of precise control of size, structure, and composition of emulsion droplets, which is pivotal to having highly controllable synthesis of polymeric particles. The use of emulsion as a particle template provides the ability to produce polymeric particles with the desired characteristics and properties [89,116,183,184].

All of these methods start with the production of an emulsion using the processes described above. Therefore, the production process can be divided into two steps: a first emulsification step to create an o/w or w/o/w emulsion, followed by a second step to form polymeric particles, which varies depending on the method used. The specific method is related to the removal of the solvent required to produce the particles. Once the solvent has been removed, the precipitation of the polymer allows the particle production and encapsulation of the active agents. The different techniques differ in the way the solvent is removed. In particular, the most used methods are emulsification solvent evaporation, emulsification solvent diffusion, salting-out, and supercritical emulsion extraction (Figure 3) [184,185].

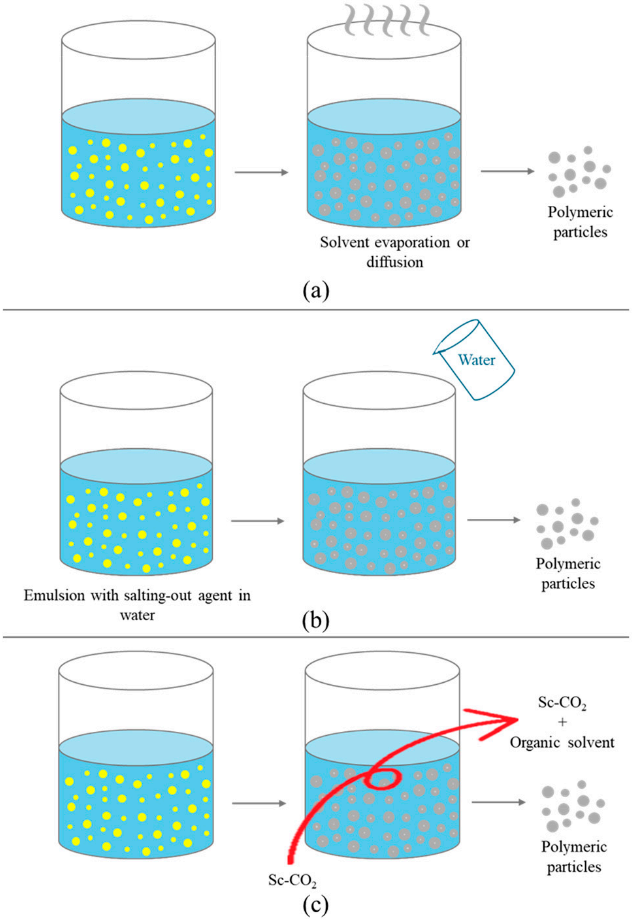

Figure 3. Polymeric particles production methods: (**a**) emulsification solvent evaporation or diffusion; (**b**) salting-out; (**c**) supercritical emulsion extraction.

4.1. Emulsion Solvent Evaporation

The emulsion solvent evaporation technique (Figure 3a) is one of the first developed methods for particle production, particularly in the pharmaceutical field. This method involves the slow evaporation of the solvent during the second step. Thanks to the solvent removal, the polymer precipitation occurs with the resulting particle production. After evaporation, which is achieved by continuous magnetic stirring at room temperature or at different temperatures depending on the type of solvent, the produced particles are recovered from the aqueous suspension obtained by centrifugation, filtration, or other techniques [186–188].

The most important parameters for size control and high encapsulation efficiency are the emulsification conditions, the type and concentration of the polymer, the solvent used, and the viscosity of the emulsion phases. The stability of the produced emulsion is fundamental to ensure the correct particle formation; therefore, the stabilizing agent plays a key role in guaranteeing good physical stability. The manipulation of these process parameters allows the size to be optimized and the encapsulation efficiency to be maximized. This method is versatile and simple; otherwise, the main disadvantages are related to the difficulty in controlling the particle size distribution due to the long evaporation time, which can increase the aggregation, and the residual solvent in the product [189].

4.2. Emulsion Solvent Diffusion

In the emulsion solvent diffusion (Figure 3a), the removal of the solvent from the oily phase occurs by diffusion from the aqueous phase and the consequent particle solidification [164]. In this case, the choice of the solvent is fundamental; in fact, the selected solvent must be partially miscible in the aqueous phase to allow the solvent diffusion. Sometimes, a dilution of the aqueous phase is necessary to increase the solvent diffusion. The produced particles are collected with the same methods described above for the emulsion solvent evaporation [148–150].

As for the emulsion solvent evaporation, the same operating parameters are fundamental to control particle production. In this case, another important parameter is the solvent. The solubility parameter and interaction parameter are fundamental to understanding the behavior of the system. A lower solvent–water interaction parameter means a higher solvent–water affinity for solvent diffusion, whereas a higher polymer–solvent interaction parameter facilitates solvent diffusion. Generally, a major affinity of solvent and polymer, as well as solvent and water, causes an increase in particle size. This method is simple and highly reproducible. The main drawback is the high amount of required water to be eliminated from the suspension, the residual solvent, and the long process time [151].

4.3. Salting-Out

The salting-out method (Figure 3b) is a variation of the emulsion solvent diffusion techniques using the salting-out effect. In this case, a salting-out agent is contained in the aqueous phase. The salting-out agent must not be soluble in the organic solvent, while the organic solvent is partially soluble in water. The most commonly used salting-out agents are magnesium chloride, sodium chloride, calcium chloride, and magnesium acetate. The used solvents are usually totally miscible with water, such as acetone and ethanol [190,191]. The correct emulsion formation is possible due to the presence of salting-out, which causes the initial immiscibility between the solvent and the water; in fact, it impedes mixing between the solvent and water. Once the emulsion is produced, it is diluted with water to reduce the ionic strength in the electrolyte and to allow the migration of the solvent from the oil phase to the water one, with the consequent solidification of the polymer. Lastly, the salting agents are usually removed by filtration, and the particles are after collected [190,192].

As before, the emulsion acts as a particle template, and the same operating process parameters influence the formed polymeric particles. The main advantage is the possibility to use less hazardous solvents; in fact, chlorinated solvents are not used. In addition, there is no need to raise the temperature, which is useful when processing heat-sensitive substances. The main disadvantages are the extensive washing step and the ability to encapsulate only lipophilic compounds [89,184,190].

4.4. Supercritical Emulsion Extraction

Supercritical emulsion extraction (Figure 3c) is part of the supercritical fluid technology that is widely used for polymeric particle preparation, such as rapid expansion of supercritical solution, supercritical antisolvent precipitation, and supercritical-assisted atomization. Supercritical fluid and dense gas technology is an interesting and effective technique of particle production that avoids most of the drawbacks of the traditional methods.

Focusing on supercritical emulsion extraction, this is the innovative version of the conventional solvent evaporation method. The principle of the process is based on the use of supercritical fluid, such as carbon dioxide (CO_2), to rapidly and selectively extract the organic solvent. Removal of the solvent causes supersaturation of the polymer in the oil phase, resulting in polymer precipitation and particle formation. This process produces a particle suspension, and the particles can be recovered by centrifugation, filtration, or other techniques. The solvent can also be recovered and recycled [193–195].

In this case, besides the parameters that affect the characteristic of the emulsion, pressure and temperature are of primary importance. The operating pressure and temperature conditions influence the extraction of the organic solvent and are, therefore, chosen to maximize solvent removal. Finally, the CO_2 flow rate is directly related to the solvent extraction rate, and it has a significant effect on the particle size and on the encapsulation efficiency [25,196].

The main advantages are the high control of particle size and morphology due to the use of emulsions and the rapid kinetics of the supercritical fluid extraction process. The use of this technique also allows the reduction of solvent residues in the particles. This technique is also versatile; it is possible to encapsulate hydrophilic and lipophilic compounds by modifying the initial emulsion. In particular, oil-in-water emulsions are used for lipophilic compounds, while water-in-oil-in-water emulsions are used for hydrophilic ones. The use of CO_2 allows for working in mild conditions, which is essential for preserving the properties of sensitive compounds. Moreover, this technique can also be carried out in continuous mode using a packed column, allowing for a possible scale-up. The main drawbacks are related to the high investment costs and to the safety issue, due to the high working pressure [25,196,197].

Several methodologies can be used for polymeric particle production. The following Table 3 provides a summary of the advantages and disadvantages of each technique in order to select the most appropriate technique.

Table 3. Advantages and disadvantages of polymeric particles production processes.

Process	Advantages	Disadvantages
Emulsion solvent evaporation	Versatile and simple	Difficulty in controlling the particle size distribution, residual solvent in the product
Emulsion solvent diffusion	Simple and highly reproducible	High amount of required water, residual solvent in the product, long process time

Table 3. *Cont.*

Process	Advantages	Disadvantages
Salting-out	Less hazardous solvents, no increase in temperature	Extensive washing step, ability to encapsulate only lipophilic compounds
Supercritical emulsion extraction	High control of particle size and morphology, reduction of solvent residues, versatile, possibility to work in continuous mode	High investment costs, safety issues

5. Conclusions

Emulsions, which consist of two immiscible liquid phases, offer excellent encapsulation systems due to their unique structure. Various production techniques are available, enabling the creation of emulsions with tailored properties for specific applications. Both laboratory-scale and industrial-scale technologies are well-established. Similarly, numerous methods exist for the production of polymeric particles, allowing customization to meet diverse requirements. Therefore, emulsion-based systems are characterized by a high degree of adaptability and versatility.

Despite the wide range of techniques, challenges remain in optimizing scalability and reproducibility, particularly for industrial applications. These aspects are particularly necessary for the promising techniques, such as membrane emulsification and microfluidization, that are only available at laboratory scale. Moreover, the development of greener processes that reduce the use of hazardous solvents is another important challenge. Further investigation is needed to refine these techniques and address the current limitations, but the high number of application sectors ensures their continued development, holding great potential for future advancements in encapsulation technologies.

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Abbreviations

The following abbreviations are used in this manuscript:

o/w	Oil-in-water emulsion
w/o	Water-in-oil emulsion
w/o/w	Water-in-oil-in-water emulsion
HIPE	High internal phase emulsion
HLB	Hydrophile–Lipophile Balance
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
DLS	Dynamic light scattering
SLS	Static light scattering
DME	Direct membrane emulsification
PME	Premix membrane emulsification

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