Review

Films based on biopolymers incorporated with active compounds encapsulated in emulsions: Properties and potential applications – A review

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Review

Films Based on Biopolymers Incorporated with Active Compounds Encapsulated in Emulsions: Properties and Potential Applications—A Review

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Abstract: Rising consumer demand for more safety, healthy and fresh-like food has given new concepts for food packaging. Besides, the growing concern with environmental issues has increased the search for materials from non-petroleum sources and biodegradable ones. Thus, active films based on biopolymers loaded with natural active compounds have potential to be used as food packaging. However, there are a lot of lipophilic active compounds that are a problem to incorporate in hydrophilic matrices, such as polysaccharides and proteins. One way to overcome these challenges is adding these compounds encapsulated in O/W emulsions. The incorporation of emulsion in biopolymeric matrix has influence in the film properties, such as mechanical, barrier, optical, among other. In this way, this review aims to point out the main characteristics of the emulsions systems encapsulating active compounds and its influence in the film properties and to present and discus critically the recent advances in the area.

Keywords: actives films; proteins; polysaccharides; lipophilic compounds

1. Introduction

Food packaging is used to maintain the safety and quality of food products during storage and transportation, protecting them against undesirable external factors. Consumer demand for convenient, safer, healthier, and fresh-like food with improved shelf life and environmental concerns has given new concepts and functions to food packaging [1]. In addition to the usual inert passive containment and protective properties, these novel food packaging should have active compounds to enhance the performance of the package system and should preferably be produced with biodegradable ingredients from renewable sources [2–4]. As a result, there is a growing request for biopolymer-based active packaging, which has stimulated studies in search of new strategies, boosting the development of a novel generation of food packaging.

Active packaging systems are produced by incorporating active ingredients into the packaging material or the package's headspace, which can release or absorb substances into or from the packaged food or from the environment surrounding the food, extending its shelf life without compromising its quality and safety [5]. The active packaging systems can perform diverse functions: i) absorbing/scavenging of substances such as carbon dioxide, oxygen, ethylene, and moisture; ii) releasing/emitting of compounds, such as ethanol, antioxidants, preservatives, flavors; iii) food component removal property (e.g., lactose, cholesterol); and iv) microbial and quality control [6].

Active films based on biopolymers are promising materials for active packaging design. In addition to the functional properties promoted by the incorporation of active compounds, such as antimicrobial and antioxidant compounds, these film types are an alternative to synthetic packaging materials, as they produced from biodegradable, renewable, and environmentally friendly materials

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[7,8]. The most common biopolymers used in the production of active films are polysaccharides (*e.g.*, starch, chitosan, pectin, cellulose derivatives, gums) and proteins (e.*g.*, gelatin, whey protein, caseinate, soy protein, zein) [9].

Regarding functionality, a wide range of active compounds have been added to the biopolymeric matrix of the active films [6,10], such as extracts from herbs and spices [11,12] or from agricultural by-products [13,14], essential oils (EO) [15,16], and lipophilic compounds [17–19]. Antimicrobial and antioxidant agents are the most studied active components since the growth of pathogenic and/or spoilage microorganisms and the oxidative degradation are the main cause of food spoilage [6].

In recent decades, interest in adding lipophilic bioactive components in films has increased, as they are powerful antimicrobial and antioxidant agents [20,21]. There are several studies incorporating directly lipophilic compounds into filmogenic matrices, however, chemical and physical stability of these films is limited [22,23]. Furthermore, these bioactive compounds have low solubility in water, due their high hydrophobicity, and are susceptible to oxygen, temperature, pH and ionic strength. These characteristics hinder the incorporation of hydrophobic functional compounds in hydrophilic matrices and can reduce their bioavailability [24,25].

One strategy to overcome these challenges is to encapsulate lipophilic bioactive compounds in the oil phase of oil-in-water (O/W) emulsions prior to their incorporation into a filmogenic solution. The use of O/W emulsions allows the dispersion of a hydrophobic bioactive compound and an oil phase in a hydrophilic matrix [17,19,26–28]. Furthermore, emulsions can protect lipophilic active ingredients against external factors and promote their controlled release [29–32].

In this context, the aim of this review is to present and discuss critically the recent advances in the design of active films incorporated with bioactive compound-loaded emulsions and to highlight how the characteristics of the emulsions can affect the film properties and their performance as active packaging. Active compound retention, active film stability, and release behavior in food simulants were also pointed out.

2. Emulsions

Emulsions are colloidal systems consisting of two or more completely or partially immiscible phases, such as oil and water. For a liquid system, one of the liquids is dispersed as droplets (dispersed phase) in another liquid continuous phase forming the single oil-in-water (O/W) or water-in-oil (W/O) emulsions [33]. More complex systems, such as water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) emulsions, can also be produced from single emulsions. In W/O/W double emulsion, smaller water droplets are dispersed in an oil phase (W/O) [34,35], which is subsequently dispersed in an external aqueous phase (W) [36]. The double emulsions can concurrently encapsulate hydrophilic and hydrophobic bioactive molecules, however the stabilization of two different interfaces during the emulsion processing and storage is still a challenge [37–39]. Figure 1 shows a schematic view of the main emulsion designs.

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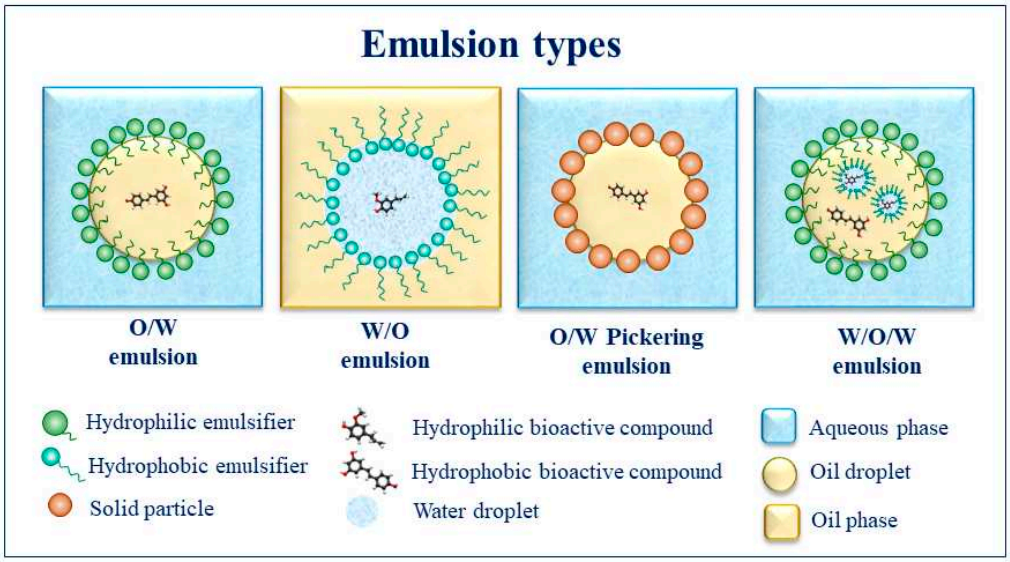

Figure 1. Different emulsion types utilized to encapsulate and protect bioactive compounds to produce biopolymer-based action films (Source: Authors).

The emulsions are thermodynamically unstable and tend to separate into an oil and an aqueous phase because the free energy of the separated phases is lower than the emulsified system [40]. However, a great kinetic stability can be reached by adding stabilizers, such as emulsifiers (surfactants, proteins, and carbohydrates) or solid particles [41,42]. These compounds can improve the stability of systems over time by retarding or preventing destabilization mechanisms such as creaming/sedimentation, flocculation, coalescence, and Ostwald ripening [43]. Differently from traditional emulsions, microemulsions are thermodynamically stable systems composed of nanometer-sized particles (formed by oil, surfactant/co-surfactant) dispersed in an aqueous phase [44] (Figure 2).

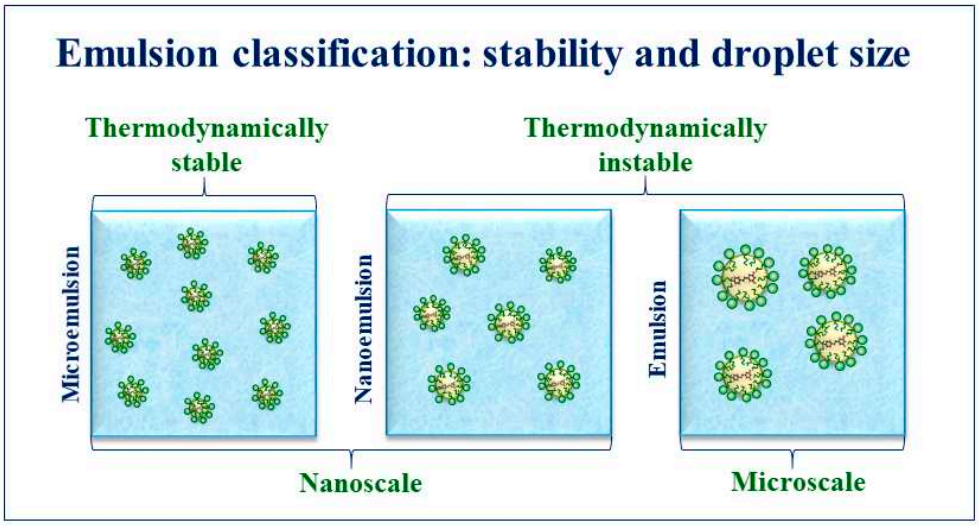

Figure 2. Classification of emulsions according to thermodynamic stability and droplet size (Source: Authors).

Emulsions can be classified according to droplet size in emulsions or nanoemulsions. Usually, nanoemulsions present droplets ranging between 20 and 200 nm, while colloidal dispersions with droplet diameters larger than 200 nm are namely emulsions [40,45]. However, different average droplet diameters are frequently used as the demarcation point between nanoemulsions and emulsions, which can range between 20 and 200nm [45–47]. Although both colloidal systems are thermodynamically unstable, a reduction in droplet size can enhance the kinetic stability and increase

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the specific surface area, improving the bioactivity of lipophilic active compounds vehiculated in nanoemulsions [45].

Stabilization by solid particles is another approach to improve the kinetic stability of emulsions, which are called Pickering emulsions. Compared to conventional emulsions, Pickering emulsions can be stable for a longer period, as micro- or nanometer sized particles irreversibly adsorb at interfaces [48]. Furthermore, this type of stabilization offers distinct advantages, especially in the field of delivery of bioactive compounds, such as good long-term kinetic stability, low cytotoxicity, controlled release under specific conditions (such as temperature, pH, light intensity, ionic strength) and targeted of the bioactive for enhanced functionality in food [49–52].

Overall, emulsified systems have been used to encapsulate various hydrophobic active compounds, such as hesperidin [24,53], curcumin [54,55], resveratrol [56], β-carotene [57], pepper oil [58] and a wide range of essential oils (e.g., oregano, lemongrass, cinnamon, clove, American mint and pectinata) [59–61], among others. The use of emulsions as encapsulating system of the bioactive compounds can prevent their degradation, preserve their bioactivity and improve their performance in different ways: i) the continuous phase and the interfacial layer of the emulsion can protect the bioactive compounds from prooxidant molecules and environmental conditions that could degrade them [55,62]; ii) allowing the incorporation and uniform distribution of hydrophobic molecules and oil phase in hydrophilic biopolymeric matrices [63,64] iii) masking undesirable flavors [65,66]; and iv) promoting controlled release of active compounds [67,68].

So, because of these advantages emulsified system such as Pickering emulsions [69–71], nanoemulsions [19,64,72] and emulsions [73,74] have been widely used to incorporate hydrophobic compounds in biopolymeric matrices. Although most active compounds encapsulated in O/W emulsions and incorporated into biopolymer matrix are hydrophobic, recently, double emulsions (W/O/W) charged with hydrophilic active compounds in the inner aqueous phase were successfully used to produce active films [75,76]. A similar W/O/W system was also used to encapsulate simultaneously hydrophilic (nisin) and hydrophobic (carvacrol) active compounds and fabricate chitosan-based films to preserve the salmon fillets [77].

3. Films incorporated with bioactive compound-charged emulsions

Figure 3 shows a schematic representation of the production system of active films incorporated with emulsions. First, the emulsion is produced with the active compound in the oil phase. After that, the emulsion is added to a biopolymeric solution and the mixture is carefully homogenized forming a homogeneous film-forming solution (FFS). The film is usually produced by casting method, in which the FFS is poured on a plate support and dried until solvent evaporation [78]. When active films are applied as food packaging, they can offer protection against light, moisture, and gas migration from/to the external environment of the packaging. Besides, they can release the active ingredients in the internal space of the package promoting an antioxidant and/or antimicrobial effect that can extend the food product's shelf life.

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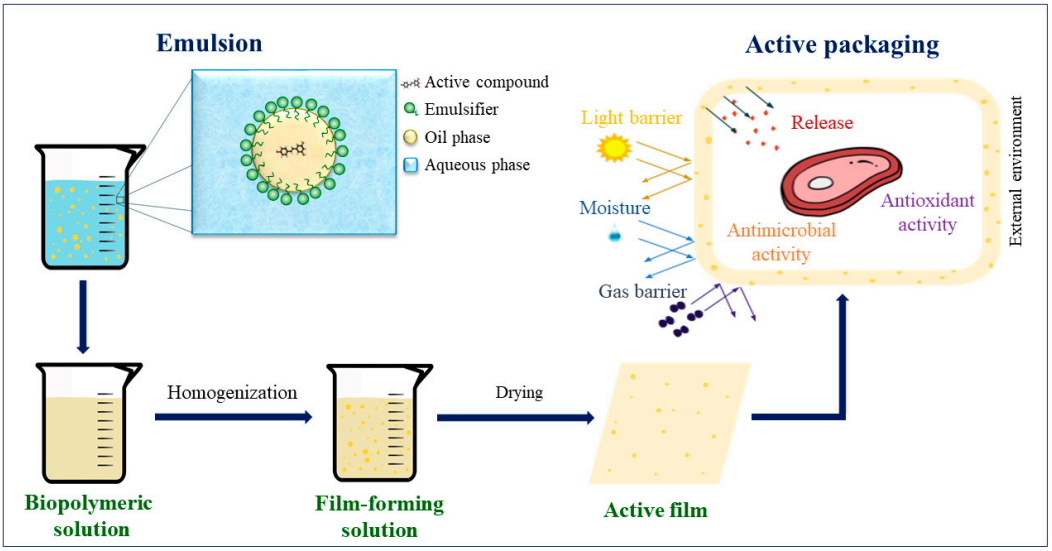

Figure 3. Scheme of the production of active packaging incorporated with emulsified systems and application simulation. (Source: [79] with modifications).

For the best of author's knowledge, the first works on development of active films by incorporation of encapsulated active compounds in nanoemulsions were carried out by Bilbao-Sáinz et al. (2010), which studied the incorporation of nanoemulsions protecting essential oil in isolated soybean protein-based films [80], and Otoni et al. (2014a) with a study of incorporation of nanoemulsion encapsulating cinnamaldehyde in pectin/papaya puree films [81]. Previously, some articles studying emulsified-films were published, nevertheless, in these cases, the emulsifying process occurred in the film-forming solution. The oil phase (containing active compounds) and emulsifier were directly added in the biopolymeric film-forming solution [82–85]. However, it is not the purpose of this review to approach this type of studies.

In the last five years, the number of published articles on emulsion-incorporated active films has increased, considering all the emulsion types (nanoemulsions, emulsions, double emulsions and Pickering emulsions (Figure 4). A search on Web of Science Core Collection using "emulsion" and "active film" as the topic and selecting the "Food Science & Technology" category led to 161 results, of which 117 were published from 2018. When other terms such as "nanoemulsion", "microemulsion", "Pickering emulsion" or "double emulsion" were added to the search it was possible to note that this research area has a significant potential to grow since the influence of emulsion (emulsion type, droplet size and nature of the emulsifier or solid particle) on the film structure is not fully understood.

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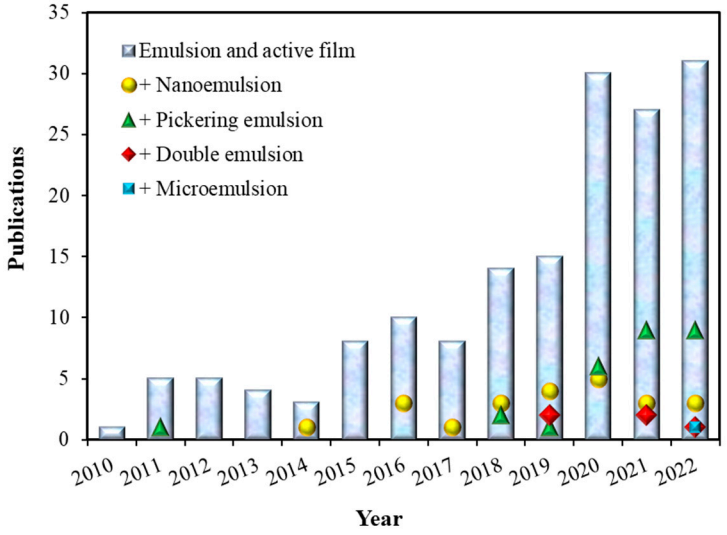

Figure 4. Number of publications using terms "emulsion" and "active film" added to the keywords "nanoemulsion", "microemulsion", "Pickering emulsion" or "double emulsion" in the "Food Science Technology" category in Web of Science Core Collection [86].

Recent studies on encapsulation of lipophilic bioactive compounds into emulsions to design of active films are presented in Table 1. The most used biopolymers for producing active films loaded with bioactive compounds encapsulated in emulsions are starch from different sources, gelatin from various sources, and chitosan, among others less common. Blends composed of two or more biopolymers have also been widely studied (Table 1).

Table 1. Summarizes some of the most recent studies that used different emulsion types to encapsulate a range bioactive compound before their incorporation into film-forming solutions.

Biopolymer	Emulsion type	Active compound	Reference
Chitosan	Pickering	Cinnamon EO	[69]
	Double emulsion	Nisin/carvacrol	[77]
	Pickering	Cinnamon and perilla EO	[87]
	Double emulsion	"Pitanga" leaf extract	[76]
	Pickering	Clove EO	[88]
	Nanoemulsion	Cinnamon EO	[89]
	Nanoemulsion	Cumin EO	[90]
	Pickering	Clove EO	[71]
	Emulsion	Cinnamon EO	[91]
	Microemulsion	Cinnamon bark oil	[92]
	Nanoemulsion	Carvacrol	[18]
Gelatin	Nanoemulsion	Lavender EO	[93]
	Double emulsion	"Pitanga" leaf extract	[76]
	Nanoemulsion	Cinnamaldehyde	[72]
	Pickering	Hesperidin	[17]
	Nanoemulsion	Eugenol	[94]
	Nanoemulsion	α-tocopherol, garlic essential oil and cinnamaldehyde	[63]

Gelatin	Nanoemulsion	Rutin	[95]
	Nanoemulsion	Ginger EO	[96]
Starch	Nanoemulsion	Curcumin	[19]
	Pickering	Ho wood, cardamom, and cinnamon EO	[97]
	Emulsion	Lemongrass EO	[73]
	Micro and nanoemulsion	Carnauba wax	[74]
	Pickering	Cinnamon EO	[98]
Whey protein (WPI)	Nanoemulsion	Bergamot oil	[23]
	Nanoemulsion	α-tocopherol	[99]
	Nanoemulsion	*Grammosciadium ptrocarpum* Bioss. EO	[100]
Pectin	Emulsion	Clove EO	[101]
	Nanoemulsion and Pickering	Marjoram EO	[102]
	Nanoemulsion	Copaiba oil	[64]
	Pickering	Cinnamaldehyde	[103]
Sodium caseinate	Nanoemulsion	Cinnamon EO	[104]
Sodium alginate	Emulsion	Cinamon EO	[105]
Soy protein isolate	Micro and nanoemulsion	Carvacrol and cinnamaldehyde	[47]
Carboxymethyl cellulose (CMC)	Emulsion	Licorice EO	[26]
Cellulose nanofibrils	Pickering	Oregano EO	[106]
Konjac glucomannan	Pickering	Oregano EO	[107]
Pullulan	Nanoemulsion	Cinnamon EO	[108]
	Emulsion	Cinnamaldehyde, thymol and eugenol	[68]
Basil seed gum	Nanoemulsion	*Zataria multiflora* EO	[109]
Chitosan/gelatin	Pickering	Cinnamon EO and curcumin	[110]
	Double emulsion	"Pitanga" leaf extract	[76]
	Nanoemulsion	a-tocopherol, cin- namaldehyde and garlic EO	[28]
	Nanoemulsion	α-tocopherol, garlic EO and cinnamaldehyde	[63]
Chitosan/Sodium caseinate blend	Nanoemulsion	α-tocopherol, garlic EO and cinnamaldehyde	[63]
Chitosan/Polylactic acid bilayer	Pickering	Thymol	[111]

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Gelatin/agar	Pickering	Clove EO	[70]
	Pickering	Clove EO	[112]
Gelatin/pullulan	Nanoemulsion and Pickering	Clove EO	[79]
Starch/PVA	Pickering	Curcumin	[22]
	Nanoemulsion	Carvacrol	[113]
	Nanoemulsion	Carvacrol	[27]
Pectin/Papaya puree	Nanoemulsion	Cinnamaldehyde	[81]
Pullulan/xanthan gum/locust bean gum	Nanoemulsion	Cinnamaldehyde, thymol and eugenol	[114]
Carrageenan/agar	Pickering	Tea tree oil	[115]
Tamarind starch/WPI	Nanoemulsion	Thyme EO	[116]
Konjac glucomannan/pullulan	Pickering	Tea tree EO	[117]

Essential oils (EOs) are the more commonly used bioactive compounds for developing biopolymer-based active films due to their natural origin, and excellent antimicrobial and antioxidant properties [10]. Among the EOs, cinnamon and clove essential oils are the mainly studied compounds (Table 1).

3.1. Emulsion-encapsulated bioactive compound versus bioactive compound in native form

Some authors have evaluated the advantages of producing active films with emulsified active compounds [22,23,118]. One way to assess this is by comparing the addition of native form of the active compound versus its emulsified form.

The comparison of adding bergamot oil directly into the WPI matrix and in nanoemulsioned form was evaluated by Sogut (2020). The films with bergamot oil nanoemulsions stabilized by nanocellulose presented higher tensile strength and elastic modulus, and lower elongation at break than those directly incorporated with bergamot oil. Moreover, nanoemulsion-charged films had lower WVP than systems incorporated with bergamot oil at the same oil concentration. The addition of nanodroplets increased the tortuosity of films, consequently reducing the mass diffusivity. The nanoemulsions decreased the UV-Vis light transmittance and increased the opacity of the films compared with control (pure WPI film) and oil direct incorporation systems. These results suggest that films with nanoemulsion can be used as light barrier. In addition, the presence of nanoemulsions stabilized by nanocellulose delayed the release of the bioactive compound in food simulant fluid (ethanol 50%). This behavior was associated with the closer structure formed by the interaction between WPI and bergamot oil in the presence of nanocellulose [23].

Curcumin-loaded Pickering emulsions and curcumin solution were incorporated in corn starch/PVA blend films [22]. Curcumin solution-film was more stretchable and resistant compared to control and Pickering emulsion systems, and a considerable decrease in tensile strength and elongation at break was observed in Pickering emulsion-films. Moreover, WVP and oxygen permeability decreased in films with the presence of Pickering emulsions. Regarding the functionality, active film with curcumin solution showed lower antioxidant activity than those with curcumin protected by Pickering emulsions. During the production process of films, the curcumin added directly into the biopolymeric matrix was more easily degraded when exposed to heating, cavitation, and drying. On the other hand, the thick interfacial layer of Pickering emulsions protected the curcumin from oxidation during the production films, preserving its bioactivity. Furthermore, Pickering emulsions also reduced the rate of curcumin degradation by light during storage, while curcumin-loaded films showed a rapid decrease in antioxidant activity over time. For the same

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reason, the emulsified films presented higher antimicrobial activity than the free curcumin-loaded one [22].

Xanthan gum-based FFS containing EOs (clove, cinnamon, and oregano) and nanoemulsified EOs were evaluated in relation to their *in vitro* antimicrobial activity [118]. In the same concentrations of essential oils, the active FFS with free active compounds was more effective in reducing microbial growth than FFS with nanoemulsified oils. This behavior may be associated with components such as crodamol (saturated triacylglycerol) and surfactant, which form additional barriers to the diffusion the EOs, controlling their release [118]. It is important to point out that the active compounds were not heated during the FFS production, and were not subjected to drying. Thus, the protective effect of emulsions from heating and during storage was not evaluated in this case.

4. Influence of emulsion characteristics in active film properties

There are many advantages to using emulsified bioactive compounds in producing active films as seen in the previous item. However, the incorporation of emulsions affects the physicochemical and functional properties of films, such as mechanical and barrier properties and antimicrobial and antioxidant activities. It is interesting to highlight that characteristics of the emulsified systems, such as emulsion type, droplet size, and emulsifier nature, can also influence the structure and biofunctionality active films, as well their performance as active packaging, as discussed in more detail below (Figure 5) [26,69,94,95].

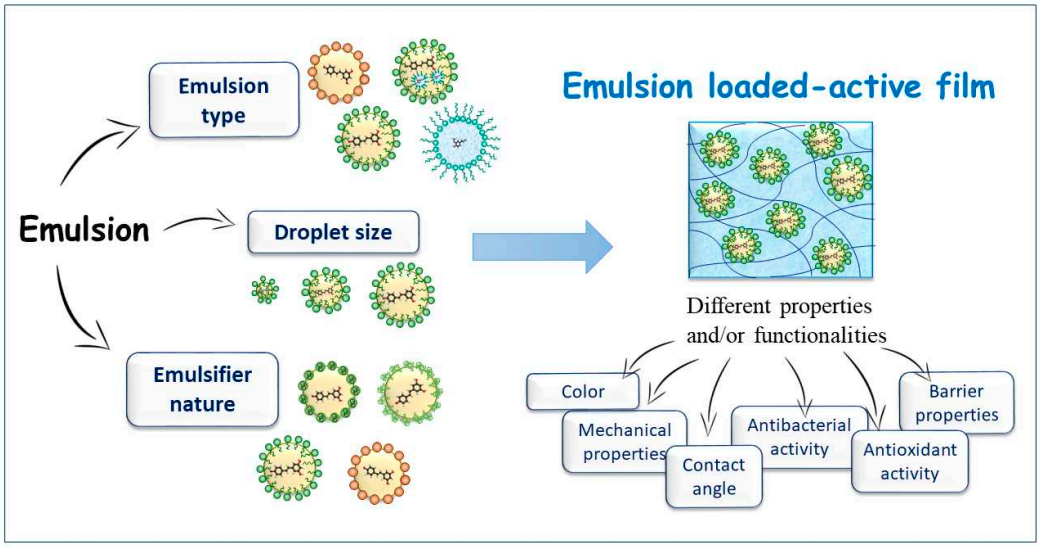

Figure 5. Characteristics of emulsified systems (emulsion type, droplet size and emulsifier nature) and their effects on structure and properties of emulsion-loaded active films (Source: Authors).

4.1. Effect of emulsion type

Different types of emulsions can be designed like emulsions, nanoemulsions, Pickering emulsions and double emulsions. These systems are produced using different homogenization techniques and stabilizers resulting in systems with distinct structures, stabilization mechanisms, and kinetic stabilities that can influence the properties of active films, such as morphology, moisture, water vapor permeability, mechanical properties.

J. Liu, Song, et al. (2022) studied chitosan films loaded with O/W emulsion or Pickering emulsions carrying cinnamon essential oil. Films loaded with O/W emulsion presented a lower water vapor permeability (WVP) than the control films; however, Pickering emulsions increased the WVP in relation to control film and film added O/W emulsion [69]. Otherwise, nanoemulsions and Pickering emulsions encapsulating clove EO reduced WVP of pullulan/gelatin-based films, but the lowest values were observed in the films containing Pickering emulsions [79]. Similar behavior was observed in pectin films added with nanoemulsion or Pickering emulsion carrying marjoram (*Origanum majorana* L.) EO. The decrease in the WVP was related to the hydrophobic nature of

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systems due to the oil phase presence, however, Pickering emulsion was more effective than nanoemulsions in reducing the WVP. Both emulsified systems increased the cross-linking between pectin chains due to filling free spaces in the pectin matrix, reducing the mobility of the pectin chains and, therefore, the migration rate of water vapor molecules [102]. Recently, double emulsion (W/O/W) has been also applied in biopolymeric films. Double emulsion carrying "Pitanga" leaf hydroethanolic extract reduced the WVP of chitosan, gelatin and chitosan-gelatin blended films [76].

Different emulsion types can affect other water related properties. For example, moisture content decreased with the addition of Pickering emulsion carrying clove EO in pullulan/gelatin-based films when addition of nanoemulsion did not affect this property [79]. Whereas moisture absorption increased with incorporation of nanoemulsions but decreased when Pickering emulsions [79]. The same behavior in moisture absorption was observed in pectin-based films charged with nanoemulsions and Pickering emulsions encapsulating marjoram EO [102]. Instead, double emulsion encapsulating "Pitanga" leaf extract, did not affect the moisture content of chitosan and gelatin films, however, solubility in water was reduced [76]. Water contact angle were improved with incorporation of emulsion and Pickering emulsion in relation to control film, but did not show difference between both, which can be attributed to an increase in oil content in the film and rougher surface of the films [69]. On the other hand, double emulsion provoked a decrease in the water contact angle of gelatin and gelatin-chitosan blended films. Authors attributed this behavior to the non-polar substances present in the hydroethanolic extract [76]. In the same way, Pickering and nanoemulsion carrying clove EO affected surface morphology of pullulan/gelatin-based films. Pickering emulsions improved the irregularity and the roughness of film's surface and the nanoemulsion reduced the roughness, which was attributed to the use of Tween 80 [79]. Double emulsion also improved the surface roughness of chitosan, gelatin and chitosan-gelatin blended films [76].

Tensile strength of Pickering emulsion-loaded chitosan films was higher than that incorporated with O/W emulsion, in addition to presenting a greater elongation at break. The cellulose nanocrystals (CNC) used as stabilizers adsorbed on the oil-water interface of Pickering's emulsions acted as reinforcement fillers for the films, mitigating the effect of breaking the continuous structure of the films promoted by the addition of cinnamon essential oil. However, both emulsions types reduced the tensile strength and elongation at break in relation to control film [69]. On the other hand, Pickering emulsions enhanced tensile strength of pullulan/gelatin-based films. However, films were less stretchable than control and films with nanoemulsions. Besides, nanoemulsions incorporation caused a reduction in tensile strength and an increase in the elongation at break of films compared to control one [79]. Nanoemulsions also provoked a decrease in films' Young modulus and tensile strength (except for sample with 2.5% of nanoemulsion) in pectin films, but it did not affect the elongation at break. Differently, Pickering emulsions increased the Young modulus and tensile strength of the films with 5 and 7.5% of emulsion. However, the elongation at break decreased in the sample with 7.5% of Pickering emulsion and increased in the sample with 5%, which showed higher elongation at break than control sample [102]. When double emulsion was added in gelatin-based films, the incorporation improved tensile strength and elongation at break, however, in chitosan films, the addition did not affect the elongation at break [76]. On the contrary, double emulsion increased the tensile strength and decrease the elongation at break of chitosan films in relation to control films. Though increasing emulsion concentration caused a reduce in tensile strength [77].

The incorporation of emulsions encapsulating cinnamon EO in chitosan films decreased the films' transparency. However, Pickering emulsion-charged films showed lower film transparency than that with O/W emulsion. This behavior was justified by CNCs used as stabilizers in Pickering emulsions, which promoted higher light scattering [69]. The same behavior was observed in gelatin, chitosan and gelatin-chitosan films charged with double emulsion [76]. Pullulan/gelatin-based films loaded with Pickering emulsions carrying clove EO exhibited higher barrier to light than films loaded with nanoemulsions [79]. The inclusion of Pickering emulsions decreased the light transmittance probably due to a shadow effect by stabilizing particles [17].

Active properties of films, such as antioxidant and antimicrobial activity, are also influenced by emulsion type. Pullulan/gelatin-based films incorporated with nanoemulsions carrying clove EO

showed higher antioxidant activity, measured by DPPH (2,2-Diphenyl-1-picrylhydrazyl) and ABTS (2,2'-azino-bis(3-ethyl-benzothiazoline-6-sulfonic acid) radical scavenging, than those incorporated with Pickering ones. This can be explained by the fact that the EO release in films charged with Pickering's emulsion was lower than in films with nanoemulsions. WPI-inulin complex used to stabilize the Pickering emulsion, adsorbed in the oil-water interface may have reduced the release of the active compound [79]. Also comparing the addition of nanoemulsion and Pickering emulsion encapsulating marjoram (*Origanum majorana* L.) EO in pectin-based films, Almasi et al. (2020) reported that antioxidant activity assessed by DPPH was higher in films containing nanoemulsions than films containing Pickering ones. This phenomenon can be caused by the decrease in the mobility of the loaded active compounds through the matrix in the films incorporated with Pickering emulsions [102]. Double emulsion encapsulating "Pitanga" hydroethanolic leaf extract improved the antioxidant activity, asssed by ABTS, DPPH and FCRC (Folin-Ciocalteau reducing capacity) of gelatin, chitosan and chitosan-gelatin blends. However, gelatin films presented the highest antioxidant activity compared to other matrices, which could be explained by the higher protective effect of gelatin compared to the other biopolymer during processing [76].

In addition to emulsion type, active properties can be affected by the emulsion concentration incorporated in biopolymeric matrix. Indeed, to define the concentration of active compounds into film-forming solutions is an important challenge. For example, in pullulan/gelatin-based films, raising the concentration of nanoemulsion and Pickering emulsions enhanced the ABTS and DPPH radical scavenging [79]. The same occurred in pectin films for both emulsions types incorporation [102]. Increasing concentration of double emulsion carrying carvacrol improved the antioxidant capacity of chitosan films measured by DPPH method [77]. This same behavior has been reported by several authors [70,93,98,107].

Other active property of interest is antimicrobial activity. Chitosan films incorporated with emulsions encapsulating cinnamon EO did not presented significantly inhibitions zone against *E. coli* and *S. aureus* in relation to control film. However, Pickering emulsion improved the inhibition zone against these bacteria. The difference behaviors between emulsions types was attributed to the limited release of the active compound from the emulsions [69]. On the contrary, there was no significant difference between Pickering and nanoemulsion carrying marjoram EO in antibacterial activity of pectin-based films [102].

4.2. Effect of emulsion droplet size

Emulsions can be produced with a wide range of droplet sizes, ranging from a few nanometers (<50 nm) to micrometers (>500 μm), depending upon the ingredients and the homogenization methods utilized to produce them. Droplet size influences important emulsion properties, such as chemical and physical stability, optical properties, rheology, and release rate. In addition, the droplet size of emulsions also affects the characteristics of active films charged with emulsions.

Different homogenization conditions in production of emulsions-loaded licorice EO changed the mean diameter of the droplets from 235.34-355.36 nm to 52.53–73.41 nm. When these emulsions were incorporated in CMC films, the roughness of the films increased with emulsions with larger particle sizes while smaller one did not affect the film roughness [26]. On the contrary, roughness parameters decreased in konjac glucomannan films with the increase in a mean diameter of Pickering emulsion droplets incorporated. Authors attributed that to the smaller number of bigger droplets in the biopolymeric matrix [119].

Water related properties, such as moisture content and water solubility were not affected by droplet sizes in starch films [74]. Unlike in konjac glucomann films the moisture content and water solubility decreased with larger droplet sizes (42.86 ± 15.27 μm) of Pickering emulsions. This effect can be attribute to hydrophobicity of oil droplets and interactions between them and the matrix that could replace partially the interactions matrix-water [119]. Evaluating the water contact angle of the films' surface, konjac glucomannan films charged with Pickering emulsions with larger droplets (42.86 ± 15.27 μm) presented higher values of water contact angle, which can be related to the increase

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in the oil phase of the emulsions [119]. Nevertheless, droplet size did not affect the water contact angle of starch films comparing the same oil concentration added in carnauba wax emulsions [74].

Comparing the influence of droplet size in WVP of carboxymethyl cellulose (CMC) film properties charged with emulsions encapsulating licorice EO, Fattahi and Seyedain-Ardabili (2021) reported that emulsions with bigger droplet sizes (235.34-355.36 nm) increased the WVP compared to the control film while smaller ones (52.53–73.41 nm) provoked a decrease in WVP [26]. Likewise, Oliveira Filho et al. (2020) observed lower WVP with addition of emulsions with nanometric droplets than micrometric droplets in starch-based films [74]. Also, Zhao et al. (2022) observed a reduction in WVP values when Pickering emulsions with smaller droplets were incorporated in chitosan/anthocyanidin films [87]. On the contrary, Z. Liu et al. (2021) reported that larger droplet sizes of Pickering emulsions decreased the WVP values of konjac glucomannan films [119].

Various emulsion droplets sizes caused a plasticizing effect was observed in CMC matrix. Emulsions with mean diameter droplets smaller than 100 nm produced films with lower tensile strength and higher elongation at break than those with bigger droplet sizes (230 to 355 nm). This change in the plasticizing may be caused by the increasing surface area of interaction in the smaller droplets with CMC matrix, weakening the CMC-CMC interactions [26]. The same effect was observed in konjac glucomannan films charged with Pickering emulsions, being that smallest droplet size (32.18 ± 30.99 μm) implied in lower film tensile strength. Elongation at break enhanced with increasing droplet size and reduced again for the biggest droplet size (42.86 ± 15.27 μm). The researchers attributed this behavior to the reorganization of emulsion droplets, as observed by confocal laser scanning microscopy [119]. Although, nanosized droplets (39.3 ± 0.7 nm) caused starch films with higher tensile strength and elongation at break and smoother microstructure than films incorporated with microsized ones (138.1 ± 0.5 nm) [74]. In contrast, tensile strength and elongation at break decreased with incorporation of Pickering emulsion with larger droplet sizes (140.5 ± 1.450 nm) in chitosan/anthocyanidin films, which can be related to the internal structure rougher and looser [87].

Changes in optical properties, such as transparency and UV-vis light barrier, can influence the application of active films. Micrometric droplets of carnauba wax emulsion raised the opacity of starch films in relation to nanometric droplets. It can be explained by the higher capacity of disperse light of larger droplets. Moreover, films charged with nanoemulsions were less opaque even than control film, which is a surprising outcome according to the authors [74]. About UV-Vis light barrier, films containing micrometric droplets presented higher barrier than the nanometric ones corroborating the opacity results [74]. Similarly, larger droplets of Pickering emulsions caused the highest opacity and UV-vis light barrier of chitosan/anthocyanidin films [87]. On the contrary, decreasing droplet sizes of Pickering emulsions reduced the light transmission of konjac glucomannan films due to greater number of smaller droplets that can promote light blocking or scattering [119].

In active properties, chitosan/anthocyanidin films charged with the smallest droplets (11.84 ± 0.130 and 13.50 ± 0.240 nm) of Pickering emulsions carrying cinnamon-perilla EO exhibited the highest antioxidant activity, assessed by DPPH. This can be due to the greater stability of these droplets that prevented the evaporation of the EO during the production of the emulsion [87]. About antibacterial effect against Gram-negative and Gram-positive bacteria, CMC-based films charged with emulsions encapsulating licorice EO with smaller droplets were more effective than the emulsion with bigger droplets. It might be caused by the higher surface-to-volume ratio of smaller droplets and the evaporation of the EO during the production of the film charged with emulsion with bigger droplets [26].

4.3. Effect of emulsifier type

The oil droplets of the emulsions can be coated by different types of emulsifiers (proteins, carbohydrates, low molecular weight surfactants) and solid particles (e.g., nano/microgels from different sources of proteins, cellulose and chitosan particles). These compounds influence interfacial layer properties, (such as charge, hydrophobicity, surface activity, and thickness) and, therefore the

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interaction of emulsions with the components of the film-forming solutions resulting in active films with distinct properties [89,94]. There are few studies comparing different kind of emulsifiers for emulsion production in the film properties.

Using different compounds to stabilize nanoemulsions carrying cinnamon EO, such as ethyl-Nα-lauroyl-L-arginate hydrochloride (LA) alone or co-stabilized by ethyl-Nα-lauroyl-L-arginate hydrochloride and hydroxypropyl-β-cyclodextrin (LH), Y. Xu et al. (2021) observed that WVP was lower for chitosan-based films with the addition of co-stabilized nanoemulsions which can be associated with the uniform distribution through chitosan matrix [89].

In tensile strength, the incorporation of LA-stabilized nanoemulsion provoking a decreasing in chitosan matrix, besides causing a reduce in the elongation at break. This stabilizer caused a disruption in the crystalline regions of chitosan matrix. However, when LH was used as co-stabilizer, films presented slightly higher tensile strength and higher crystallinity. Furthermore elongation at break was lower than the control film but higher than when LA-stabilized nanoemulsion was used [89]. Changing emulsifier also had influence in mechanical properties of gelatin-based films. Nanoemulsions encapsulating eugenol stabilized by sodium caseinate caused higher tensile strength, higher stiffness and lower stretchability as compared with nanoemulsions stabilized by soy lecithin. Furthermore, sodium caseinate implied lower surface roughness of film than with soy lecithin [94].

Emulsifier type can also affect the active properties of biopolymeric films. Higher antioxidant activity, measured by ABTS method, was observed in gelatin films incorporated with sodium caseinate-stabilized nanoemulsion in comparison with lecithin-stabilized ones. Authors attributed this fact to a better retention of eugenol in oil droplets when sodium caseinate was used as stabilizer [94]. Antimicrobial effect of active chitosan-based films against *E. coli* was more effective when nanoemulsion encapsulating cinnamon EO co-stabilized with LH was incorporated. LH enhanced the uniformity of EO distribution through chitosan matrix and presented a protective effect on EO and LA stabilizer. Similar behavior was observed against *S. aureus*, but the antibacterial effect was higher than against *E.coli* [89].

Table 2 summarizes the main properties that were influenced by emulsion characteristics.

Table 2. Summarizes the influence of emulsion characteristics in biopolymeric films properties in relation to a control film.

Property	Emulsion type			Droplet size		Emulsifier	Reference
	Emulsion	Nanoemulsion	Pickering	Smaller	Bigger		
WVP	Decreased	-	Increased	-	-	-	[69]
	-	Decreased	Decreased	-	-	-	[79]
	-	Decreased	Decreased	-	-	-	[102]
	-	-	-	Decreased	Increased	-	[26]
	-	-	-	Decreased[2]	Decreased	-	[74]
	-	-	-	Decreased	Increased	-	[87]
	-	-	-	Decreased	Decreased[2]	-	[119]

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	-	-	-			Decreased[3]	[89]
Moisture absorption/ content	-	Increased	Decreased	-	-	-	[79]
	-	-	-	No effect	No effect	-	[74]
	-	-	-	No effect	Decreased[2]	-	[119]
	-	Increased	Decreased	-	-	-	[102]
Water contact angle	Increased	-	Increased	-	-	-	[69]
	-	-	-	Increased	Increased	-	[119]
	-	-	-	No effect	No effect	-	[74]
Surface roughness	-	Decreased	Increased	-	-	-	[79]
	-	-	-	No effect	Increased	-	[26]
	-	-	-	Increased	Decreased[2]	-	[119]
Tensile strength	Decreased	-	Decreased	-	-	-	[69]
	-	Decreased	Increased	-	-	-	[79]
	-	Decreased	Increased	-	-	-	[102]
	-	-	-	Decreased[2]	Decreased	-	[26]
	-	-	-	No effect	Decreased	-	[87]
	-	-	-	Decreased[2]	Decreased	-	[119]
	-	-	-	Decreased[2]	Decreased	-	[74]
	-	-	-	-	-	Increased[3]	[89]
	-	-	-	-	-	Increased[4]	[94]

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	Decreased	-	Decreased	-	-	-	[69]
	-	Increased	Decreased	-	-	-	[79]
	-	No effect	Increased/ decreased*	-	-	-	[102]
Elongation at break	-	-	-	Increased	Increased[2]	-	[26]
	-	-	-	Increased	Decreased	-	[87]
	-	-	-	Increased	Increased	-	[74]
	-	-	-	-	-	Decreased[3]	[89]
	-	-	-	-	-	Decreased[4]	[94]
	Decreased	-	Decreased	-	-	-	[69]
UV-vis light barrier	-	-	-	Increased	Increased[2]	-	[74]
	-	-	-	Increased	Increased[2]	-	[87]
	-	-	-	Increased[2]	Increased	-	[119]
	-	Highest	Lowest	-	-	-	[79]
Antioxidant activity[1]	-	Highest	Lowest	-	-	-	[102]
	-	-	-	Highest	Lowest	-	[87]
	-	-	-	-	-	Highest[4]	[94]
	No effect	-	Effect	-	-	-	[69]
Antimicrobial activity[1]		No effect	No effect	-	-	-	[102]
	-	-	-	Higher effect	Lower effect	-	[26]
	-	-	-	-	-	Higher effect[3]	[89]

*Depending of emulsion concentration; [1] In comparison to film with emulsion; [2] In comparison with smaller droplets addition; [3] LH addition; [4] Sodium caseinate.

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5. Active film stability and bioactive compound retention

Some active compounds, like EO, could evaporate from the film during the drying process or storage due to its high volatility [120]. Active compounds can be lose by diffusion from the film interior to its surface and by convection from film surface to environmental surrounding [92]. Therefore, retention of these compounds in the film matrix and its stability over time need to be evaluated. Evidently, the loss of active compounds imply that active films can lose their antibacterial and antioxidant activity over time.

Chu et al. (2020) reported significant EO losses during film drying process and during 6-days of storage of pullulan-based films loaded with nanoemulsions carrying cinnamon EO. Decreasing droplet size of the nanoemulsion caused less loss of EO, which could be related to the homogeneous internal structures of these films, as observed by scanning electron microscopy (SEM) and other physical properties. Pullulan matrix was not able to entrap the high amount of oil droplets, which caused its flocculation during film formation, leading to porous structure and faster release rate of active compound [120]. Contrarily to these results, Gahruie et al. (2017) observed that for higher initial concentration of *Zataria multiflora* EO encapsulated into nanoemulsions incorporated in basil seed gum films, lower was its loss during storage at room temperature. Nevertheless, they also observed that 50% of the active compound was lost in the first day of storage [109]. Ma et al. (2016) produced chitosan films loaded with emulsified cinnamon bark oil and kept them for 7 days at room temperature. During this period, films incorporated with microemulsion were more efficient in retaining the active compound than the control one [92].

Comparing the influence of different stabilizers for nanoemulsion, Y. Xu et al. (2021) observed that chitosan matrix charged with nanoemulsion co-stabilized with LH showed higher retention of cinnamon EO than when it was used only one stabilizer (LA) in the nanoemulsion. So, addition of LH to stabilize nanocmulsion promoted a encapsulation of the EO [89]. On another work, retention rate of cinnamon EO in chitosan films was higher when EO was added in conventional emulsion form than Pickering emulsion form [69]. These authors attributed this fact to larger sizes of Pickering emulsion droplets, which caused a bigger pathway for EO which could increase its volatilization [69].

It is worth noting that retention capacity of an active compound in a biopolymer matrix during film production and storage generally depends on matrix structure, composition and interactions [121]. Furthermore, emulsion type, droplet size and concentration of active compound in the matrix can influence in retention properties and stability of the films, as can be seen in the examples cited above.

6. Release properties in food simulants

Release process of an active compound from a biopolymeric matrix occur in three steps, which starts with the solvent penetration into the matrix, provoking a relaxation and swelling of the biopolymeric chains, facilitating the active compound diffusion to the surrounding medium [111]. A quick release occurs in the first hours followed by a deceleration in the release rate and, in the final, almost a constant rate is reached [19]. The fastest release in the first phase can be related to encapsulated compounds that are in or near the film surface. The second phase is associated with the molecules inside the matrix, which show a slow diffusion through the film caused by specific interactions with the biopolymeric chains [122].

For packaging application, active films will be in contact with food products. So, it is important to understand how active molecules are released and their migration process from the film to different kinds of foods [123]. For this purpose, release studies have been performed in food simulants [68,104,105,111,114].

Evaluating the release profile of nanoemulsified curcumin from banana starch matrix, Sanchez et al. (2022) reported a maximum release value in simulant for lipophilic foods (50% ethanol w/v). This fact could be explained by hydrophobic character of curcumin [19]. There are a lot of factors that could influence the oil release from a biopolymeric matrix as film structure and composition, presence of hydrogen bonds and solvent type [124].

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Zhang et al. (2022) studied the release properties of oregano EO encapsulated in Pickering emulsion from konjac glucomannan films in different food simulants, considering standard food simulants for fatty foods (95% aqueous ethanol), oil-in-water emulsions and alcoholic food (50% aqueous ethanol) and aqueous-based food (distilled water). They observed that the release rate of EO reduced with increasing ethanol concentration in the simulant. At the higher ethanol concentration, the solvent was not capable of diffuse easily into the biopolymeric matrix, what slowed the release rate. Furthermore, the solvent polarity decreased with the increment in ethanol concentration [125]. Xu et al. (2020) observed a significant decrease in the release in glycerol solution (60%) with the increasing Pickering emulsion concentration carrying cinnamon EO loaded in chitosan films. It can be attributed to the enhancement in the interaction between biopolymeric matrix and OSA-modified gum Arabic, which was used as stabilizer for the Pickering emulsion [91]. Dammak et al. (2017) reported release rate was faster in lower concentrations of nanoemulsions encapsulating rutin from gelatin films [95].

Shen et al. (2021) evaluated the release rates of nano and Pickering emulsions encapsulating clove EO loaded in pullulan-gelatin films in fatty foodstuff simulant (ethanol 95%) and observed that EO concentration was insignificant in the release rate but emulsion type showed significant effect. Films incorporated with nanoemulsion had higher release rates than the films with Pickering emulsions [79]. A similar behavior with pectin-based films loaded with Pickering and nanoemulsions encapsulating marjoran EO was observed by Almasi et al. (2020) at the same conditions. However, in this case EO concentration was significant and the release was faster at higher concentrations for both type of emulsions [102]. On the contrary, Hua et al. (2021) reported a decreasing in the release of clove EO encapsulated in Pickering emulsions with the increase in nanoparticles concentrations in chitosan matrix in ethanol 95% as simulant [88]. Chitosan-based films incorporating conventional emulsion encapsulating cinnamon EO presented slower release than similar films with Pickering emulsion [69].

As can be seen there are several factors that affect the release of active compounds in the medium in these films. Emulsion type, food simulant, biopolymeric matrix, interaction between emulsion and matrix are some of them. Besides studying the release in food simulants, it is very important to verify the performance of these films in real systems.

7. Applications of active films incorporated with emulsions

In addition to study the influence of emulsions incorporation into de biopolymeric matrix, active film performance as food packaging or coating is very important. Therefore, some researches have been applying these films in some foodstuffs [87,90,93,98,126,127].

Dini et al. (2020) studied an edible coating composed of chitosan solution loaded with nanoemulsion carrying cumin EO and observed that combinations of active coatings extended 8 days of beef loins shelf life compared to control group while the combination of active coating and gamma irradiation extended 15 days of shelf life under refrigerated storage [90]. Pérez-Córdoba et al. (2022) applied gelatin/chitosan-based film activated with nanoemulsified garlic EO and α-tocopherol for mortadella conservation. Results showed that active film was effect against bacteria growth [127]. Yuan et al. (2022) applied chitosan solution loaded with double emulsion (W/O/W) carrying nisin in the inner aqueous phase and carvacrol in oil phase as coating for salmon fillets. During storage in a refrigerator (4°C), coated fillets showed the lowest values of pH, water loss, total viable counts, total volatile basic nitrogen and TBARS values, meaning increased shelf life of the salmon fillets [77].

Sun et al. (2021) evaluated the effects of gelatin films incorporated with nanoemulsions encapsulating lavender EO for preservation of cherry tomatoes. They reported an antioxidant activity and antibacterial properties of the active films against *E. coli*, *S. aureus* and *Listeria monocytogenes*, sustained release characteristic and a good heat-sealing performance, which is important to produce food packaging bags. These active films were effective in reducing weight loss, inhibiting microorganisms' growth and delaying the titratable acids and phenolic compounds degradation of cherry tomatoes, extending its storage time [93]. Zhao et al. (2022) studied the preservation of red sea bream wrapped with anthocyanidin/chitosan films charged with cinnamon-perilla EO encapsulated in Pickering emulsions. They observed that active films with emulsions and anthocyanidin were

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capable of maintaining the concentration limit of total volatile basic nitrogen until 12 days of storage while control reached this limit in 6th day. Besides, these packages maintained low thiobarbituric acid values after 14 days of refrigerated stored, enhancing the shelf life of fish fillets in 6-8 days [87].

Ghoshal and Shivani (2022) applied tamarind starch/whey protein concentrate blended films charged with nanoemulsion encapsulating thyme EO as tomato packaging. In 14 days of storage, total acidity and total soluble solids were higher in control fruits, and the active packaging retarded the weight loss in tomato fruits. In sensory evaluation, there were significant high scores in appearance, firmness, flavor and overall appearance detected by panelists for packaged tomatoes. Active films were able to delay the ripening process and provide better quality to the tomatoes fruits [116]. J. Liu, Li, et al. (2022) produced a gelatin/chitosan matrix charged with Pickering emulsion carrying cinnamon EO and free curcumin and applied it for pork meat preservation and monitoring freshness. The color of the film changed according with the variation of pH of the meat, due to the presence of curcumin. Besides, the total volatile basic nitrogen was lower than control film when the film containing Pickering emulsion carrying cinnamon EO. Thus, this film has potential to be applied as active packaging and freshness indicator for pork meat [110]. J. Liu, Song, et al. (2022) also applied chitosan film charged with Pickering emulsion encapsulating cinnamon EO for pork meat preservation. Active film kept the freshness of the meat and was capable of maintain structural integrity during the storage time comparing to control film [69].

These examples demonstrate the potential of biopolymeric active films incorporated with emulsions charged with active compounds in preservation and extending shelf life of foodstuffs. However, more application studies need to be performed in others food systems.

8. Final remarks

Active films based on biopolymers have attracted a lot of attention from researchers in recent years, due to be an eco-friendly material and to minimize the use of chemical additives in the food. The focus of the recent studies is on lipophilic active compounds, such as essential oils, in the emulsified forms, because the difficulties of its incorporation in hydrophilic biopolymeric matrices. However more recently some authors have evaluated some hydrophilic compounds in the emulsified form to incorporate into active films.

Emulsion-based systems, in addition to further the incorporation of non-polar compounds, act as a protector for these compounds. The comparison between the active compound in natural form and in emulsified form have shown this effect in the compound concentration, antioxidant and antimicrobial properties of the films and in its stability during storage.

There are several kinds of emulsions, but the most loaded in active films are common emulsions, nanoemulsions and Pickering emulsions. This review reports that the emulsion type has influence in the film properties, such as mechanical, barrier and optical ones. In addition, droplet sizes and emulsifier used to stabilize the emulsion can interfere in the film properties. The effect of emulsifier type need to be studied more because currently there are only few researches evaluating its influence.

Emulsion characteristics affects the antimicrobial and antioxidant activities of the active films and its release to the surround media. So, it is important to highlight the objective of the use of these active films to choose the better emulsion type and production parameters to produce the active packaging.

The application of these films in real systems need to be more studied. This review reports that some applications were effective in extend the shelf life of some food stuffs. However, more studies of migration and the interference in the taste and flavor need to be done.

Despite of bipolymeric matrices incorporated with emulsions encapsulating active compounds present potential to be used as a food packaging, there are a few concerns to be point out to be applied in commercial scale. One of these problems are its high water vapor permeability rate and high solubility in water. Moreover, the effects of compound migration and biodegradability of these system must be studied.

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