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Pickering emulsions stabilized by polysaccharides particles and their applications: a review

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Abstract

Pickering emulsions stabilized by polysaccharide particles have attracted extensive research interest in the food, biopharmaceutical and cosmetic industries due to their ability to edibility, protect bioactive substances, and control the release of bioactive substances. This paper reviewed research progress in using natural polysaccharides, modified polysaccharides by physical or chemical method and polysaccharide complexes as particles to form and stabilize Pickering emulsions. In particular, the application of Pickering emulsions stabilized polysaccharide particles in encapsulation and delivery of food bioactive ingredients, fat substitutes, and modulation of lipid digestion, was discussed. Finally, the future prospects of Pickering emulsions stabilized by polysaccharide particles were discussed.

Keywords: polysaccharides; pickering emulsions; application; particles.

Practical Application: Pickering emulsions can be potentially used as new zero trans fat margarine products and encapsulation and delivery of food bioactive ingredients such as β-carotene, curcumin, inulin.

1 Introduction

A Pickering emulsion is a distinctive emulsion discovered by Ramsden and developed by Pickering (Linke & Drusch, 2018). In contrast to conventional emulsions, Pickering emulsions are surfactant-free emulsions stabilized by fine solid particles. Currently, the stabilization mechanism of Pickering emulsions is based on mechanical barrier theory (Aveyard et al., 2003) and three-dimensional viscoelastic particle network theory (Lagaly et al., 1999). As shown in Figure 1, the tiny solid particles with good wettability can be adsorbed on the oil/water interface. And these small particles further rearranged on the droplet surface to form a single or multi-layer dense solid interfacial film. The desorption energy of solid particles at the oil-water interface is much greater than the thermal energy, so the adsorption of particles is irreversible. The film provides a strong spatial barrier and electrostatic protection for the emulsion droplets and prevents the aggregation of droplets, thus achieving long-term stability of Pickering emulsions (Wang et al., 2020a). In general, Pickering emulsion type is determined by the wetting properties of the solid particles, and in the same way as O/W emulsions stabilized by hydrophilic surfactant agents (high HLB), hydrophilic particles facilitate the stabilization of O/W Pickering emulsions. As shown in Figure 2, O/W-type emulsions are more likely to be generated when the contact angle (θ) of solid particles in the oil-water phase composition is less than 90°. Conversely, W/O emulsions are more likely to be produced when the contact angle of solid particles is greater than 90°. As shown in Figure 3, compared to other traditional emulsions using surfactants, Pickering emulsions have low emulsifier dosage, high emulsion stability, low toxicity, high safety, wide and inexpensive sources of colloidal particles, and are less susceptible to external environmental influences (Jiang et al., 2020; Yang et al., 2017). As a result, Pickering emulsions have attracted a great deal of attention from researchers.

As shown in Figure 4, from 2008 to 2021, the number of papers researching Pickering solutions has increased year by year. Meanwhile, with the development of technology, studies have been conducted to explore the practical applications of Pickering emulsions. The preparation of new food material stabilized Pickering, the stabilization mechanism of food grade Pickering emulsion and functional active substance delivery system have become international research hotspots. Food-grade Pickering emulsion stabilized particles mainly include proteins, starch, cellulose and their derivatives, etc. Among them, polysaccharides are of great interest in food processing due to their wide sources, low price and low irritation. However, most colloidal particles of plant origin are usually too hydrophilic or hydrophobic to produce Pickering emulsions with low stability. In order to solve the above problems, many researchers have prepared highly stable Pickering emulsions with starch, cellulose, chitosan and other polysaccharide particles, supplemented with ultrasound, high-speed homogenization, high-pressure homogenization and other means (Wani et al., 2016; Miskeen et al., 2021; Zou et al., 2021; Yi et al., 2020). Therefore, Pickering emulsions prepared on the basis of polysaccharide particles have a very wide application prospect in the food field, including improvement of oxidative stability of oils and fats, preparation of liquid oil-based fat substitutes. In this paper, we begin with an overview of recent progress in the formation and properties of Pickering emulsions stabilized by natural polysaccharides, modified polysaccharides, and polysaccharide complexs. Meanwhile, we summarized applications of edible Pickering emulsions. Finally, the review puts forward future research trends of edible Pickering emulsions.

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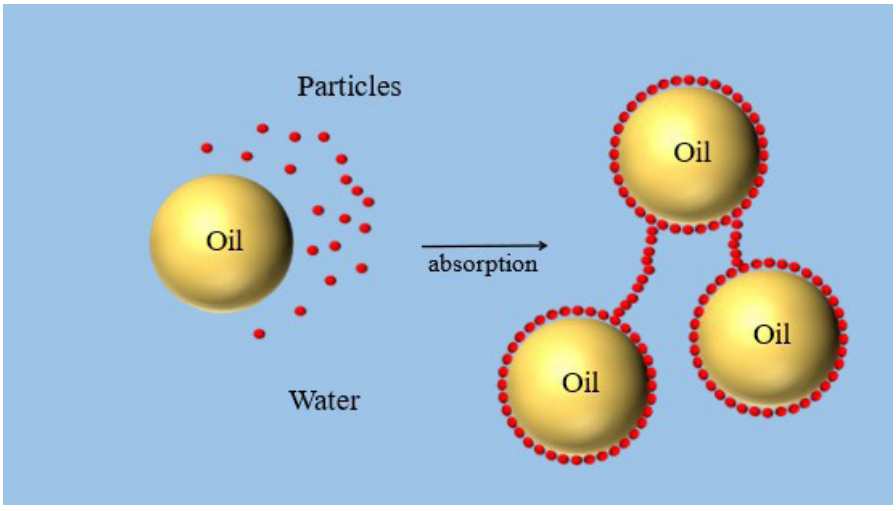

Figure 1. Mechanism of the stability of Pickering emulsion.

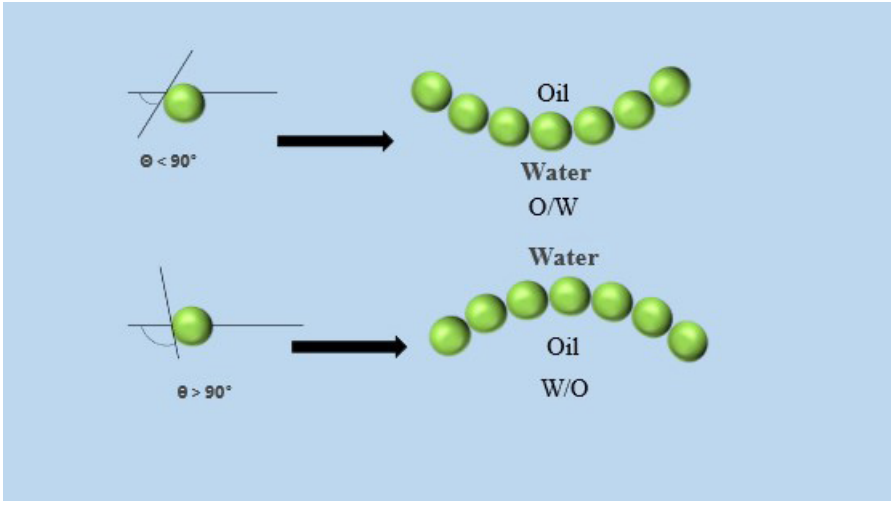

Figure 2. Difference in contact angle of solid particles with different wettability at the oil-water interface.

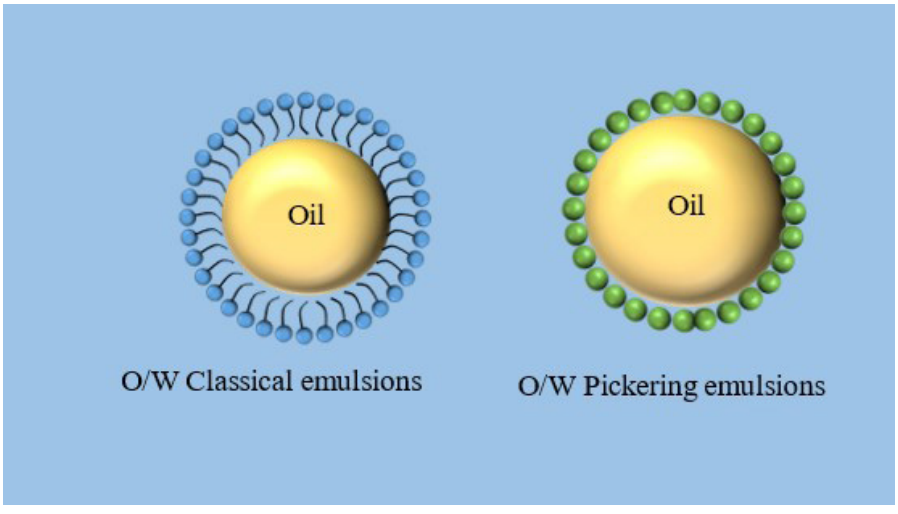

Figure 3. Comparison of Pickering emulsion and traditional emulsion (surfactant-based).

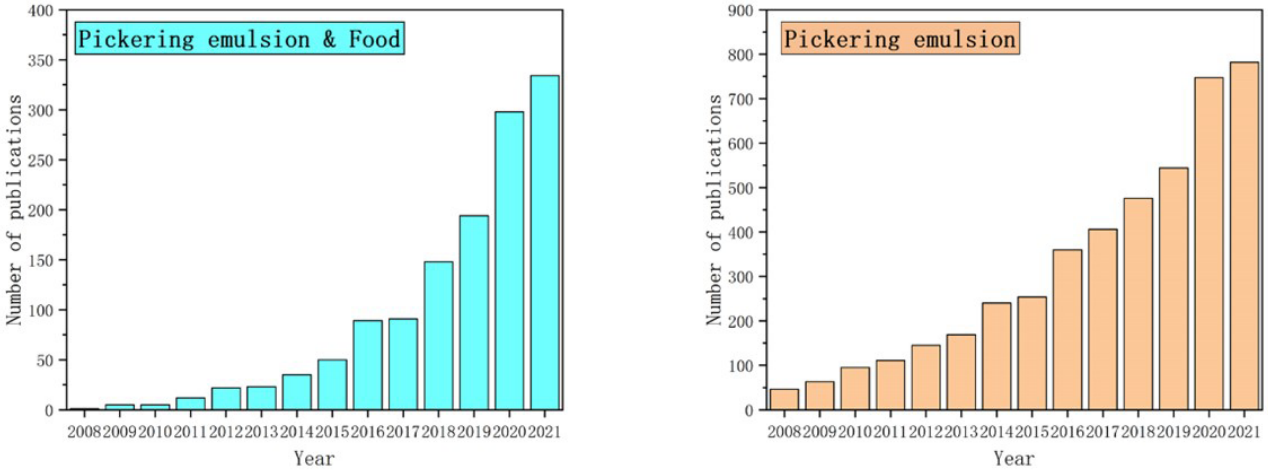

Figure 4. Publication number of Pickering emulsions per year. Data was obtained from "Web of Science" on March 2022.

Table 1. The preparation of Pickering emulsion stabilized by polysaccharide particles.

Particles as stabilizers	Modified methods	Particle size	Reference
Rice, tapioca, corn, wheat and potato starches	OSA esterification	47.79-148.8 μm	(Simsek et al., 2015)
Waxy maize starch nanocrystals	OSA esterification	0.5-1.3 μm	(Jo et al., 2018)
Quinoa starch	Dodecenyl succinic anhydride (DDSA) esterification	95.8-28.1 μm	(Li et al., 2019a)
Cellulose nanocrystals	OSA esterification	20-250 μm	(Li et al., 2018)
Cellulose nanocrystals	Cinnamoyl chloride acylation	8-62 μm	(Zhang et al., 2018)
Microcrystalline cellulose	Carboxymethyl cellulose adsorption	7-22 μm	(Ahsan et al., 2019)
chitosan	ltrasound-assisted emulsificatio	22.3-5.5 μm	(Costa et al., 2018)

2 Pickering emulsion stabilized by a single polysaccharide particle

Currently, polysaccharide particles from plants were attracting research interest due to their greater advantages in sustainability, safety, economy and ethics. In recent years, modified starch, cellulose, chitosan and other polysaccharides were widely used in the construction of Pickering emulsions. In Table 1, for reference, we summarized the studies of Pickering Emulsion stabilized by polysaccharide particles reported in some literatures reported in the past five years.

2.1 Starch

Starch is a macromolecular carbohydrate formed by the polymerization of glucose molecules and is found in a variety of plants such as corn, potatoes and rice (Tavernier et al., 2016). It is one of the important components of food and the main source of carbohydrates in the human diet. Natural starch exists mainly in granular form with diameters ranging from 0.5 μm to 100 μm. A small amount of starch has structural proteins, which give it a certain emulsifying power. So native starch granules have potential as food-grade Pickering stabilizers (Tavernier et al., 2016). However, most native starches are not suitable for the preparation of stable Pickering emulsions due to their large particle size. Therefore, native starches need to be modified by chemical or physical methods to reduce the granule size and improve the hydrophobicity of the granules (Wang et al., 2020b). So as to adjust the interface behavior of particles, improve their amphiphilicity, and achieve the purpose of preparing stable Pickering emulsion (Zhu, 2019). The methods commonly used by researchers to reduce the size of starch particles (Liu et al., 2019) include acid hydrolysis, organic solvent precipitation, high-pressure treatment, ultrasonic treatment, ball milling etc. To reduce the size of starch granules, researchers often use physical methods such as ball milling and heating to reduce the size of starch granules to improve their ability to stabilize Pickering

emulsions. Although heat treatment of starch granules can also increase the hydrophobicity of starch granules, the size of starch granules may become larger after heat treatment (Asghari et al., 2016). Also the particle size of starch can be reduced by acid hydrolysis of starch. For example, Zhou et al. (2020) prepared waxy maize starch nanocrystals (SNCs) for the first time using dry-heated oxalic acid hydrolysis, the results showed that the size of the obtained SNCs was 46.58-197.15 nm, the yield of SNCs prepared by this method was as high as 89.6% (Li et al., 2014). In terms of improving the hydrophobicity of granules. Researchers often enhance the hydrophobicity of starch granules by chemical modification with octenyl succinic anhydride (OSA) to increase their affinity for oils and fats (Agama-Acevedo & Bello-Perez, 2017). Generally speaking, the higher the degree of OSA modification of starch, the better the emulsification of starch granules (Matos et al., 2018). Ye et al. (2017) prepared Pickering emulsions using OSA-modified starch nanoparticles (SNPs), and the emulsions showed no phase separation and good stability after 30 days of storage. At present, besides OSA modification, there are lauric acid modified starch (García-Tejeda et al., 2018), octenyl succinate starch (Li et al., 2019b), acetylated starch (Qian et al., 2020) can enhance the hydrophobicity of starch granules and the stability of forming Pickering emulsion. Although there are still many doubts about chemically modified starches, several published studies (Mahadevan et al., 2014) have confirmed that there are no safety problems with chemically modified starches and that chemically modified starches are safe to use. OSA, as the most commonly used modifier, has been approved by the FDA for use in food, and OSA modified starch granules have been commercialized, which have been widely used in food and pharmaceutical applications. Epichlorohydrin can also be used for the modification of starch, Luo et al. (2022) prepared Quinoa starch microparticles using epichlorohydrin as a cross-linking agent and synthesized it by reversed-phase emulsion polymerization. The results showed that the crystallinity of Quinoa starch microparticles decreased significantly, and their adsorption properties and thermal stability were significantly improved compared with those for Quinoa starch.

2.2 Chitin/chitosan

Chitin is the second most abundant polysaccharide in nature after cellulose, and its main source is extracted from the shells of crustaceans and microorganisms in the ocean. Chitin contains hydroxyl groups in its backbone, in addition to amino groups (Yang et al., 2017), and thus exhibits different charged properties and dependence on the pH of the system. When the pH value in the system is less than 6, chitin is positively charged, so its charged nature can be used to prepare the corresponding particles, while when the pH value in the system is higher than 6, the amino group is deprotonated and becomes an uncharged polymer, so its polymeric properties can be used to prepare the particles.

Chitosan is a derivative of chitin, and chitosan is deacetylated to chitosan (CTS). The presence of a large number of amino and hydroxyl groups in the main chain of the CTS molecule causes it to exhibit typical pH dependence in solubility in water. When the degree of deacetylation is greater than 75%, the aqueous solution of CTS will shift towards gelation. Under alkaline conditions, CTS forms self-aggregates with increased hydrophobicity and improved affinity for oil. Since CTS under alkaline conditions possesses certain emulsification properties and also exhibits good biocompatibility and antibacterial properties, CTS is a commonly used functional molecular encapsulant in cosmetics and pharmaceuticals (Han et al., 2020; Lim et al., 2020; Sharkawy et al., 2020). There have been numerous experiments to demonstrate that CTS self-aggregating particles can successfully stabilize Pickering emulsions. CTS is mainly used as Pickering emulsifier in the form of nanocrystals. Traditionally, the common preparation methods for chitosan nanocrystals (CHINCS) are acid hydrolysis, TEMPO oxidation and ultrasonication. Tian et al. (2019) used sodium tripolyphosphate (TPP) as a modifier to modify CTS hydrophobically and produced hydrophobic CTS-TPP submicroparticles by ionic gelation under acidic conditions. The results showed that the Pickering emulsion with 0.6% w/v CS - TPP had the best chemical stability and 52.33% of citral remained after 14 days of monitoring. Ho et al. (2016) found that treating CTS with ultrasound induced CTS self-aggregation, causing CTS to depolymerize and form smaller monodisperse polysaccharide particles, ultimately stabilizing Pickering emulsions with up to 70% oil phase volume fraction. Meanwhile, Wang & Heuzey (2016) prepared CTS-stabilized Pickering emulsions with an average diameter of less than 1.7 μm and stable for 5 months by sonicating CTS at high frequencies without adding any surfactant or cross-linking agent. The studies of the two aforementioned authors illustrate that ultrasound treatment can disrupt and disperse the structure of CTS aggregates and improve their emulsification and the stability of their emulsions. The emulsion type can also be controlled by the response of CTS to pH. Mwangi et al. (2016b) prepared CTS pellet precipitates by adjusting the pH of CTS acetate solution to above the CTS 'pKa value and investigated the effect of internal and external factors on the stability of their Pickering emulsion. The results show that CTS particle-stabilized Pickering emulsions have the property of responding to environmental stimuli, which indicates that CTS particle-stabilized Pickering emulsions will have a wide range of application prospects in food and pharmaceutical fields with special requirements (Mwangi et al., 2016a). It is not uncommon to report that CTS-based Pickering emulsions are stable under acidic conditions, but how to obtain modified CTS particle emulsifiers under acidic conditions in a simpler and less expensive way is still one of the main research directions to improve the utilization of CTS.

2.3 Cellulose

Cellulose, as a non-starch polysaccharide, is a linear macromolecule whose chemical structure consists of a repeating ring of β-1,4-linked D-glucans (Kedzior et al., 2017; Liu et al., 2019). It is widely found in various plant cell walls, wood pulp as well as in bacteria (Laitinen et al., 2017). The natural cellulose structure generally contains a crystalline region and a non-crystalline region. The glucose molecule chains in the non-crystalline region are arranged extremely irregularly, which easily exposes the hydroxyl groups at the edges of its chains and thus exhibits a certain degree of hydrophilicity, while the crystalline region exhibits a certain degree of hydrophobicity,

so cellulose particles are also excellent emulsion stabilizers for Pickering emulsions Cellulose particles with emulsification effect can be obtained by acid digestion of cellulose. Common cellulose particles include Cellulose nanocrystals (CNCs) (Kalashnikova et al., 2013), Cellulose nanofibrils(CNFs) (Winuprasith & Suphantharika, 2013), Regenerated cellulose, bacterial cellulose. All of these cellulose particles have been shown to stabilize Pickering emulsions. Among them, CNCs are now commercialized and the Pickering emulsions prepared from them have great application prospects. However, after sulfuric acid treatment, sulfate groups are introduced on the surface of CNCs thus making CNCs negatively charged. This highly charged nature makes CNCs very hydrophilic and poses certain limitations for the preparation of Pickering emulsions. Therefore, researchers have devised a series of methods to be proposed to solve the above problems. The main idea is to improve the emulsification performance by reducing the surface hydrophilicity of CNCs or improving hydrophobicity through various physical and chemical modifications. Kalashnikova et al. (2013) found that CNCs obtained with cotton cellulose and bacterial cellulose could not be effectively adsorbed at the oil-water interface when highly charged. Hydrolysis of bacterial cellulose by the addition of hydrochloric acid could shield the surface charge of CNCs and could significantly improve the emulsification ability of CNCs. As with starch granules, researchers can also physically and chemically modify cellulose granules. Usually, Pickering emulsions stabilised by CNCs are prepared using shearing, sonication or a combination of both as emulsification technique (Chen et al., 2019). However, chemical modification to improve the emulsification properties of cellulose particles is currently more effective There are two main chemical modification methods in the mainstream. After OSA modification, the surface hydrophobicity of cellulose nanocrystals (CNCS) is greatly improved, and the emulsification performance of CNCS is also significantly improved (Chen et al., 2018). The advantage is that even though the concentration of modified cellulose particles is very low, it is possible to prepare Pickering emulsions with a stable gel-like high internal phase. And when CNCS was modified with appropriate sodium ethyl lauryl alginate, the surface properties and aggregation state of CNCS could be improved. Pickering emulsions prepared when only a small or large amount of LAE is present tend to be stable, otherwise the prepared Pickering emulsions will have large droplet size and break easily (Bai et al., 2018).

3 Pickering emulsions stabilized by polysaccharide complexe particles

Since natural polysaccharides carry more hydroxyl groups and are therefore more hydrophilic and less emulsifiable. Pickering emulsions stabilized by a single polysaccharide-based particle do not perform satisfactorily in practice. People are more likely to use composite colloidal particles in practical applications. Composite colloidal particles can improve the emulsification of emulsions compared to single particles, and they help to resist environmental stresses (e.g., temperature, pH, ionic strength) and enhance the stability of emulsion gel systems. Current polysaccharide-based composite colloidal particle combinations broadly include polysaccharide-protein, polysaccharide-polysaccharide, and polysaccharide-ploy phenols as shown in Figure 5, Table 2 summarizes these food-grade particles and some of these examples are described in detail below.

3.1 Polysaccharide–protein complex particles

Proteins are a class of amphiphilic macromolecules that are common in living things and can adsorb at interfaces to reduce the energy of liquid interfaces (Lam & Nickerson, 2013), thus achieving stabilization of foams or emulsions. In addition, proteins can also self-assemble at the interface and form granular aggregates (Dickinson, 2008). This creates a strong spatial barrier at the interface between the foam and the emulsion. Existing studies have found that microgel particles prepared from soy protein, pea protein, and peanut protein (Burgos-Díaz et al., 2019; Ning et al., 2020) have been shown to be useful for preparing Pickering emulsions, but the addition of polysaccharides can improve their performance. Proteins are more lipophilic than

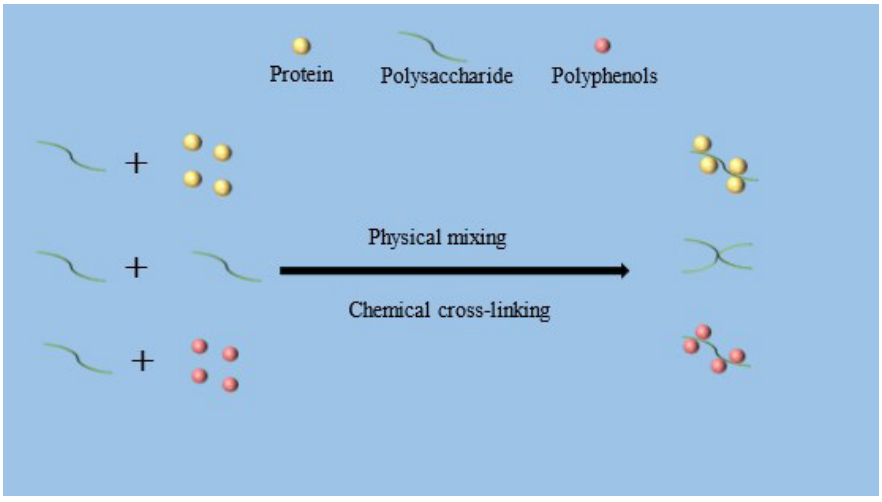

Figure 5. Schematic representation of the fabrication of complex particles.

Table 2. The preparation of complex particles and Pickering emulsions.

Complex particles	Particle shape	Particle size	Reference
Gliadin–chitosan complex particles	Spherical	575.7-601.9 nm	(Zhou et al., 2019)
Chitosan–starch complex nanogels	Nanogel	378.2 nm	(Li et al., 2019c)
OSA starch/chitosan complexes	Not available	116.8-491.5 nm	(Yan et al., 2019)
β-cyclodextrin–glucan complex particles	Spherical	104.48 nm	(Hu et al., 2020)
Phosphorylated cellulose Nanocrystal(P-CNC)/modified-chitosan (GCh) nanoparticles	Spherical	300-350 nm	(Baek et al., 2019)
Chitosan–caffeic acid complex particles	Not available	378-583 nm	(İlyasoğlu et al., 2019)
Lysozyme/xanthan gum nanoparticles	Inerratic spherical shape	50-76 nm	(Xu et al., 2018)

hydrophilic due to their carboxyl group structure, so they are biased towards the oil phase at the interface, but the resulting emulsions are not very stable and therefore require hydrophilic modification. In contrast to Pickering emulsions prepared using only polysaccharide particles as stabilizing particles, polysaccharide-protein complex particles have stronger emulsifying properties as Pickering stabilizers. These particles are formed mainly by electrostatic or charge interactions, including electrostatic attraction, hydrogen bonding, hydrophobic interactions, etc. The polysaccharides are highly hydrophilic and are often used in combination with proteins to construct solid particles in emulsions. Thus polysaccharide-protein complexes can better improve the stability of Pickering emulsions, and the addition of polysaccharides to protein particle-based Pickering emulsions can also be used to enhance their gastrointestinal conditioning effects. For example, the addition of inulin to Pickering emulsions stabilized by lactoferrin particles retards their in vitro gastric digestion, and currently protein-polysaccharide complex particles can be produced by physical mixing, enzymatic cross-linking, chemical cross-linking, and merad reactions. They are usually classified into covalent and non-covalent complexes depending on their complexation.

3.2 Polysaccharide–polysaccharide complex particles

The combination of polysaccharides and polysaccharides can also be used as a stabilizer for Pickering emulsions. Polysaccharide-polysaccharide complexes are formed mainly by electrostatic interactions between polysaccharides of opposite charges. The advantage over polysaccharide-protein complexes is that conditions such as ionic strength and pH do not need to be strictly controlled, which will also greatly enhance the performance of polysaccharide complexes as interfacial stabilizers for Pickering emulsion. Chitosan is the only known natural cationic polysaccharide, and researchers have mostly used it in complexes with other polysaccharides to prepare Pickering emulsions. For example, starch-chitosan complex particles and cellulose-chitosan complex particles. Baek et al. (2019) prepared nanocomposites from modified chitosan with phosphorylated cellulose nanocrystals by ionic gelation method. With increasing amount of chitosan, the nanocomposites changed from rod-like morphology to hard spheres and random coil morphology. Pickering emulsions prepared from nanocomposites have better stability over three months without aggregation and phase separation compared to chitosan-based Pickering emulsions. Li et al. (2019c) prepared chitosan hydrochloride and carboxymethyl starch complex nanogels by covalent cross-linking method and successfully applied the nanogels to the preparation of Pickering emulsions. Pickering emulsions prepared from this gel showed a high degree of stability at pH 6 and above.

3.3 Polysaccharide–polyphenol complex particles

Polysaccharides can also be used to form particles with natural small molecule polyphenols to prepare Pickering emulsions. Natural plant components polyphenols are of great interest because of their various healthful physiologically active functions. However, due to the problem of poor solubility, the efficacy of polyphenols is not fully exploited when they enter the human body. Therefore, the application of polyphenols to Pickering emulsions is important to address the bioaccessibility of polyphenols and to expand the functionality of Pickering emulsions. For example, chitosan lacks a conjugated structure and therefore has a weak antioxidant capacity. However, if polyphenolic crystals are added to chitosan, the antioxidant capacity of chitosan will be significantly increased, resulting in a strong ability to inhibit the oxidation of oils and fats. Compared to the small molecule surfactants used to stabilize conventional emulsions, the polyphenol crystals used for Pickering emulsion stabilization have particle sizes ranging from a few hundred nanometers to a few tens of microns, and the particles are mostly polyhedral, rod-shaped, spherical, or irregular in shape. Such studies on polyphenol particles in the oil-water community were first carried out by Luo et al. (2011). They found that some common polyphenols can be used to stabilize Pickering emulsions, such as curcumin, quercetin, rutin, etc. (Zembyla et al., 2019a, b). And the work of Duffus & Norton (2016) demonstrated the ability of water-insoluble polyphenol crystals, such as curcumin and quercetin, to effectively stabilize Pickering emulsions. Polyphenols and polysaccharides driven by hydrogen bonding and hydrophobic forces can be obtained as promiscuous particles for emulsion stabilization. The particles can form a dense particle layer with a certain thickness at the oil-water interface. For example, Li et al. (2019b) used the self-

assembly of tannic acid and β-glucan to form colloidal particles with an average particle size in the range of 300-900 nm that are nearly spherical. The use of polyphenol crystal particles to make Pickering emulsion is a relatively simple emulsification method, however, the current research field of this type of Pickering emulsion is relatively empty, and the application of polyphenol as stabilizer should be broadened, especially the development of polyphenol nanoparticles and the control of polyphenol crystal particle shape and size.

4 Application of Pickering emulsion stabilized by polysaccharide particles

4.1 Encapsulation and delivery of food bioactive ingredients

With the concept of nutritious and healthy diet gaining popularity, a large number of functional active substances have been used in food systems. However, a functional active substance such as coenzyme Q10, β-carotene (Tumer & Tulek, 2022), curcumin (Sun et al., 2022), inulin (Souza et al., 2020) etc. has poor water solubility and easy oxidation and decomposition, which makes it difficult to add directly into food. For example, coenzyme Q10 and curcumin are prone to loss when exposed to light, and their stability during storage cannot be maintained even after solubility problems are solved. Pickering emulsion as a special emulsion loading system, in addition to loading hydrophobic functional active substances, also has for adsorption on the water-oil interface of the particle layer for the carrier in the disperse phase to provide a physical barrier to block the external light source, to ensure the stability of some susceptible to photodegradation, UV degradation load as shown in the Figure 6. In addition, the network structure of food-grade particles in the continuous phase of the emulsion can achieve the effect of slow release, which is incomparable to conventional emulsions. For example, Pickering emulsions prepared by chitosan and corn protein are less toxic and easily biodegradable, and colloidal particles are adsorbed at the oil-water interface to form a dense layer of solid particles, which can effectively control the diffusion of functional active substances inside the emulsion droplets, and certain internal polymers can interact with the load, so the slow release of functional active substances can be better achieved. For example, Zhang et al. (2017) used hydrophobic calcium alginate (MCA) stabilized Pickering emulsion encapsulated with curcumin to investigate the release performance of the emulsion and found that the 4-h emulsion release in simulated gastric fluid at pH 1.5 was only 3%, while the release in simulated intestinal fluid at pH 6.8 reached 37% in the same time, indicating that MCA -Pickering emulsions have good pH sensitivity and slow release performance. Wang & Heuzey (2016) prepared Pickering emulsions by adjusting the pH of aqueous chitosan solutions worth to self-polymerized chitosan nanoparticles by ultrasound, When the pH value of chitosan aqueous solution was increased from 3.5 to 6.5, the stability of the emulsion was significantly enhanced with a maximum stability time of 2-5 months, indicating a clear advantage of Pickering emulsion in the encapsulation of functional active substances. Shah et al. (2016) used chitosan-triphosphate nanoparticle-stabilized Pickering emulsion to load curcumin, and only about 14% mass fraction of curcumin was degraded after 24 h of storage away from light, and this system was significantly more protective of curcumin than conventional methods.

4.2 Fat substitutes

Due to the poor plasticity of animal fats and their high saturated fat content, hydrogenated vegetable oils have been used for decades to improve the plasticity of fats, but this can lead to the production of harmful trans fats (Wei & Huang, 2019). The safety of trans fats in hydrogenated vegetable oils has long been a major concern, and medical studies have shown that trans fats can produce serious health risks (Brownell & Pomeranz, 2014; Mozaffarian et al., 2010). Therefore, it is important to look for high-quality, low-cost alternatives to hydrogenated vegetable oils. Pickering are a potential alternative product. When the internal phase ratio of emulsion is higher than 80%, the high internal phase Pickering emulsion is very close to margarine in terms of composition and properties, which is a potential substitute for margarine and can effectively avoid the intake of trans fat.

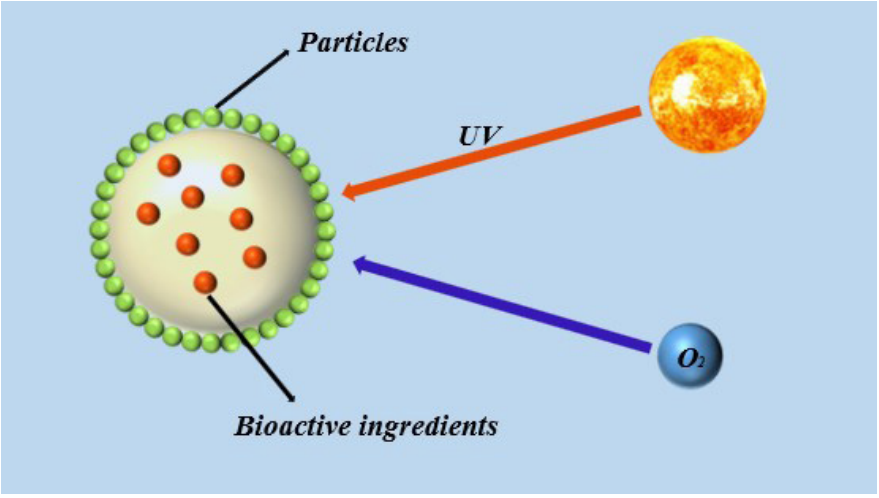

Figure 6. The solid particles adsorbed on the oil-water interface can provide a physical barrier to weaken the degradation of nutrients.

Pickering emulsions based on ethyl cellulose and camellia seed oil can be used as a substitute for cream in frozen yogurt and ice cream. Sensory evaluation and physicochemical characterization showed that Pickering emulsion-based products have more satisfactory food quality. Pickering emulsions can also be used in place of butter in cakes, while Pickering emulsion-based cakes can reduce calorie intake and extend shelf life without changing their color and texture (Feng et al., 2020). Zeng et al. (2017) was able to prepare stable Pickering high-internal phase emulsions with up to 83% internal phase at low concentrations (0.5-2%) of wheat alcohol soluble protein/chitosan composite particles. The extruded high internal phase Pickering emulsion droplets formed an interpenetrating 3-D network structure, which imparted viscoelasticity and plasticity to the emulsions. This experiment confirmed the protective effect of Pickering high internal phase emulsions on curcumin, and the content of primary oxidation products in HIPEs was slightly lower than that of the feedstock oil. It can be used as a potential substitute for partially hydrogenated vegetable oils. The results of all these experiments suggest that polysaccharide-based Pickering emulsions may replace hydrogenated vegetable oils and improve the nutritional value of foods, but their effects on functional properties and sensory attributes also need to be considered.

4.3 Modulation of lipid digestion

Pickering emulsions can be designed to control the digestion and absorption of lipids in the gastrointestinal tract, thereby increasing satiety and reducing appetite. CNCs have now been shown to inhibit fat in Pickering emulsions by reducing the ability of lipase to reach the oil droplets. It has also been shown that the rate and extent of lipid digestion can be regulated by selecting suitable particles as Pickering stabilizers (Sarkar et al., 2018). Wei & Huang (2019) found that the digestibility of oleogel-based Pickering emulsions stabilized by ovotransferrin fibers was higher than that of oleogels, indicating a greater degree of lipolysis. Other studies have also shown that ChNs can be used to impede lipid digestion may have important implications for the design and fabrication of structured emulsions with controlled lipid digestibility that could provide the basis for the development of novel products that may promote satiety, reduce caloric intake and combat obesity (Tzoumaki et al., 2013). The use of Pickering emulsions stabilized by polysaccharide-based particles to modulate lipid digestion and absorption has attracted widespread interest. For example, cellulose nanocrystals, chitin nanocrystals, starch particles and chitosan have been widely used to modulate the digestion and absorption of lipids. According to a previous study, Researchers investigated the impact of a naturally-derived particle stabilizer, cellulose nanocrystals (CNC), on the gastrointestinal fate and digestion of corn oil-in-water Pickering emulsions (Bai et al., 2019). The results were found to be effective in preventing droplet incorporation in the mouth and stomach. This is due to the formation of a dense, impermeable CNC coating around the oil droplets. As shown in Figure 7, Other studies have reported that the intestinal mucus layer can prevent CNCs from reaching epithelial cells, and this sequestration may also lead to reduced absorption of saturated lipids from CNC-stabilized emulsions, which may be used to regulate lipid absorption (Mackie et al., 2019). In addition the rate and extent of lipid digestion in tributyl stabilized Pickering emulsions showed significantly lower than in protein stabilized Pickering emulsions. The release of free fatty acids (FFA) was confirmed by experiments. After 60 minutes of digestion, only 6% of FFA was released from the tributyl stabilized Pickering emulsion, while 26% was released from the protein stabilized Pickering emulsion (Xiao et al., 2018). This is because proteins adsorbed at the interface are easily replaced by bile salts, as they form a thin mobile interfacial layer only after hydrolysis by proteases in the stomach and small intestine. In contrast, chitin nanocrystals attach so strongly that they are not readily replaced by bile salts and form a barrier that prevents lipase from reaching the lipids.

In summary, these studies suggest that polysaccharide-based Pickering emulsions can be designed to modulate lipid digestion, with the ultimate effect depending on the nature of the resulting interfacial coating. And their ability to regulate lipid digestion may lead to the development of diet-like foods.

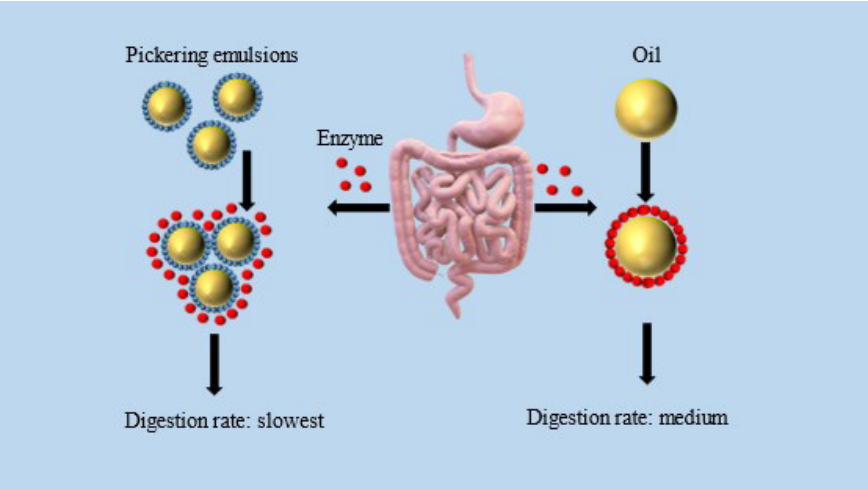

Figure 7. Schematic representation of the digestion of Pickering emulsions (left) and bulk oil (right) in the gastrointestinal tract.

5 Conclusions and future prospects

Pickering emulsions have gained popularity among researchers in recent years because of their enhanced stability and environmental friendliness compared to conventional emulsions, and the related products have also started to develop rapidly. The consumption and production of margarine in China is on the rise year by year. However, the main component of margarine, partially hydrogenated vegetable oil, contains harmful trans fats. There is enough evidence that trans fats have the risk of cardiovascular disease, diabetes, cancer, etc. Therefore, the search for high-quality, low-cost alternatives is a bottleneck that needs to be addressed. There is no doubt that Pickering emulsions are a very promising alternative. With the modification of some colloidal particles and the development of more nascent colloidal particles, Pickering emulsions will have good rheological properties, digestibility and freeze-thaw stability, providing more possibilities for their use in food applications. Although the application is very promising, there are still many challenges. On the one hand, it is difficult to maintain the stability of Pickering emulsions due to the more complex and variable environment of the actual food production process. On the other hand, most experiments have been conducted in the laboratory and have not been commercially developed on an industrial scale. Future research should focus more on improving the stability of Pickering emulsions in food production processes and exploring greener and more efficient Pickering emulsion preparation methods to exploit the commercial value of Pickering emulsions in the food sector.

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