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**Emerging Pickering emulsion films for bio-based food packaging applications**

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**Abstract**

Bio-based films have attracted great attention in food packaging for the biodegradable properties of these films. However, the mechanical strength, antibacterial, antioxidant and barrier properties of these films are struggle to meet practical application requirements. Adding multifunctional hydrophobic substances in Pickering emulsions into hydrophilic bio-based films is a newly developed strategy to improve the physicochemical properties. In this review, we summarize the preparation and applications of Pickering emulsions contained bio-based films. The first part introduces different polysaccharides and proteins-based Pickering emulsions that have been used to fabricate degradable food packaging films. Different form of films, for instance, self-support films and coatings are discussed in the second part. In the third part, antibacterial, antioxidant, barrier and optical properties of films have been systematically discussed. The last part introduces the applications of the films, particularly, the preservation of various meat, vegetable and fruit.

**Keywords:** Pickering emulsions, Food packaging, Polysaccharides, Nanomaterials, Films

## 1. Introduction

Petroleum-based polymers have been widely used as food packaging materials for their properties of high strength, cheap and light weight .

. However, synthetic polymers degrade slowly in the natural environment and cause severe environmental pollution, such as microplastic pollution (do Sul & Costa, 2014; Tang et al., 2021). Polysaccharides and proteins enhance film forming, biodegradable and other practical properties and there are many publications involving such biopolymers in food packaging fields (Ding, Hu, Lan, & Wang, 2020). Yet, most of the biopolymers-based packaging films are still in the experimental stage, unusual films can be used to enhance poor barrier, mechanical and hydrophilic properties but their practicality is problematic. Strategies for incorporating nanofillers, blending other bio or synthetic polymers, chemical treatment, and physical modification have been widely used to enhance the physicochemical properties.

Pickering stabilized emulsions for food applications have been recently developed as an alternative to the use of conventional surfactants such as Tween 20 and sodium dodecyl sulphonate (SDS) (Murray, Ettelaie, Sarkar, Mackie, & Dickinson, 2021; Sarkar & Dickinson, 2020). They are advantageous because they can be safe, biodegradable, stable and economic, making them very attractive for use in packaging applications. (Gonzalez Ortiz, Pochat-Bohatier, Cambedouzou, Bechelany, & Miele, 2020)

Incorporating multifunctional Pickering emulsions into the polymer matrix to make different bio-based packaging films with enhanced physicochemical features has attracted attention (Niro, Medeiros, Freitas, & Azeredo, 2021). Pickering emulsions are emulsions stabilized by solid particles or nanofibers which adsorb onto the interface between the water and oil phases (Berton-Carabin & Schroën, 2015; Lou, Wen, Wang, & Ni, 2023). Nano sized polysaccharides and proteins such as nano-cellulose, chitin, starch, zein, phytoparticles (Jafari, Sedaghat Doost, Nikbakht Nasrabadi, Boostani, & Van der Meeren, 2020) and whey protein isolate have been used as stabilizer to prepare Pickering emulsions which can be incorporated into polymer matrix to fabricate food packaging films or coatings. The incorporation of Pickering emulsions into the film can directly enhance the antibacterial and antioxidant properties for the multifunction of the substances in the oil phase.

Essential oils (EOs) are concentrated hydrophobic liquids with excellent antibacterial and antioxidant properties that have been widely used in Pickering emulsions. Whilst their hydrophobic properties dominate their solubility behavior, all essential oils contain polar components which distinguish their behavior from the triacylglycerols which are the major components of vegetable oils. EOs are also different chemically from vegetable oils, which comprise mainly esterified fatty acids, while Eos are volatile at room temperature and formed from terpenes (Bakkali, Averbeck, Averbeck, & Waomar, 2008). The presence of hydrophobic and phenolic compounds with hydroxyl groups (-OH) in EOs are responsible for antibacterial and antioxidant activities (Dorman & Deans, 2000) which are able to disrupt the cell membrane of the bacteria (Xue, Davidson, & Zhong, 2013). Oregano, lemon, clove, grapefruit, marjoram essential oil have been used to enhance the antibacterial and antioxidant properties of bio-based films (Mukurumbira, Shellie, Keast, Palombo, & Jadhav, 2022; Perumal et al., 2022; Rout et al., 2022). Other biologically active substances, such as thymol and curcumin, have also been added into the films or coatings (Ahmed et al., 2022). Pickering emulsion containing films can evenly disperse the active components such as EOs. The release behaviors of the active materials from the film can be controlled accurately in a homogenous film which is critical if it is to extend the shelf-life of foods (Tavassoli et al., 2023). Another advantage of Pickering emulsion containing systems is that a homogenous film enhances the water vapor barrier properties of the film. The water vapor permeability (WVP) of a film containing Pickering emulsions reduced due to the increased tortuous path caused by the emulsions and hydrophobic compounds in the oil phase (Yang et al., 2023). As to the oxygen permeability of the films, in some cases, the oxygen permeability of the films enhanced in that the high solubility of nonpolar oxygen molecules in the oil phase. In other cases, the oxygen permeability of the films reduced with addition of Pickering emulsions for the high crystallinity characteristics of the polymeric stabilizer.

Bio-based food packaging films have made great progress due to the development of biopolymer nanomaterial stabilized Pickering emulsions. In this article, we comprehensively review recent advances in biopolymer stabilized Picking emulsions which can be incorporated into a polymer matrix to fabricate food packaging films. Different forms of Picking emulsions contained packaging films are discussed. Antibacterial, antioxidant, barrier, optical properties and the different foods preservation behaviors of the Pickering emulsions-based packaging films are systematically reviewed (Fig. 1). The aim of this review is to present the latest progress of biopolymer nanomaterials stabilized Pickering emulsions-based food packaging and provide perspectives in the development of new bio-based food packaging films.

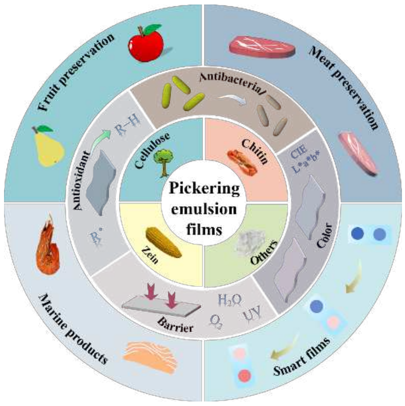


Fig. 1. Schematic illustration of this review

## 2. Different biopolymeric Pickering emulsions

Biopolymeric nanomaterials stabilized Pickering emulsions with characteristics of biocompatibility and biodegradability have been widely researched in different engineering fields (Ribeiro, Morell, Nicoletti, Quiles, & Hernando, 2021). In particular, polysaccharide nanomaterials such as cellulose, chitin, and protein nanomaterials of zein and whey protein isolate have been used to stabilize the Pickering emulsions which can be incorporated into the biopolymer matrix to fabricate different food packaging films. In this section, various biopolymeric nanomaterials-based Pickering emulsions which can be used to prepare food packaging films are discussed.

### 2.1 Cellulose nanomaterials stabilized Pickering emulsions

Cellulose is the most widely distributed and abundant polysaccharide in nature. It has been heavily researched in various fields (Ding et al., 2021; Mokhena & John, 2020). A series of nano-cellulose including cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs) can be prepared through enzymatic hydrolysis, mechanical stirring, or chemical treatments (Bu et al., 2022; Kargarzadeh et al., 2018) (Fig. 2. (a-c)). The raw materials are commonly derived from plants (straw, wood, fruits), sea animals (tunicates) and waste biomass (paper, plant leaf) (Q. Li et al., 2021). Cellulose nanomaterials include bacterial cellulose nanocrystals (BCNCs) and bacterial cellulose nanofibrils (BCNFs) that can also be derived from some some bacteria. Cellulose nanomaterials have the characteristics of low cost, safety, environment-friendly, easily available and can be used as a stabilizer to stabilize Pickering emulsions (Fujisawa, Togawa, & Kuroda, 2017). Cellulose nanomaterials can replace the traditional chemical surfactant to pursuit more suitable Pickering emulsions.

Among cellulosic materials, CNCs are commonly applied nanomaterials to stabilize Pickering emulsions due to the broad range of applications (Sneh Punia Bangar, Whiteside, Dunno, Cavender, & Dawson, 2023) and contributes to multiple functions of Pickering emulsions. For instance, CNCs isolated from cotton showed spherically shaped droplets and good dispersibility and has been applied to stabilize oregano and cinnamon essential oil Pickering emulsions. CNCs can effectively keep oil droplets from accumulating with each other improving bacterial inhibition against (Oun, Shin, & Kim, 2022) (Fig. 2. (d, e)). Likewise, superb polydispersity was seen in cinnamon essential oil-based CNC stabilized Pickering emulsions, remaining stable even after a month of storage. Moreover, the variations in concentration from both CNCs and cinnamon essential oils affected the emulsion droplet size (J. Liu et al., 2022). Different concentrations of CNCs are  play a significant role in thermal stability and storage time of corn oil loaded emulsions (Kasiri & Fathi, 2018). CNCs can be also serve as stabilizers in acrylate epoxidized soybean oil loaded Pickering emulsions, exhibiting obvious improvement of emulsion deformation recovery capacity and viscosity as the content changes. The concentration of CNCs was determined as crucial factor in emulsion rheological properties, and better water vapor resistance was performed accordingly in Pickering coatings (R. Liu et al., 2021).  CNC stabilized oleic acid Pickering emulsions incorporated into chitosan coatings, improve stability and hydrophobicity; thereby extending the shelf-life of fruits(Deng, Jung, Simonsen, & Zhao, 2018). Though CNC stabilized Pickering emulsions have been extensively researched, modified CNCs with designed properties can better stabilize Pickering emulsions.

Chemical modification is one of the most widely used methods for the preparation of CNC derivatives that improve the stability of Pickering emulsions. For instance, octylamine modified CNCs display stronger ability in preventing oil droplets from creaming than unmodified CNCs, as a result of the grafted hydrophobic moieties on the surface (G. Xu et al., 2022) (Fig. 2. (f, g)). 3-aminopropyltriethoxysilane (APTES) modified CNCs reach a more stable dispersion in acrylate epoxidized soybean oil Pickering emulsions, enhancing the hydrophobicity in comparison with pristine CNCs (X. Tian, Wu, Wang, Zhang, & Lu, 2022). Aliphatic succinic anhydride modified CNCs were selected as a more advantageous stabilizer in starch-beeswax nanocomposite emulsions than unmodified ones, due to the amphiphilic character of dodecyl succinic anhydride CNCs (Trinh, Smith, & Mekonnen, 2022). Likewise, ethyl lauroyl arginate modified CNCs provide potent suppression against gravitational separation in cinnamaldehyde-based Pickering emulsions, resulting in a more uniform and stable emulsions (K. Zhang, Ren, Harper, & Li, 2022). Another commonly used modification method is to oxidize the hydroxyl groups on the cellulose. In oregano essential oil Pickering emulsions, CNCs made from microcrystalline cellulose via the oxidization ammonium persulfate efficiently inhibited the growth of four microorganisms when mixed with them (Y. Zhou et al., 2018). Sulfuric acid hydrolyzed CNCs can be used to stabilize Pickering emulsions. The electrostatic repulsion force endowed the modified CNCs with the ability to emulsify the cinnamon essential oil Pickering emulsions. When TEMPO-oxidized CNCs in the same oil phase emulsion grafted with polyethyleneimine, receiving an improved emulsification properties (M. Wu, Yang, Chen, Lu, & Wang, 2021).

Cellulose nanofibrils is another nano-cellulose frequently used to stabilize the Pickering emulsions (Q. Li et al., 2021; A. A. Wardana, Wigati, Tanaka, & Tanaka, 2023; Ata Aditya Wardana, Wigati, Van, Tanaka, & Tanaka, 2023). Although CNCs and CNFs are perfect stabilizers, there are some notable differences in the observation of morphology between them. Unlike short rigid rod-like crystals, CNFs with semi-flexible structure of long fibrils, exhibit better emulsifying capacity by forming a three-dimensional structure network in the oil-water surface (Fig. 2. (h, i)). CNF stabilized tea tree essential oil Pickering emulsions present good stable and thermal properties, attributed to a light white appearance and invariability under thermal treatment (Bu et al., 2022). Similarly, the stabilization by CNF was applied to clove essential oil loaded Pickering emulsions as well, displaying excellent polydispersity in emulsions (S. Roy & J.-W. Rhim, 2021). Furthermore, creaming phenomena were effectively restrained over time in CNF stabilized sunflower oil Pickering emulsions, primarily owing to the  networks of particles. And the emulsion viscosity was determined by the endowed crystallinity and length of CNFs,  associated with the mechanical treatment (Costa, Gomes, Tibolla, Menegalli, & Cunha, 2018). CNF stabilized peanut oil Pickering emulsions showed high stability whilst stored for more than 3 months, as a resultof changed surface wettability through different $FeCl_3$-catalyzed formic acid hydrolysis. Particularly, better stabilization is achieved in CNF stabilized Pickering emulsions through the alteration of ionic strength (W. Liu et al., 2022). In addition to the stability given by CNFs, the thermal and mechanical properties of edible composite films can be promoted in the presence of soybean oil Pickering emulsions, depending on the concentration of oil.

Cellulose nanofibrils also exhibit desired excellent performance through chemical modification (Qasim et al., 2023). The surface of oxidized CNFs is negatively charged, creating electrostatic repulsion between nanofibers and facilitating the dispersion in cinnamon oil based Pickering emulsions (Jian Liu et al., 2022) (Fig. 2. (j, k)). Moreover, the oxidized CNFs can fabricate a complex system with the cationized CNFs through electrostatic attraction, therein the opposite charge reaction from both CNFs stabilizes them at the interface and plays a vital role in emulsion stability (Shi et al., 2022). Although other modified CNFs have been prepared and used to fabricate Pickering emulsions, yet, these kinds of Pickering emulsions have seldomly been applied mixed with a biopolymer matrix to fabricate bio-based films. In view of excellent performance of the CNFs and stabilized Pickering emulsions, various modified CNFs and its stabilized Pickering emulsions should have promising future in the preparation of multifunctional bio-based food packaging films.

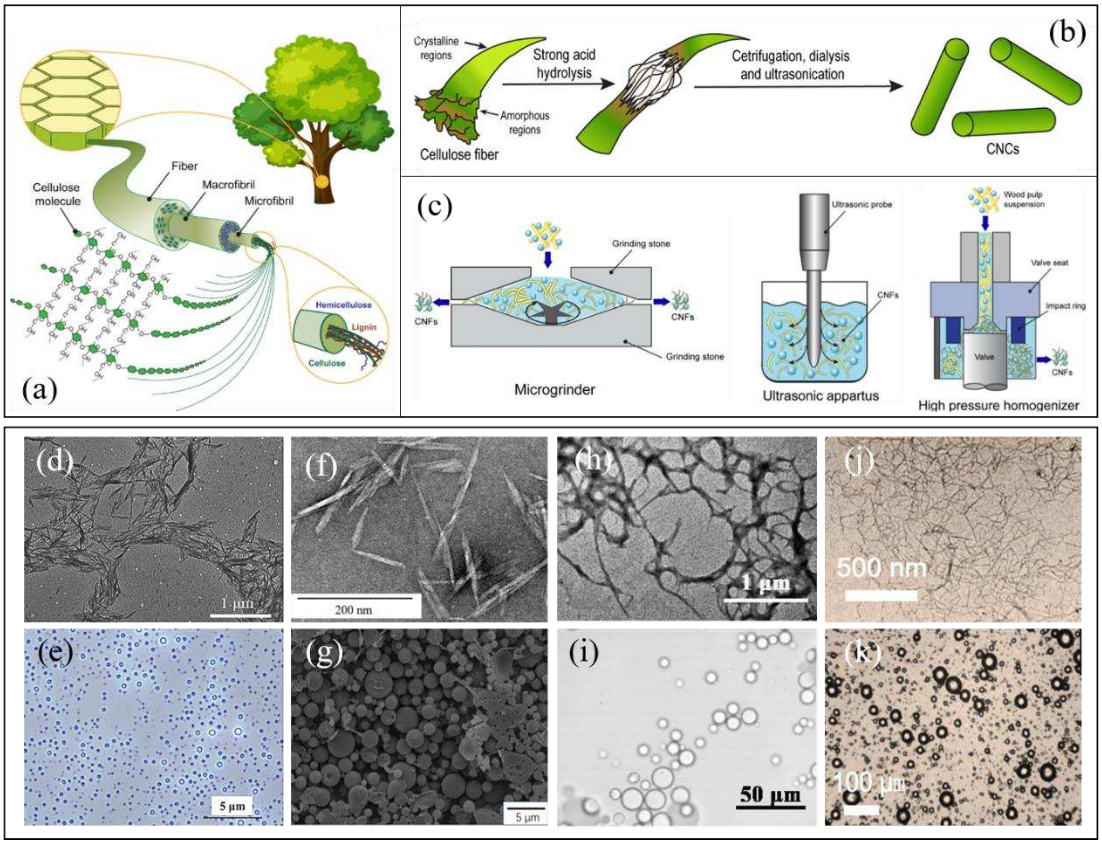


Fig. 2. Diagram shows the source and fibrous structure of cellulose (a), the process of fabrication of cellulose nanocrystals (b), three main methods for fabricating cellulose nanofibers (c), [Reprinted with permission from (Ghasemlou, Daver, Ivanova, Habibi, & Adhikari, 2021). Copyright 2021 Elsevier], the morphology of cellulose nanocrystals and its stabilized Pickering emulsions (d, e),

[Reprinted with permission from (Oun et al., 2022). Copyright 2022 Elsevier], the morphology of octylamine-modified cellulose nanocrystal and its stabilized Pickering emulsions (f, g), [Reprinted with permission from (G. Xu et al., 2022). Copyright 2022 American Chemical Society], the morphology of cellulose nanofibers and its stabilized Pickering emulsions (h, i), [Reprinted with permission from (Y. Zhang et al., 2020). Copyright 2020 Elsevier], the morphology of modified cellulose nanofibers and its stabilized Pickering emulsions (j, k), [Reprinted with permission from (Jian Liu et al., 2022). Copyright 2022 Elsevier].

Apart from those CNCs and CNFs derived from biomass, two other kinds of nanomaterials (BCNFs and BCNCs) of bacterial origin can also be prepared and applied to fabricate Pickering emulsions (Huang et al., 2014; Reiniati, Hrymak, & Margaritis, 2017; Xia et al., 2023) (Fig. 3. (a, b)). BCNFs can be used as an excellent stabilizer in peanut oil Pickering emulsions, with good dispersion and lower surface tension (Fig. 3. (c-e)). But high oil concentration will lead to the reduction of intensity (Zhai, Lin, Liu, & Yang, 2018). BCNCs may cause discontinuity between oil droplets, thus resulting in poor water barrier properties. While in palm olein loaded Pickering emulsions, the emulsions dispersed uniformly in the presence of BCNC stabilization. The incorporation of a calcium-crosslinked alginate system (Medeiros et al., 2022) enhanced opacity and opposite increased water vapor permeability. Moreover, an emulsion consisting of cinnamon essential oil and BCNCs has the potential to create a cage-like structure accompanied by the addition of gelatin, showing unique overall stability. Particularly, lower concentration of oil in BCNCs system result in smaller particles, which is distinct from the conventional Pickering emulsions (Razavi et al., 2020). Although the CNCs or CNFs derived from bacteria have been developed to prepare Pickering emulsions, the research on this topic is insufficient because sources of bacterial cellulose are not as extensive as that of biomass cellulose. However, BCNF and BCNC stabilized Pickering emulsions will in future be prepared and incorporated in the fabrication of bio-based packaging films as food, chemistry and packaging science devlopes.

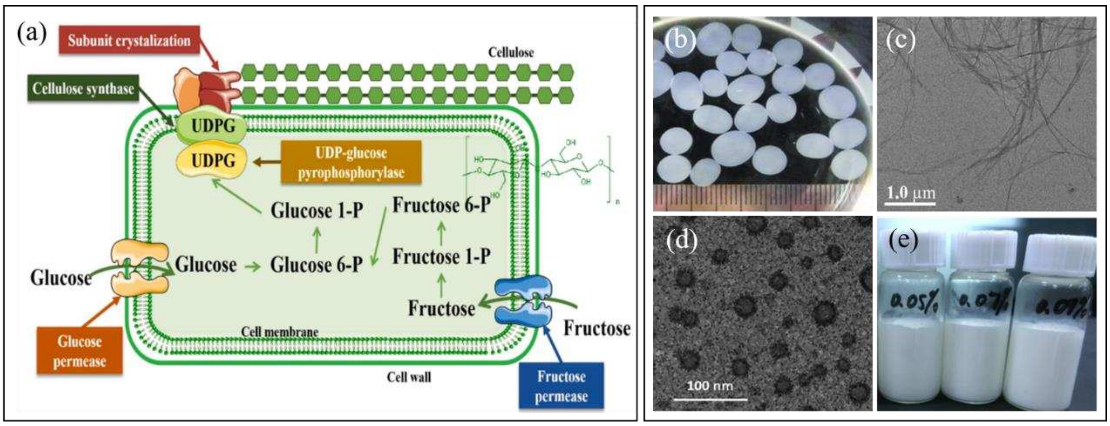


Fig. 3. Diagram shows the process for synthesizing bacterial cellulose (a), [Reprinted with permission from (Qian et al., 2022). Copyright 2023 Elsevier], optical photograph of bacterial cellulose beads (b), [Reprinted with permission from (Qian et al., 2022). Copyright 2023 Elsevier], transmission electron microscopy image of bacterial cellulose nanofibers (c), transmission electron microscopy and optical images of bacterial cellulose nanofibers stabilized Pickering emulsions (d, e) [Reprinted with permission from (Zhai et al., 2018). Copyright 2018 Elsevier].

## 2.2 Chitin and chitosan nanomaterials stabilized Pickering emulsions

Chitin is the second most abundant biomass on the earth after cellulose (Hu et al., 2018; Hu et al., 2021). The structure of chitin is like cellulose. Chitin is mainly extracted from the shells of Marine crustaceans, possessing varying properties including biocompatibility, biodegradability, sustainability, and renewability (Bai et al., 2022; Lv et al., 2022). Despite the enormous annual production of chitin in nature, it is an under-utilized biomass resource. Fabrication of chitin-based nanomaterials applied in food science can greatly promote the development of this biomass (Liao, Zhou, Hou, Zhang, & Huang, 2023; Y. Liu et al., 2023).

From chitin, chitin nanocrystals (ChNCs) and chitin nanofibers (ChNFs) can be obtained. Chitin nanocrystals are mainly obtained from crab or shrimp shells through hydrolysis (Fig. 3. (a-c)). Prepared chitin nanocrystals with positive charge can be used to stabilize Pickering emulsions (Jimenez-Saelices, Trongsatitkul, Lourdin, & Capron, 2020; J. T. Xu et al., 2023) (Fig. 3. (d)). Chitin nanocrystals can also adsorb at oil-water interfaces and form a network in the continuous phase (Barkhordari & Fathi, 2018). In addition, the chitin nanocrystal network can form between emulsion droplets. These two properties together confer the resultant Pickering emulsions with high stability which can be adjusted by adjusting the pH or adding salts into the system. Concentration has an influence on Pickering emulsions (Y. Zhu et al., 2020); increasing the concentration of the chitin nanocrystals results in a high internal phase Pickering emulsions (HIPPEs) with an internal phase up to 96 % (Perrin, Bizot, Cathala, & Capron, 2014). The stabilization ability of the chitin nanocrystals can also be adjusted by chemical modification or complexation with other substance.

While chitin breaks down into fibrous structures, a range of superior material properties would be exhibited, because of the increased surface-volume ratio. ChNFs showed better emulsify properties than the ChNCs at the same concentration and ChNF stabilized Pickering emulsions showed high stability when the concentration was higher than 0.8 wt%. The stability of emulsions was affected by the concentration of the chitin nanomaterials and higher concentration results in higher stability. Also, the crystal structures and lengths of the nanofibers have influence on the Pickering emulsions. In a mixture of ChNF and divinylbenzene emulsions, the dispersive ability of the droplets of two diverse ChNFs differs depending on crystal structures and lengths. Obviously, the chitin nanofibers with shorter fibrils as well as greater surface charge present better dispersibility (Kaku, Fujisawa, Saito, & Isogai, 2020).

With the extensive application of nano-filling materials for improving edible films, chitosan nanoparticles (ChiNPs) are emerging as a potential novel material for stabilizing Pickering emulsions and food packaging (Gasti et al., 2022; W. H. Meng, Sun, Mu, & Garcia-Vaquero, 2023; R. Zhao, Guan, Zheng, et al., 2022). Chitosan nanoparticles are usually fabricated at pH 6.5 through self-assembly. Chitosan nanoparticle-stabilized Pickering emulsions demonstrate increased stability as the droplet size decreases (W. Meng, Sun, Mu, & Garcia-Vaquero, 2022). Chitosan nanoparticles can also be prepared through crosslinking with tripolyphosphate (TPP). TPP-crosslinked chitosan nanoparticle stabilized Pickering emulsions show high stability against varying pH and ionic strength. Chitosan can also complex with other macromolecules forming nanoparticulate structures due to the positive charge of the chitosan. Gum arabic, casein, zein and gelatin have also been complexed with chitosan to prepare nanoparticles which can be used to stabilize Pickering emulsions (Sharkawy, Barreiro, & Rodrigues, 2020). Many authors have reviewed the preparation of chitin and chitosan nanomaterials stabilized Pickering emulsions (Bai et al., 2022; Barkhordari

& Fathi, 2018; Jimenez-Saelices et al., 2020; Kaku et al., 2020; Lee, Tarté, & Acevedo, 2021; Liao et al., 2023; Y. Liu et al., 2023; Lv et al., 2022; Perrin et al., 2014; Sharkawy et al., 2020; Sun, Zhao, Liu, Li, & Li, 2019; J. T. Xu et al., 2023; Yuan, Hong, Lian, Zhang, & Liimatainen, 2020; Y. Zhu et al., 2020). Though chitin and chitosan nanomaterials showed excellent properties and can be used to stabilize Pickering emulsions, further development of chitin and chitosan science is needed

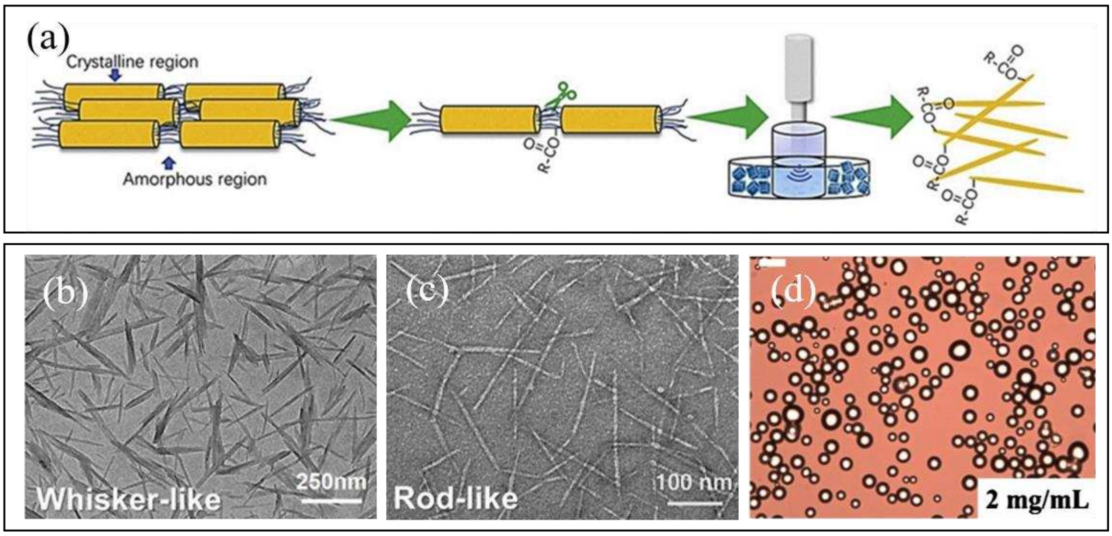


Fig. 4. Diagram showing the process of fabricating chitin nanocrystals (a), [Reprinted with permission from (Yuan et al., 2020). Copyright 2020 Elsevier], transmission electron microscopy images of chitin nanocrystals (b, c), [Reprinted with permission from (Liao et al., 2023). Copyright 2023 Elsevier], optical images of chitin nanocrystal stabilized Pickering emulsions (d), [Reprinted with permission from (Jimenez-Saelices et al., 2020). Copyright 2020 Elsevier].

**2.3 Zein colloidal particles stabilized Pickering emulsions.**

Proteins are biological macromolecules frequently utilized as stabilizers and emulsifiers in Pickering emulsions (C. Z. Wang et al., 2022), in addition to polysaccharides. For example, Zein is an alcohol soluble protein obtained from maize (Song, Xiong, Shi, Yuan, & Gao, 2022) which can safely be used as a stabilizer in Pickering emulsions result due to its disintegration into zein colloidal particles (ZCPs) by self-assembly (Du et al., 2023; M. Li & He, 2021; Wei et al., 2021). However, due to polymerization of the hydrophobic area, the resultant Pickering emulsions often delaminate, demulsified or even leak, induced by ZCPs. So, it is inappropriate to consider the ZCPs as favorable particles due to the resultant hydrophilicity at the interface. ZCPs are better employed with other biopolymers, such as chitosan, cellulose nanomaterials, pectin and so on to stabilize emulsions (Cui et al., 2023; Sun et al., 2019; B. Wu et al., 2022; Yao et al., 2023).

As for the composite of ZCPs and chitosan, the homogeneous and individual droplets show improved stability in the presence of quercetin (Ma, Huang, Yin, Yu, & Yang, 2021). Zein and chitosan composite particles reduce oil release, for example in the case of cinnamaldehyde essential oil Pickering emulsions, which reach an optimized stabilizing effect at the ratio 20:1 (Y. Wang et al., 2022). In contrast, the complex system of ZCPs and CNCs synergistically maintained higher physicochemical stability by coating droplets, thereby inhibiting lipolysis. In this case CNCs functioned as an inner layer while ZCPs served as the outer one (Wei et al., 2021) (Fig. 4. (a-c)). Another bioactive substance that often blinds to ZCPs is pectin, which can be extracted from multifarious fruits, endowing effective stabilization in conjunction with ZCP, for example achieving sustainable utilization of hawthorn fruit waste to create products with added value. (Jiang et al., 2020). Likewise, gellan gum (GG), a water-soluble polysaccharide exuded from the bacterium Sphingomonas elodea whilst fermenting under aerobic conditions, comprises both high acyl and low acyl gellan. As expected, it is of greater benefit to Pickering emulsions due to the existence of low acyl gellan which is absent from zein. Furthermore, there is a close correlation between the concentration of GG and the wettability of the zein/gellan gum composite, with the latter being determined by the former (Jiang et al., 2021).

In addition to the above, amino acids can also bind to zein by non-covalent bonds to form colloidal particles, thereby altering structure and transforming function. For instance, combination with glutamic acid brought about changes in the secondary structure and wettability of zein, along with improved Pickering emulsion stability as a consequence of hydrophobic and electrostatic interactions. To some extent, plant-based polyphenols and zein perform in similar ways.. Adzuki bean seed coat polyphenol (ABSCP), a plant polyphenol sourced from the adzuki bean, demonstrated an increasing lipid oxidative stability in Pickering emulsions via covalent binding. In particular, the inherent color of ABSCPs (red and yellow) imparts an extraordinary characteristic appearance onto Pickering emulsions.

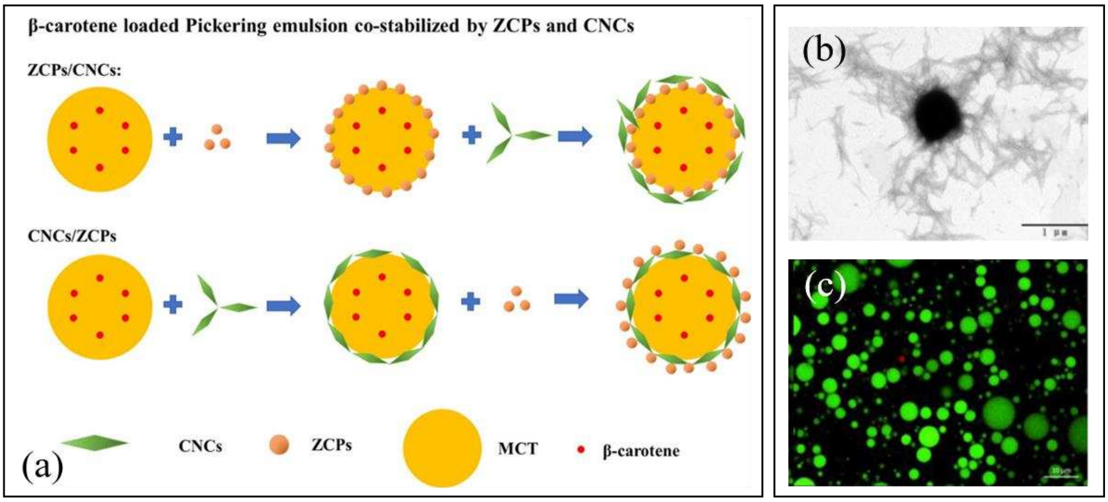


Fig. 4. Diagram shows (a) the process of zein nanoparticle fabrication for stabilized Pickering emulsions, (b) transmission electron microscopy images of cellulose nanocrystals modified zein nanoparticles, (c) confocal laser scanning microscopy images of zein nanoparticles stabilized Pickering emulsions [Reprinted with permission from (Wei et al., 2021). Copyright 2021 American Chemical Society].

## 2.4 Other biopolymeric nanomaterials stabilized Pickering emulsions

Nanomaterials derived from cellulose, chitin, and zein have been widely applied to the fabrication of Pickering emulsions which can then be used to prepare composite films. Other biopolymeric nanomaterials, such as whey protein isolate (WPI), collagen and starch have also been used to stabilize Pickering emulsions and prepare composite films (Ran et al., 2023). Whey protein isolate (WPI), the major constituents of which are β-lactoglobulin and α-actalbumin, rank as the most suitable biopolymers for the encapsulation of hydrophobic bioactive compounds owing to the existence of both hydrophobic and hydrophilic amino acids. Nevertheless, WPI often combines with inulin to play a joint role in Pickering emulsions, because of the higher core material encapsulation that the combination of proteins and short chain polysaccharides can provide (T. Zhang et al., 2021). WPI-inulin stabilized Pickering emulsions and Tween 80 prepared emulsions are blended to activate films. The loaded essential oil includes marjoram essential oil, cumin seed essential oil and clove essential oil. When the pH value is higher than the isoelectric point of WPI, Pickering emulsions exhibit a higher negative zeta potential that accords with the negative charge of WPI, finally delivering perfect stability because of electrostatic repulsion between droplets (Almasi, Azizi, & Amjadi, 2020; Hemmatkhah, Zeynali, & Almasi, 2020; Shen et al., 2021). Collagen is a fiber-like structure protein which is the most abundant protein in mammals. It can be used to stabilize cinnamon-perilla essential oil Pickering emulsions. Collagen stabilized Pickering emulsions can be incorporated into chitosan to prepare composite films with enhanced physicochemical properties.

In addition to protein nanomaterials, other polysaccharide such as nanosized starch can be used to stabilize Pickering emulsions and prepare composite films (López-Pedrouso, Lorenzo, Moreira, & Franco, 2022; T. Xu et al., 2020). Native starch can be used to stabilize Pickering emulsions due to its structure. The stabilization ability of native starch granules is mainly affected by the source, shape and size of the starch. Modified starch with enhanced hydrophobic properties showed improved emulsifying ability. Octenyl succinic acid modified starch can be applied to stabilize curcumin-loaded Pickering emulsions. Modified starch stabilized Pickering emulsions can be incorporated into a starch and polyvinyl alcohol mixture to fabricate an intelligent film. The starch is an easily available and cheap polysaccharide which has been widely used to stabilize Pickering emulsions (Lee et al., 2021). However, starch-based Pickering emulsions have seldomly been used to fabricate composite films. Different kinds of starch-based Pickering emulsions can be blended with various polymer matrix to fabricate bio-based food packaging films. Other biopolymer nanomaterials stabilized Pickering emulsions that have been used to fabricate packaging films can be found in Table 1.

Table 1. Summary of preparation of biopolymer nanomaterial stabilized Pickering emulsions that have been used to fabricate biopolymeric packaging films

| Particles | Raw materials | Preparation method | Bioactive substance | Emulsion type | Ref |
|---|---|---|---|---|---|
| CNCs | Cotton fibers from Whatman filter paper | $H_2SO_4$ hydrolysis and post-purification | Oregano essential oil / cinnamon essential oil | O/W | (Oun et al., 2022) |
| CNCs | Purchased from Tianjin Woodelfbio Cellulose Co., Ltd. | — | Cinnamon essential oil | O/W | (J. Liu et al., 2022) |
| CNCs | Kudzu (Pueraria montana) vines | De-polymerization and $H_2SO_4$ hydrolysis | Clove bud oil | O/W | (Punia Bangar et al., 2022) |
| Aliphatic succinic anhydride-modified CNCs | Obtained from CelluForce Inc. | — | Cornstarch and beeswax | O/W | (Trinh et al., 2022) |

| | | | | | |
|---|---|---|---|---|---|
| +CNCs | | | | | |
| Sulfated CNCs and Octylamine-modified CNCs | Provided by the Process Development Center, University of Maine | — | Linseed oil | O/W | (G. Xu et al., 2022) |
| OCNCs (TOCNC-g-PEI) | Sugarcane | Mechanical grinding | Oregano essential oil and soybean oil | O/W | (M. Wu et al., 2021) |
| CNFs | Citrus peels | Homogenization | Soybean oil, curcumin | O/W | (Valencia, Nomena, Mathew, & Velikov, 2019) |
| OCNFs | Provided by Tianjin Woodelfbio Cellulose Co., Ltd. | — | Cinnamon oil and curcumin | O/W | (Jian Liu et al., 2022) |
| BCNCs | Dried membranes from Biosmart Nanotechnology | Mill and $H_2SO_4$ hydrolysis | Palm olein, probiotic bacteria | O/W | (Medeiros et al., 2022) |
| BCNCs | Komagataeibacter sucrofermentans | Static fermentation and $H_2SO_4$ hydrolysis | Cinnamon essential oil, fish gelatin | O/W | (Razavi et al., 2020) |
| WPI | Obtained from Source Leaf Biology | — | Clove essential oil, inulin | O/W | (Shen et al., 2021) |
| ZCPs | Purchased from Yuancheng Co. Ltd. | Glacial acetic acid hydrolysis, homogenization and ultrasonication | Clove essential oil | O/W | (Y. Xu et al., 2020) |
| ChNCs | Chitin powder from shrimp shells, | HCl hydrolysis | Paraffin oil | O/W | (Jimenez-Saelices et al., 2020) |
| ChiNPs | Obtained from Sigma-Aldrich | Acetic acid hydrolysis and ultrasonication | Soybean oil and hesperidin | O/W | (Dammak, Lourenço, & Sobral, 2019) |

— means not reported in the referenced article

## 3. Different form of films

Polysaccharide nanomaterial stabilized Pickering emulsions can be incorporated into a biopolymer matrix to prepare different functional films (Fig. 5). Single biopolymer/Pickering emulsions or binary biopolymers/Pickering emulsions self-support films or coatings can be fabricated mainly by the method of blending and casting.

### 3.1 Self-support films

#### 3.1.1 Single biopolymer/Pickering emulsions films

Self-support films attract a lot of attention in the food packaging field and generally consist of biopolymers like proteins, polysaccharides, lipids and other edible substances, with the characteristic of non-toxic, biodegradable, biocompatible and so on (Y. Xu et al., 2020). A self-supporting film is a type of film that does not require any substrate or support to maintain its shape and structure. Edible films of a hydrophilic nature will lead to high water permeability and low firmness, thus resulting in adverse effects on the shelf life of food. For this reason, plant essential oil-based Pickering emulsions and other materials are incorporated into the edible matrix to fabricate composite films, improving the water barrier as well as antibacterial property of films (Fig. 5. (b, c)). Biopolymers of starch, gelatin, chitosan and konjac glucomannan has been blended with Pickering emulsions to fabricate self-support films.

As a promising edible matrix, chitosan enjoys wide popularity in food packaging due to natural antibacterial property and excellent film-forming ability. Clove essential oil Pickering emulsions containing stabilizing zein colloid particles, achieve compatibility and homogeneity in composite film after incorporation, despite the hydrophilicity of chitosan and the hydrophobicity of essential oils. Meanwhile, the strong smell of plant oils can be eliminated and physicochemical performance of film can be greatly improved (Y. Xu et al., 2020). In addition, antibacterial and water barrier properties can be enhanced via the incorporation of cellulose nanocrystal stabilized cinnamon essential oil loaded Pickering emulsions, whose enhancement effect depends on the content of cinnamon essential oil or cellulose nanocrystal (J. Liu et al., 2022). Moreover, when incorporating clove essential oil based and zein- sodium caseinate stabilized Pickering emulsions into a chitosan film, improved mechanical, water permeability and release-suppressing properties are obtained as compared to pure chitosan film (Hua et al., 2021).

Starch is one of the most favored materials to fabricate biofilms, owing to its low cost, ready availability and good biodegradability (H. J. Wu et al., 2023). Still, starch needs to be mixed with other active compounds to address the limitation of its inherent hydrophilicity. Rod-like chitin nanocrystal stabilized paraffin oil Pickering emulsions can be incorporated into a starch matrix, aiding uniform dispersion and preserving the mechanical properties of the original matrix (Jimenez-Saelices et al., 2020) (Fig. 5. (d, e)). In addition, konjac glucomannan is a natural polysaccharide that can be applied in edible composite film incorporated with zein–pectin stabilized oregano essential oil Pickering emulsions that benefit antibacterial activity, antioxidant activity and controlled-release. More importantly, the edible film can be used in improved food packaging (S. Zhang et al., 2022).

Gelatin film is a kind of typical edible matrix often combined with Pickering emulsions. Soybean oil loaded Pickering emulsions stabilized by chitosan nanoparticles and encapsulated hesperidin were incorporated into gelatin films, exhibiting improved microstructural performance and antimicrobial properties (Dammak et al., 2019). Similarly, the incorporation of dihydromyricetin-soybean oil based dialdehyde cellulose nanocrystals stabilized Pickering emulsion, provided increased stability and improved gelatin based film water barrier, mechanical strength, antioxidant and UV-blocking properties (J. Xu et al., 2021). Single biopolymer/Pickering emulsion composite films showed enhanced physical and chemical properties, however, some properties can be further improved by adding another biopolymer matrix.

### 3.1.2 Binary biopolymers/Pickering emulsions films

Since physical cross-linking structures can be formed with several different biopolymers, two or more polysaccharides often blend together to construct a double network matrix before their incorporation into Pickering emulsions, thus enhancing the inadequacies of each and greatly improving the mechanical properties (Fan et al., 2023; P. X. Zhao et al., 2023; F. Zhou et al., 2023). For instance, blended carrageenan and agar film shows water barrier and mechanical property enhancement, despite the high water solubility of carrageenan and the poor mechanical performance of agar (S. Roy & J.-W. Rhim, 2021). Konjac glucomannan and Pullulan can form a double polymer matrix via hydrogen bonding, increasing the dispersion of konjac glucomannan (F. Zhou et al., 2023). On the other hand viscosity will decrease with the excessive addition of cellulose nanofibrils stabilized tea tree essential oil Pickering emulsions, as a result of the interaction between the emulsions and the biopolymers (Bu et al., 2022).

The sol-gel properties of gelatin facilitate the formation of composite films with other biopolymers and Pickering emulsions. Oxidized cellulose nanofiber stabilized cinnamon oil Pickering emulsions can be incorporated into gelatin-chitosan film, improving the tensile strength and water resistance of the films. In particular, the addition of curcumin to a gelatin-chitosan dispersion not only increases the bacteriostatic effect, but also functions as freshness indicator in food packaging (Jian Liu et al., 2022) (Fig. 5. (f-i)). A mixture of gelatin and agar is ordinarily used as a binary biopolymer matrix to overcome the disadvantages of low water resistance and limited functionality. The blended film exhibits a smooth and flat surface even with Pickering emulsions, highlighting the compatibility of the binary composite films (S. Roy & J.-W. Rhim, 2021).

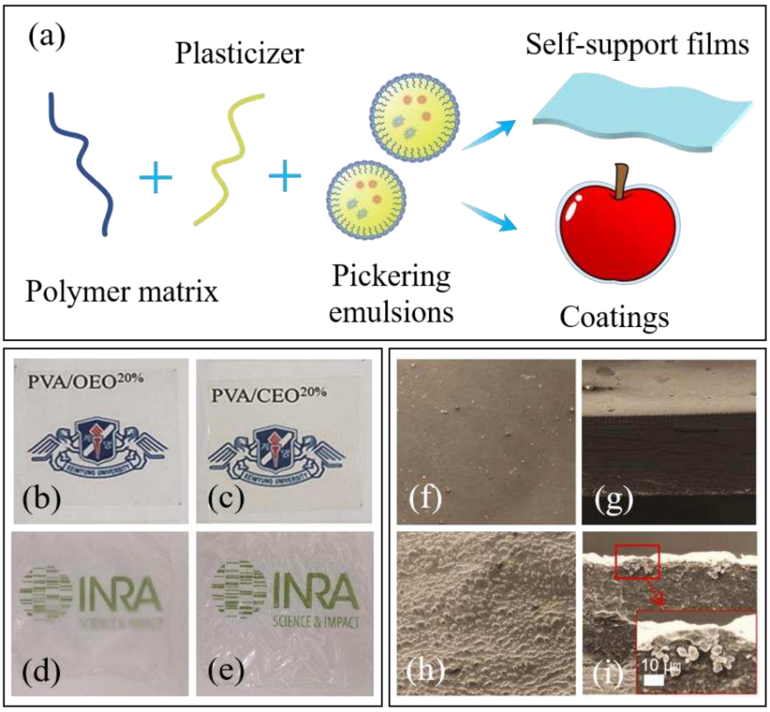


Fig. 5. Diagram shows (a) the process of fabricating Pickering emulsion-based self-support films and coatings, (b, c) optical images of polyvinyl alcohol/Pickering emulsions, [Reprinted with permission from (Oun et al., 2022). Copyright 2022 Elsevier], (d, e) starch/chitin nanocrystals stabilized Pickering emulsion composite films, [Reprinted with permission from (Jimenez-Saelices et al., 2020). Copyright 2020 Elsevier], (f-i) scanning electron microscope images of gelatin/chitosan composite films containing cellulose nanofiber stabilized cinnamon oil Pickering emulsion [Reprinted with permission from (Jian Liu et al., 2022). Copyright 2022 Elsevier].

### 3.2 Coatings

Coatings are another form of active packaging applied in food, functioning as an appealing approach to food preservation with numerous advantages such as effectiveness, and low-cost. In general, lipid compounds, including carnauba, shellac, paraffin and beeswax, are indispensable materials in edible coatings. And in order to enhance the poor mechanical properties of the pure wax components, polysaccharides are usually combined as well. Pickering emulsions are equally significant in the process of edible coating fabrication, as a kind of emulsifier and compatibilizer in the composite system. Aliphatic succinic anhydride-modified and unmodified cellulose crystals are added for instance to starch-beeswax mixed solution, serving as Pickering emulsion stabilizers. The prepared coatings exhibit superb performance in the preservation of fruits, improving the structural hardness and maintaining commercial appearance meanwhile. In particular, the coatings can be easily washed away by 40°C water, catering for consumers who dislike the consumption of coatings (Trinh et al., 2022). Cellulose nanofibril and carboxymethyl chitosan complexes are also used to stabilize Pickering emulsions, accompanied by a mixture of beeswax solution in edible coatings. It has been shown that Pickering emulsion loaded coatings display antibacterial properties as well as structural integrity, which is greatly beneficial for the maintenance of the freshness of berry fruits (Xie et al., 2020).

Some biopolymers combined with essential oil loaded Pickering emulsions can also be fabricated into coatings. Since more active compounds are preserved in coatings due to the slower release of oils, essential oil loaded Pickering emulsions coatings may have excellent antibacterial activities. Cinnamon essential oil loaded chitosan Pickering emulsion (CH-PE) coating is employed for preserving mangoes, benefitting from stabilization by cellulose nanocrystals. Compared to the pure chitosan and chitosan-cinnamon essential oil coatings, the greater reduction of water vapor permeability and water solubility endows these coatings with better performance in postharvest storage. More importantly, better controlled release for cinnamon essential oil is achieved in CH-PE coatings (Yu, Xu, Zhou, Zou, & Liu, 2021). Cinnamon essential oil loaded carboxymethyl cellulose-polyvinyl alcohol based coatings prepared through Pickering emulsions method show remarkable strong antifungal ability for bread slice preservation, and the impact is even more effective than the films, on account of the larger contact area between active ingredients and bread slices (Fasihi et al., 2019). In addition, while oleic acid is involved in the cellulose nanocrystal stabilized chitosan Pickering emulsions coating, a wide range of variation in emulsion stability will be achieved by the addition of oleic acid. And appropriate concentration leads to effective decrease for ethylene content, thus extending the shelf life of pears (Jung, Deng, & Zhao, 2020).

## 4. Properties of Pickering emulsions-based films

Pickering emulsions containing various active compounds such as essential oil can enhance the antibacterial and antioxidant properties of composite films. In addition, Pickering emulsions can structure composite films improving their barrier properties.


Fig. 6. Diagram illustrates the antibacterial [Reprinted with permission from (Gao et al., 2020). Copyright 2020 The Royal Society of Chemistry], antioxidant, barrier and color properties [Reprinted with permission from (Jian Liu et al., 2022). Copyright 2022 Elsevier] of Pickering emulsion-based composite films.

### 4.1 Antibacterial properties

Packaged food can be harmed by different kinds of bacteria that grow and regenerate during storage and transportation, causing health risks for consumers and economic losses ((M. Wu et al., 2021). To prevent this, many smart packaging methods and bioactive compounds have been developed to make antibacterial films, and the most effective and popular ones are based on essential oils (B. R. Tian, Liu, Yang, & Wan, 2023). Plant sourced essential oils have a significant influence on the inhibition of bacteria and microorganisms, owing to the presence of terpene and other aromatic compounds (Dai et al., 2023; Fasihi, Noshirvani, & Hashemi, 2023; K. Zhang et al., 2022). Antibacterial mechanisms mainly act through the destruction of the bacterial cell membrane, since the increased permeability of bacterial cell wall results in the leakage of cytoplasm and subsequent alteration to the functions of bacterial membrane (Almasi et al., 2020; L. Zhang et al., 2010; Lingling Zhang et al., 2013).

Oregano essential oil exhibits antimicrobial properties against L.monocytogenes and E.coli in active TEMPO-oxidized cellulose stabilized Pickering film, significantly extending the shelf life of food (M. Wu et al., 2021) (Fig. 7. (a, b)). Furthermore, marjoram essential oil, a variety of origanum majorana similar to oregano, shows remarkable inhibition of S. aureus (Gram-positive) and E. coli (Gram-negative) bacteria similar to clove essential oil Pickering emulsions (Almasi et al., 2020; Y. Xu et al., 2020). Other than S. aureus and E. coli, clove essential oil in soybean protein and microfibrillated cellulose (MFC) composite film similarly displays remarkable antibacterial activities against Bacillus cereus and Salmonella enteritidis, and the influence can be improved through the increasing the content of MFC (Ortiz, Salgado, Dufresne, & Mauri, 2018). Likewise, cinnamon oil is widely used in Pickering films for its antibacterial properties as well, but the inhibition zone areas may decrease over time due to evaporation of the volatile components Moreover, optimizing the ratio of cinnamon oil and cellulose nanocrystals in Pickering emulsions improved the antibacterial activity of the film, otherwise the cellulose nanocrystals act as a route for the leakage of cinnamon oil (Jian Liu et al., 2022; J. Liu et al., 2022).

A commonly used food flavoring, cumin seed essential oil, plays a critical role in prohibiting the growth of microbes, especially for the psychrophilic and mesophilic aerobes. However, when added to inulin and whey protein isolate loaded Pickering emulsions, the co-stabilizing effect will be weakened (Hemmatkhah et al., 2020). Tea tree oil, a class of oils which is little researched, and derived from melaleuca alternifolia leaves, possesses a variety of bioactive compounds such as sesquiterpenes, monoterpenes and so on. Notably it prevents both S. aureus and E. coli bacteria from developing in cellulose nanofiber stabilized Pickering emulsions, and the influence on the former is stronger. The different antibacterial effects may be ascribed to the differing structures of the bacterial cell walls (Bu et al., 2022; S. Roy & J. W. Rhim, 2021). Originating from the Lamiaceae family, melissa officinalis L. essential oil is considered an attractive functional oil for Pickering films with powerful antibacterial effects, greatly enhancing the suppression of S. putrefaciens with increasing effect with increasing amount (Borchers & Pieler, 2010). Lemon myrtle essential oil is another category of oils with superior antimicrobial ability, traditionally providing benefits in phototherapy using the herb leaves. It displayed improving suppression for E.coli in chitosan-coated alkali lignin stabilized films (L. Liu, Swift, Tollemache, Perera, & Kilmartin, 2022).

Compared with the antibacterial effects directly from the essential oil in Pickering films, the active ingredients from the plants alone sometimes contribute to the inhibition of microbes as well. Thymol, for example, is found naturally in many plants and can be added in maize germ oil Pickering film to function as an antibacterial agent. Thymol suppresses S. aureus and E. coli, and the effect on S. aureus increases greatly when the loading reaches 20% (J. Y. Zhu, Tang, Yin, & Yang, 2018). Most essential oils exhibit outstanding antibacterial activity, usually accompanied by antifungal effects, providing an indispensable property in Pickering films. Essential oil-cinnamaldehyde based Pickering emulsions can effectively inhibit the growth of Botrytis cinerea when added in films (K. Zhang et al., 2022) (Fig. 7. (c)). In addition, cinnamon essential oil performs complete prohibition for molds and yeasts both in carbohydrate-based active films and coatings (Fasihi et al., 2019).

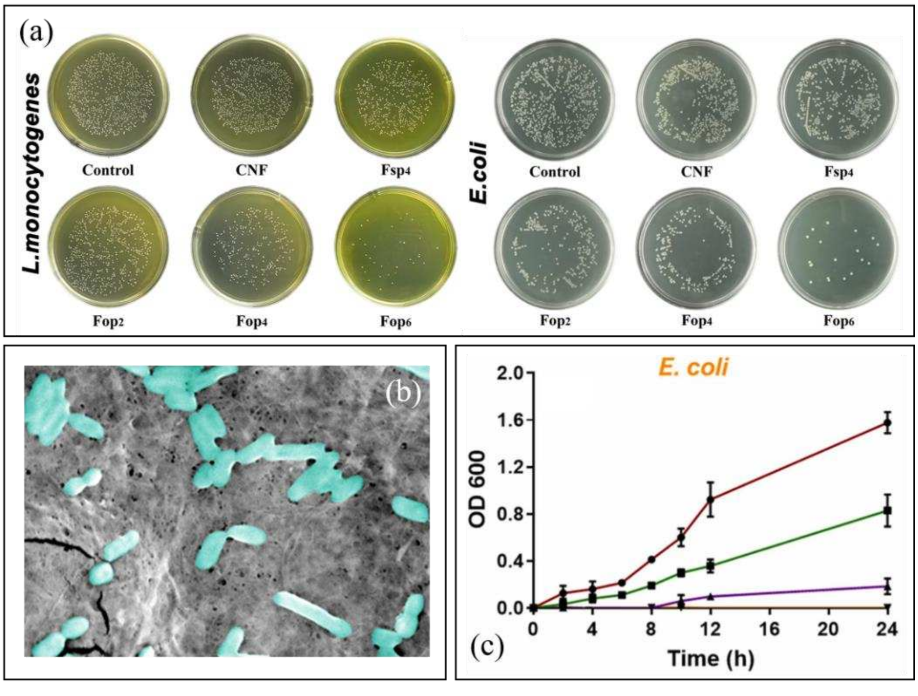

Fig. 7. (a) The antibacterial properties of cellulose nanofiber films containing cellulose nanocrystals stabilized oregano essential oil Pickering emulsions against *Listeria monocytogenes* and *Escherichia coli*, [Reprinted with permission from (M. Wu et al., 2021). Copyright 2021 Elsevier], (b) transmission electron microscopy images of cellulose nanofiber based composite film against *Escherichia coli*, [Reprinted with permission from (M. Wu et al., 2021). Copyright 2021 Elsevier], (c) antibacterial properties of PVA films containing cellulose nanocrystals stabilized cinnamaldehyde Pickering emulsions, [Reprinted with permission from (K. Zhang et al., 2022). Copyright 2022 Elsevier].

### 4.2 Antioxidant properties

Lipid peroxidation and other oxidation phenomena often happen in food despite the package outside, lead to a series of nutritional loss and spoilage (J. Xu et al., 2021; J. Y. Zhu et al., 2018). Fortunately, antioxidant films can be realized through the scavenging of some free radicals, like ABTS and DPPH radicals, improving food quality.

Many essential oils possess excellent antioxidant activities, owing to the bioactive compounds that they contain. For instance, the clove essential oil loaded films show improvement in antioxidant ability, and a better scavenging rate for ABTS when compared with DDPH (Ortiz et al., 2018; S. Roy & J.-W. Rhim, 2021). Marjoram essential oil and oregano essential oil based Pickering films show increased DPPH scavenging activity (Almasi et al., 2020; S. Zhang et al., 2022). While tea tree oil scavenging of ABTS is slightly higher level than DDPH because of the different water solubility (S. Roy & J. W. Rhim, 2021). Cinnamon essential oil acts similarly, and the intrinsic cinnamaldehyde is an important source of the antioxidant effects. Droplet size may be another factor that influences antioxidant activity, since reducing size expands the reaction area between surface and oxygen, further enhancing antioxidant capacity (Fasihi et al., 2019).

Other compounds may function as antioxidant materials. Obtained from Curcuma longa L, curcumin can serve as an indicator of food quality and is an effective scavenger of free radicals. Actually, it is beneficial for curcumin to remove free radicals, due to the straightforward extraction of H atom by highly reactive carbon atom between two methoxyphenol rings. And the protection provided by Pickering emulsions makes it work better (D. Liu, Dang, Zhang, Munsop, & Li, 2021). Dihydromyricetin (DMY), a natural compound extracted from Ampelopsis grossedentata leaves, is generally considered to be an oxidation resistant substance. In dihydromyricetin loaded Pickering films, superior antioxidant ability is displayed through the effective elimination of ABTS, in response to the gradual increasing addition of DMY (J. Xu et al., 2021).

### 4.3 Barrier properties

#### 4.3.1 Barrier to water vapor

Water vapor permeability (WVP) is a measure of barrier effectiveness in food packaging, indicating significant correlation between the applicability of packaging and food quality. Reducing or eliminating water diffusion contributes to relatively stable food quality, and thereby extends the shelf life of the food (S. P. Bangar, Whiteside, Dunno, Cavender, & Dawson, 2022). In practice, many factors should be considered regarding the WVP in Pickering emulsion containing films. The addition of Pickering emulsions is reported to be conducive to the reduction of WVP, primarily due to the increased tortuosity caused by emulsions droplets, and the simultaneous hindrance of water diffusion due to hydrophobic compounds, resulting in significantly diminished WVP as the content of Pickering emulsion increases (Almasi et al., 2020; Shen et al., 2021; J. Xu et al., 2021). Plant essential oils may also lead to lowered WVP in Pickering films, since their inherent nonpolarity and hydrophobicity greatly impede water diffusion. (Farajpour, Emam Djomeh, Moeini, Tavakolipour, & Safayan, 2020; S. Roy & J. W. Rhim, 2021). In particular, effective emulsifiers such as zein colloidal particles hamper the permeability of water. The hydrophobic amino acids contained in zein crystals limit the adsorption of water molecule by the films, thus, reducing the water vapor permeability (Farajpour et al., 2020; S. Zhang et al., 2022).

#### 4.3.2 Barrier to oxygen

Oxygen permeability is a measure of the extent to which gas molecules dissolve in packaging film matrix, and it can be used to measure the rate of gas passing through the films. However, due to the potential oxidation and unpleasant odor caused by the oxygen, low oxygen containing Pickering films are preferred (J. Y. Zhu et al., 2018). It is supposed that film thickness has a positive effect on reducing the oxygen permeability, due to the tortuous path of oxygen molecule caused by the complex structural properties of stabilized particles. It can be specifically expressed as the fiber structure and crystallization property of microfibrillated cellulose in films, and complicated network structures formed in films (D. Liu et al., 2021; Ortiz et al., 2018). Furthermore, beeswax exhibits poor oxygen barrier ability in the films, because it may increase the absorption of oxygen molecules while the diffusion of non-polar oxygen lowers the surface tension. Consequently, whilst starch-beeswax based films have improved oxygen permeability compared to beeswax, pure starch films display much better oxygen barrier capacity (Trinh et al., 2022). Moreover, in active cellulose nanofibril films, the decreased oxygen barrier ability is accompanied by improved water vapor properties as the concentration of emulsion increases (M. Wu et al., 2021).

#### 4.3.3 Barrier to UV light

The property of UV-blocking is important in food packaging, because it can protect food from undesirable changes in flavor and unnecessary degradation in nutrients, induced by the direct exposure to UV (J. Xu et al., 2021). To endow Pickering films with a UV barrier function, several UV absorbed substances has been explored. Bioactive groups such as aromatic compounds, phenols and cinnamaldehyde molecules exhibit effective UV barrier properties Gelatin films with dihydromyricetin have strong UV blocking ability because both gelatin and dihydromyricetin have groups that absorb UV light. This makes them more suitable for food packaging applications (J. Xu et al., 2021). Moreover, some plant essential oils and compounds often present excellent UV barrier performance, especially in Pickering films. For example, clove essential oil Pickering emulsion loaded chitosan film shows better UV blocking ability than pure chitosan film (Hua et al., 2021). The same effect can appear in the cinnamon essential oil Pickering emulsions based composite film, where the curcumin also acts as UV absorbing substance that improves the UV barrier ability in addition to its indicator role (Jian Liu et al., 2022).

### 4.4 Color and optical properties

Color, a crucial feature of food appearance, is determined by various factors such as emulsion particle scattering of light, light transmittance, pH conditions and so on, that can directly affect consumers' appetite for food products (L. Liu et al., 2022). The transparency of Pickering films is a favorable characteristic that attracts many researchers, whereas most of them create opaque sample films whilst seeking UV-blocking properties. Light transmission is the major factor that influences the color, so many Pickering films have increased opacity, such as clove essential oil and zein-NaCas loaded chitosan films (Hua et al., 2021). Nevertheless, clove essential oil contained gelatin/agar film shows transparent appearance in conjunction with a pale yellow color, related to concentration (S. Roy & J.-W. Rhim, 2021). The color of films may change in buffer solutions with different pH as well, due to the structural alterations of internal curcumin (Jian Liu et al., 2022). Occasionally, zein nanoparticles also increase the opacity of Pickering films due to scattering of light and interactions between film matrix with the nanoparticles (Farajpour et al., 2020).

## 5. Application of the Pickering emulsions-based packaging films

Pickering emulsion-based packaging films and coatings with different excellent properties can be used to extend the shelf-life and indicate the freshness of various foods. The preservation and sensing of meat, marine products, and fruit using Pickering emulsion-based packaging films are reviewed in this section.

### 5.1 Application in meat preservation

As the demand for meat products grows, so does the need for better quality meat. To keep the meat products fresh and prevent them from spoiling during transport, new types of films or coatings can be used for packaging (Fig. 8. (a)). A film suitable for packaging needs a series of conditions, including antibacterial and antioxidant properties, which can provide consumers with better appearance, flavor and high nutrient content. Cumin seed essential oil loaded paper extends the shelf-life of hamburger beef, resulting in subtle change of pH value, water holding capacity and color during storage in the presence of the paper (Hemmatkhah et al., 2020). Moreover, curcumin and gelatin-chitosan based Pickering film is effective in pork preservation, owing to the antioxidant and antimicrobial activities from the contained cinnamon oil. Similarly, the cinnamon oil-based Pickering emulsions loaded chitosan composite active film extends the shelf life of pork (J. Liu et al., 2022) (Fig. 8. (b, c)).

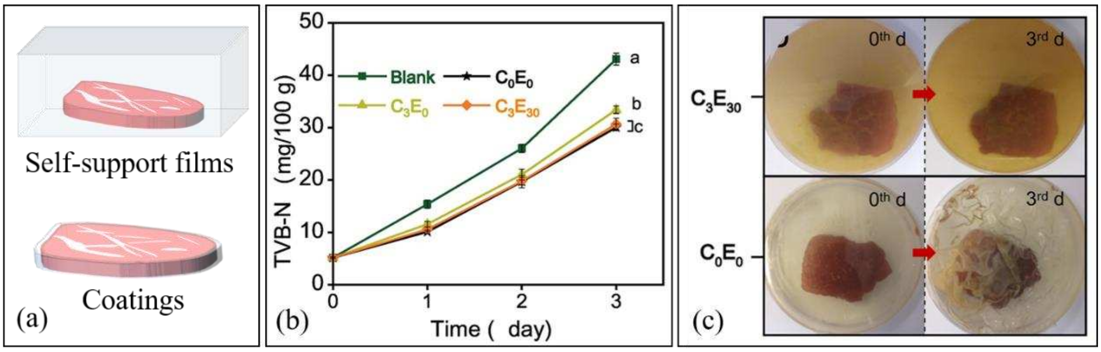


Fig. 8. Diagram (a) Pickering emulsion-based self-support films and coatings which can be used as packaging films (b), total volatile basic nitrogen (TVB-N) changes of the pork after storing for different days (c), Digital images of the pork after storing for 0 and 3 days, [Reprinted with permission from (J. Liu et al., 2022). Copyright 2022 Elsevier].

### 5.2 Application in marine products preservation

Marine products are rich in nutrition, such as ω-3 polyunsaturated fatty acids and protein in red sea bream, and protein and minerals in shrimp. But during storage, their protein can degrade and their lipid can oxidize, which can lower their commercial value. Pickering film packaging can be applied to improve the current situation, primarily focusing on thiobarbituric acid (TBA) and total volatile basic nitrogen (TVB-N), which indicate the spoilage degree of fat-rich foods and protein-rich foods respectively. Red sea bream is a valuable fish with delicious flavor, full of fat, protein and trace elements. Research shows that cinnamon-perilla essential oil Pickering emulsions/collagen protein/chitosan nanoparticles/anthocyanidin film exhibit lower TBA values and TVB-N contents with the extension of storage time, achieving a preservation effect (R. Zhao, Guan, Zhou, Lao, & Cai, 2022). Also, wrapping with chitosan nanoparticle-based Pickering emulsion films can help preserve the quality of anthocyanin in terms of sensory evaluation and texture. Anthocyanin loaded cinnamon oil Pickering nanoemulsions have even better antimicrobial effect. And each combination can keep the red sea bream fillets fresh for longer. (R. Zhao, Guan, Zheng, et al., 2022). The freshness of shrimp can be maintained by active films as well. Lavender essential oil Pickering emulsions loaded gelatin films inhibit microorganism growth, endowing the films with a beneficial preservation effect (J. Wang et al., 2022) (Fig. 9. (a, b)).

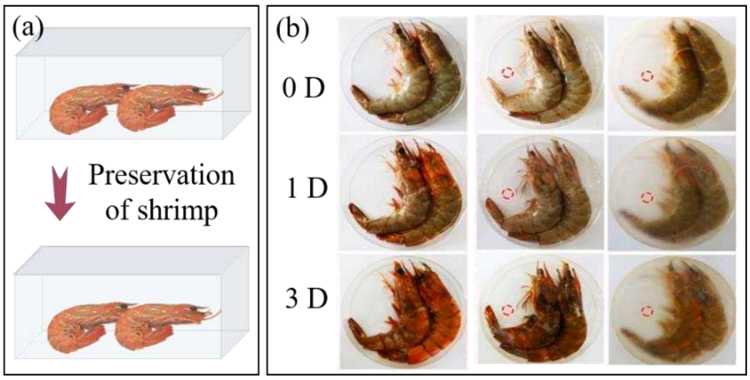


Fig. 9. Diagram (a) the preservation of shrimp by Pickering emulsions-based self-support films (b), Digital images of the shrimp at day 0, 1 and 3 after covering with different films, [Reprinted with permission from (J. Wang et al., 2022). Copyright 2022 Elsevier].

**5.3 Application in fruit preservation**

As the provider of many nutrients, fruits enjoy a wide popularity throughout the world. However, their natural perishability can easily contribute to deterioration even when stored at low temperature, and approaches to prolong the shelf life of fruits are a focus issue to be investigated. Respiration and transpiration are two main factors leading to deterioration in the post-harvest stage, resulting in weight loss. Generally speaking, the commercial value of the fruits will be severely reduced when the weight loss reaches 5% (Punia Bangar et al., 2022). On this occasion, different kinds of packaging films are created for climatic and non-climatic fruits.

As a kind of climatic fruit, 'Bartlett' pear is grown in Europe and Western Asia. The superficial scald and ripeness of pears can be greatly delayed by covering with cellulose nanocrystal-chitosan and oleic acid Pickering emulsions coatings, which functions as an effective barrier which depends on the appropriate concentration of the oleic acid (Jung et al., 2020). Mango is another climatic fruit abundant in nutrients, always accompanied by dark spots and color changing on the surface during storage. In response, chitosan-cellulose nanocrystals stabilized cinnamon essential oil Pickering coatings effectively maintain the quality of mangoes, reducing dark spots, delaying peel yellowing, lowering weight loss and keeping firmness, thus retaining the commercial value of mangoes to a large extent (Yu et al., 2021). In addition, starch-beeswax edible coatings applied to the surface of bananas and apple slices, display superb freshness preservation. In the presence of coatings, the browning phenomena and firmness of bananas are greatly improved. More importantly, the intrinsic color of the coatings does not affect the appearance of fruits (Trinh et al., 2022).

As for non-climatic fruits, red grapes can be kept longer while in contact with starch films with CNCs stabilized Pickering emulsion containing clove bud oil, improving firmness, weight and total soluble solids (Punia Bangar et al., 2022). Another possible way to keep fruits fresh is to prevent the growth of microbes, which are the main cause of spoilage. For example, films made of konjac glucomannan and zein–pectin with oregano essential oil can preserve strawberries well, with a strong antibacterial effect from the start of storage (S. Zhang et al., 2022). Besides, CNCs-ethyl lauroyl arginate-cinnamaldehyde Pickering emulsions containing films alleviate the deterioration of strawberries, owing to their enhanced water barrier property accompanied with lower weight loss (K. Zhang et al., 2022) (Fig. 10).

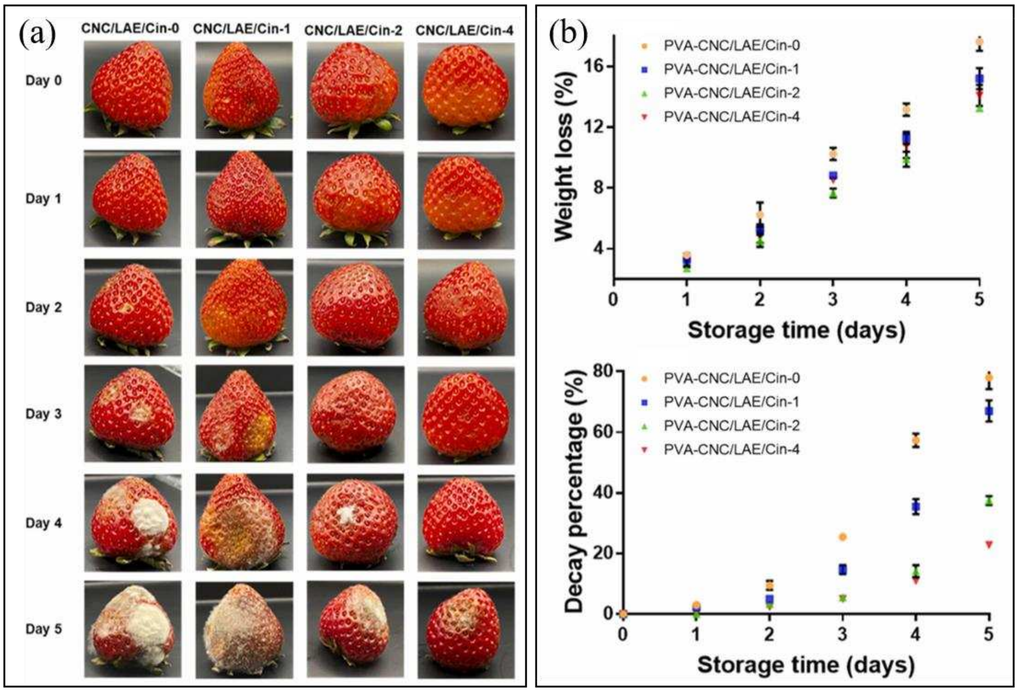


Fig. 10. (a) Images of strawberries packaged with different cellulose nanocrystals stabilized Pickering emulsions/PVA composite films after storing for different days (b) plots of associated decay and weight loss, [Reprinted with permission from (K. Zhang et al., 2022). Copyright 2022 Elsevier].

## 5.4 Application in sensing films

Pickering emulsions containing bio-based films not only may preserve foods, but also can be used to detect the freshness of the foods since the color of the film will change with the level of deterioration (R. Li, Zhuang, Feng, Wang, & Zhu, 2023). It is an intuitive and effective approach for the variation of color can be observed directly by naked eye (Jian Liu et al., 2022). Natural dyes such as alizarin and curcumin have been incorporated into the Pickering emulsions to fabricate composite films which can detect the freshness of meat. Curcumin is a common natural pigment widely used in food intelligent packaging, indicating the quality of protein-rich foods through measuring the total volatile basic nitrogen content of food. OCNF-stabilized cinnamon oil Pickering emulsions and curcumin loaded gelatin/chitosan film can serve as freshness indicator in pork preservation, due to the pH sensitivity of curcumin. Alterations in pH are accompanied by color changes varying from brown to saddle brown (Jian Liu et al., 2022). Likewise, curcumin-loaded Pickering emulsions with corn starch and polyvinyl alcohol film can be used for monitoring fish freshness, since the colors of the film change with the spoilage of fish (D. Liu et al., 2021). Lavender essential oil loaded gelatin based film can function as a real-time pH and biogenic-amines indicator because of the incorporation of alizarin, generally a variation from yellow to red brown, thus monitoring the freshness of shrimp (J. Wang et al., 2022). Though Pickering emulsion-based films face many challenges as intelligent indicators, the films should have a bright future for smart packaging applications. Further applications of Pickering emulsion-based films or coatings in the food packaging field can be found in Table 2.

Table 2. Summary of properties and applications of Pickering emulsions-based films or coatings

| Pickering emulsions(PE) | Film matrix | Form of films/coatings | Properties of films | Application | Ref |
|---|---|---|---|---|---|
| OCNFs-stabilized cinnamon oil | Chitosan, gelatin | Edible composite film | WVP, antibacterial, antioxidant, UV-blocking, transparent, mechanical | Pork preservation | (Jian Liu et al., 2022) |
| CNCs-stabilized cinnamon essential oil | Chitosan | Edible composite film | WVP, antibacterial, transparent, mechanical, oil-release control | Pork preservation | (J. Liu et al., 2022) |
| Collagen-stabilized perilla essential oil | Chitosan | Edible composite film | WVP, mechanical, UV-blocking, antioxidant, | Red sea bream fillet preservation | (R. Zhao, Guan, Zhou, et al., 2022) |
| CNCs-stabilized clove bud oil | Starch | Edible composite film | WVP, antibacterial, mechanical | Red grapes preservation | (Punia Bangar et al., 2022) |

| | | | | | |
|---|---|---|---|---|---|
| CNCs-stabilized oleic acid | Chitosan | Edible coating | WVP, oil incorporation control | Bartlett pears preservation | (Jung et al., 2020) |
| CNCs-stabilized Cinnamon essential oil | Chitosan | Edible coating | WVP, lower water solubility(WS), antioxidant, oil-release suppressing | Mangoes preservation | (Yu et al., 2021) |
| Zein–pectin nanoparticle-stabilized oregano essential oil | Konjac glucomannan | Edible composite film | WVP, antioxidant, antibacterial, mechanical, oil release-suppressing | Strawberries preservation | (S. Zhang et al., 2022) |
| CNCs/ethyl lauroyl arginate (LAE) stabilized cinnamaldehyde | Polyvinyl alcohol | Edible composite film | WVP, antibacterial, WS, mechanical, UV-blocking, transparent | Strawberries preservation | (K. Zhang et al., 2022) |
| CNCs stabilized beeswax and corn starch | Starch | Edible coating | WVP, oxygen permeability, mechanical, coating washability | Fresh bananas, strawberries, and fresh-cut apples preservation | (Trinh et al., 2022) |

**6. Conclusions and future perspectives**

Biopolymer-based films have attracted great attention as food packaging materials addressing the serious environmental and health concerns caused by non-degradable petroleum-based packaging materials. Advances in the development of new materials and technologies enable the preparation of multifunctional Pickering emulsions. These biopolymer stabilized Pickering emulsions offer promise once incorporated into a biopolymer matrix for fabricated food packaging films with enhanced physicochemical properties. Pickering emulsion containing food packaging films or coatings with excellent mechanical, antibacterial, antioxidant and barrier properties can be used to preserve various meat, vegetable and fruit. Yet, most of the research remains at lab scale and a lot of effort is still required to improve the films to meet practical applications. New Pickering emulsions should be developed to better blend with the polymer matrix for fabricating food packaging films with certain properties. More active materials are needed to be explored to expand the application of the bio-based films which can be used to preserve some newly developed foods. The technologies needed for the fabrication of Pickering emulsion-based food packaging films is undeveloped and more new technologies could be found for the preparation of different forms of films, such as multi-layer films.

Though Pickering emulsion-based food packaging films have made some progress, future developments should also be considered to fabricate a bio-based food packaging film with enhanced properties. The effect of film structure in the dry state on film performance is not well studied, which leads to inconsistent results. More experiments are needed to enhance all the performance aspects consistently. Different crosslinkers with designed structures and functions need to be developed to enhance various properties of the films. Essential oils are the main source of functional substances. There is not enough research on how other kinds of active substances can be embedded and perform in the film. Active substances that can have both antibacterial and sensing functions should be investigated. Though bio-based packaging films are generally considered safe, thorough toxicity studies of the films still need to be performed. More studies should be carried out to reveal the degradable behavior and environmental impact of the films. As to the application of the films, current studies largely focusing on the preservation of the meat and fruit. More detailed research of the films in preserving other kinds of foods should be conducted. All in all, Pickering emulsion-based films with excellent properties show promise in the field of food packaging despite the many difficult challenges which need to be addressed in the future.

## CRediT authorship contribution statement

**Fuyuan Ding**: Writing-review & editing, Project administration, Funding acquisition, Chart design. **Siman Long**: Writing-original draft, Writing-review & editing. **Xiaowei Huang**: Chart design. **Megan Povey**: Review & editing. **Xiaobo Zou**: Supervision, Review & editing.

## Declaration of competing interest

The authors declared that they have no conflicts of interest in this work.

## Data availability

Data will be made available on request.

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