Advances in the preparations and applications of nanochitins

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ARTICLE INFO

ABSTRACT

Chitin is a widely available polysaccharide, biodegradable, insoluble in most solvents and with low antigenic properties. Chitin nanoparticles such as nano whiskers and nanofiber (CHNF) can form a stable and uniform dispersion. The nanoparticle suspension shows the properties of crude chitin as well as the properties of high aspect ratio, high surface area, low density, and hydroxyl group, N-acetyl group and the residual amine group on its surface can also be chemically modified. This review describes nanochitin preparation technologies and food applications. Specifically, the role of nanochitin in modulating fat-soluble bioavailability and saltiness perception was investigated. Fat-soluble vitamins incorporated into CHNF are less available for digestion. Whereas hyaluronic acid and cancer-treatment drugs can be delivered through the skin to targeted locations via chitin nanogels. Interestingly, CHNF enhances saltiness perception via ionic binding with taste receptors. At pH < 7, the amino group chelates chloride, thus releasing sodium for interaction with salt receptors. This mechanism may allow salt reduction in food formulations. Furthermore, nanochitins express surfactant properties and strengthen composite food packaging (starch- or gelatin-based, gelatin nanocomposite, nanocellulose/nanochitin membranes coating F-SiO$_2$ suspensions). This paper can help build a better understanding of the opportunities of nanochitin as functional food ingredient.

1. Introduction

Chitin, a polysaccharide of glucosamine, is the second most abundantly available natural biopolymer after cellulose. This aminopolysaccharide can be beneficial to human health (Chen & Cheung, 2014). First of all, it can reduce the level of aortic cholesterol and triglycerides because upon binding with dietary lipids, which reduces their intestinal absorption (Koide, 1998). In addition, it can inhibit the *in vitro* growth of microorganisms, such as Candida. Also, it can be very useful in prevention of infection of wounds because of the activities of antibacterial and anti-yeast of chitin Koide (1998). It can also increase the activities of hepatic antioxidant enzymes (Chen & Cheung, 2014). The chemical structure of chitin is similar to that of cellulose (Shahidi, Arachchi & Jeon, 1999) with the main difference laying in the existence of acetamide groups in chitin Dutta, Duta and Tripathi (2004). Because of its low antigenicity, low toxicity, and biodegradability, chitin is recognized as a biocompatible material (Krajewska, 1991; Muzzarelli, 1980), attracting great attention by many industries and producing about 10

billion tons by mollusks, crustaceans, fungi, algae and insects each year (Zargar, Asghari & Dashti, 2015).

Nanostructure is common for chitin, particularly in the form of nanofibrillar composites (Ehrlich et al., 2008). It has been identified in numerous matrices, such as mushrooms, shellfish and the mineralized structures of diatoms and sponges (Brunner et al., 2009; Ehrlich et al., 2007a,b). Marine organisms produce them via the process of biomineralization: the synthesis of materials needed for the organism's growth. Composites of chitin with minerals, such as calcium and silica, confer structural integrity and mineral reserve to the organism, particularly when arranged into nanofibers (Ehrlich, 2010a,b). In recent years, simultaneously with the exponential growth in the number of research projects on nano-scaled cellulose, the isolation and extraction of nanosized crystalline chitin, also called chitin nanocrystals (CHNC) or whiskers, have attracted great interest. The concept of supercontinuum generation (SG) has been introduced in 2016, highlighting the effect of light (across ultraviolet, visible, and infrared domains) in stimulating structural rearrangement in chitin nanofibers

(Ehrlich et al., 2016). In the crab's exoskeleton, chitins are present in the form of nanofibers, composed of crystalline and amorphous domains, and can be downsized into chitin nano-whiskers/nano-crystals (Salaberria, Labidi & Fernandes, 2014). The fibrils of 3 nm in diameter can be individualized by a series of chemical treatments and grinding processes from a fiber of 60 nm in diameter which is coated by proteins. Similarly, the cell walls of fungi are composed of a chitin nanofibers (CHNF) network which is mainly embedded in a matrix of $\beta-1,3$-glucan (Michalenko, Hohl & Rast, 1976) fibers further assemble into bundles, which form horizontal planes. These planes superposed in a helicoid stacking, creating a twisted plywood structure. There are tubules like ribbons running through the pore canals in z-direction. A stack of layers that have rotated 180° is referred as Bouligand structure. These repeated structures form the exocuticle and endocuticle of crustaceans (Bouligand et al., 1972; Chen, Lin, McKittrick & Meyers, 2008). Nanofibers are generally defined as a diameter of less than 100 nm and a length-diameter ratio of over 100 (Li & Xia, 2004; Xia et al., 2003). The same characteristic of Bouligand structure can be also found in collagen networks in compact bone, cellulose fibers in plant cell walls and other fibers (Giraud-Guille, 1998). Generally, nanochitin can be extracted from their sources with various methods. Numerous advanced techniques have been implemented to study such complex structures: chromatography, diffraction, electrophoresis and spectroscopy (Tsurkan et al., 2021). It is noteworthy to mention that at least 3 allomorphs have been identified: α, β and γ. The most abundant conformation is α, where layers follow alternate directions. The β allomorph consists of unidirectional layers, whereas the γ structure has a change in direction every 3 layers (Kaya et al., 2016; Tsurkan et al., 2021).

Chitin nanofibers (CHNF) are generally prepared from the exoskeletons of crabs and prawns by removing proteins and minerals with sodium hydroxide (NaOH) and hydrochloric acid (HCl). Sodium chlorite (NaClO$_2$) is used to remove the associated components when chitin is extracted from mushroom due to its different organizational structure and ingredients of mushroom cell walls (Ivshina, Artamonova, Ivshin & Sharnina, 2009) mainly because of the highly branched glucans that are attached on the wall (Zivanovic, Buescher & Kim, 2003).

The properties of nanofibers are different from those of micro-sized fibers due to their high surface to volume ratio and a highly porous mesh (Ramakrishna et al., 2006). Recent work has showed that CHNF were successfully used to stabilize Pickering oil-in-water emulsification, such as soybean oil, acrylated soybean oil, and epoxidized soybean oil (Ben Cheikh, Mabrouk, Magnin, Putaux & Boufi, 2021). Several studies on digestion system implemented in vitro have been reported that nanochitin has the potential to inhibit lipid digestion. A slower lipid digestion may induce more satiety (Zhou et al., 2020). Furthermore, it has similar effects on reducing the bioaccessibility of vitamins and β-carotene (Zhou et al., 2020, 2021)(Zhou et al., 2020). Another application is entrapping and modulating the efficacy of different active ingredients. The block-copolymers chitin nanofibrils-hyaluronan showed potential to increase the delivery and effectiveness of active ingredients at level of the skin layers (Morganti et al., 2013). The increasing skin penetrability attributed by chitin nanogel is also reported to be useful for transdermal delivery of anti-cancer drugs for its biocompatibility and biodegradability (Mangalathillam et al., 2012). Hence, nanochitin, as a biopolysacchride has great prospect in the field of functional food, cosmetic and drugs.

In this review, top-down and bottom-up preparation are introduced, and recent applications of nanochitin and mechanism in food industry are reviewed. This article serves as an introduction of the present preparation and the powerful potential utilization of nanochitin in the food industry, covering the mechanism of emulsifying and water vapor resistance, which systematically sorted out the previous works at the present stage, contributing to build a better understanding of the previous limitation in the food industry and provide ideas for future.
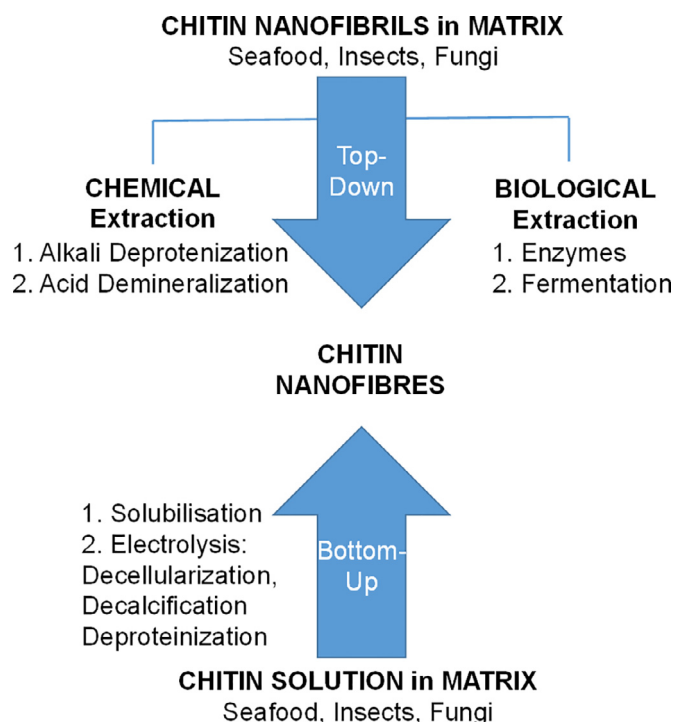
Fig. 1. Approaches to chitin isolation.

2. Discussion

2.1. Preparation

Generally, the methods for preparing nanochitin can be divided into two categories: top-down and bottom-up (Fig. 1). The top-down method is used to separate nanochitin from other materials (shell or exoskeleton), going from chitin nanofibrils to nanofibres. The bottom-up method is applied to dissolve chitin to the molecular level, going from chitin solution to nanofibers (Yadav et al., 2019). Chitin macromolecules are regenerated in precipitant or self-assembly. Then, they are assembled into nano-scale chitin through electrospinning and wet spinning methods.

Chitin is closely associated with proteins and other inorganic materials like calcium carbonate and lipids extensively in crustaceans sources, owing to multiple deproteinization and demineralization treatments while extracting. Deproteinization is carried out predominantly using NaOH or KOH, however other reagents includes Na2CO3, NAHCO3, K2CO3, Ca (OH)2, Na2S, CaHSO3, and Na3PO4. The effectiveness of deproteinization depends on temperature, alkaline concentration and ratio of solution to shells. Normally a mean incubation time of 0.5 to 6 h is needed for deproteinization whereas it would only take 1 to 3 h to achieve demineralization using diluted acids like HCl at room temperature, as longer process might degrade chitin. A higher amount of acid accounts for complete elimination of minerals, although it might cause chitin depolymerization (Arbia, Arbia, Adour & Amrane, 2013; Charoenvuttitham, Shi & Mittal, 2006; Hajji, Ghorbel-Bellaaj, Younes, Jellouli & Nasri, 2015), therefore EDTA has been recommended for the same, than HCl. Chemicals like CH3COOH and H2SO4 has also been reported to be used as effective solvent for demoralization, as HCl has been regarded as harsh chemical effecting intrinsic properties of purified chitin following structural depolymerization (Arbia et al., 2013; Charoenvuttitham et al., 2006). Chitosan can be extracted deacetylating chitin by alkaline regents at elevated temperature followed by several wash until it reaches neutrality. Ehrlich et al. (2016) proposed rapid and green novel method to obtain chitosan using microwave assisted deacetylation following acid and alkali treatments accounting extraor-

dinary reduction of time with very high degree of deacetylation DD% (El Knidri, El Khalfaouy, Laajeb, Addaou & Lahsini, 2016). The degree of deacetylation (DD%) is defined by the molar fraction of deacetylated units in the chitin chain influencing the intrinsic factors of chitin and chitosan like viscosity, solubility, polymer conformation and flexibility (Arbia et al., 2013).

Chemical extraction is regarded to be highly expensive, therefore biological isolation/extraction of chitin were proposed using proteolytic enzymes or microorganisms (Arbia et al., 2013; Hajji et al., 2015), and lactic acid-producing microbes (Arbia et al., 2013) resulting higher molecular weighted chitin forms with retained nutritional quality of by-products than compared to chemically processed. It has been reported that biotechnological processes yield more supernatant with enriched bioactive molecules like biopeptides and so on. Hajji et al. (2015) reported production of chitin from crab crustacean waste using protease-producing six strains of Bacillus species with higher degree of deproteinization independent of added substrate/glucose molecules (Hajji et al., 2015), The use of organic acids like lactic acid produced by microbes are eco-friendly in nature promising low cost of process (Arbia et al., 2013).

2.1.1. Top-down preparation of nanochitin

Chitin, a natural biological macromolecules material, can be formed by N-acetylglucosamine molecules after a series of multistage regular hierarchical structures. The "top-down" method usually requires two steps to extract the pure chitin nanoparticles: alkali deproteinization and acid demineralization (Klinger et al., 2019; K. Nowacki et al., 2020). Firstly, purify the chitin that binds with protein and other impurities. Alkaline (KOH or NaOH), enzymatic hydrolysis, acid (HCL), and bleaching (CH3CH2OH or NaClO3) treatment have been proved that is feasible and efficient to remove proteins, minerals, lipids and pigments (Gopi, Pius & Thomas, 2016; Marchessault, Morehead & Walter, 1959; Morin et al., 2002; Zeng, He, Li & Wang, 2012). A recent development is the extraction of nanochitin with ascorbic acid aqueous solutions (Bogdanova et al., 2019). After purification, the extract can be stored in the form of powder by drying or kept in suspension until subsequent treatments proceed.

The second step is to downsize the purified chitin, obtaining the ideal nano size of chitin. Recent studies on the micro-fibrosis of purified chitin reported the treatments of acid hydrolysis, TEMPO-mediated oxidation, mechanical (Bamba, Ogawa, Saito, Berglund & Isogai, 2017; Fan, Saito & Isogai, 2008, 2010; Ifuku, Hori, Izawa, Morimoto & Saimoto, 2015; Zou, Lin, Xu, Lin & Zhan, 2018). Microwave-assisted extraction has from marine demosponges been developed as new technology to isolate chitin scaffolds in tridimensional (3D) conformation. This process consists of 4 steps, three of which are repeated 4 times. Steps 1 is a pure microwave extraction in water solution. Steps 2 and 3 are alkali deproteinization and acid demineralization, respectively. Step 4 is a depigmentation with hydrogen peroxide (Klinger et al., 2019). Similarly, microwave-assisted extraction has proven successful in chitin isolation from spiders (Machałowski et al., 2019). Advantages of these technologies are the limited impact on chitin structure, while disadvantages reside in long times and use of solvents.

2.1.2. Bottom-up preparation of nanochitin

To obtain a chitin solution from the shells of crustaceans or from mushrooms the first step is to dissolve in a specific solvent. Secondly, formation of the nano-size-chitin by electrospinning, self-assembly, and dissolution-regeneration is required (El Knidri, Belaabed, Addaou, Laajeb & Lahsini, 2018; Jung et al., 2018; Shamshina et al., 2016). Reports showed that fibres exhibit a varying degree of difference based on solution concentrations (Min et al., 2004). A recent technology proposed an electrochemical method. Briefly, demosponges are decellularized, decalcified and deproteinized in an electrolysis cell consisting of platinum anode, platinum cathode and platinum current collector, separated by a cation exchange membrane (Nowacki et al., 2020a). In the first step the

sponge is placed in the catholyte, producing a cell-free skeleton (decellurization). In step 2, the skeleton is placed in the anolyte and purified of the calcium, producing a decalcified skeleton (decalcification). In step 3 the decalcified skeleton is placed again in the catholyte, where it is purified of protein, silica and pigments, producing a colourless 3D scaffold is (Nowacki et al., 2020a).

Bottom-up methods are considered more "green" due no or reduced use of solvents and shorter processing times. Limitations reside in minor modifications of the native structure. Therefore, a combination of top-down and bottom-up technology has been proposed for coral (*Cirrhipathe ssp*), with electrochemical and alkali treatments. In the first step, the coral was placed in the catholyte. In step 2, sodium sulfate was introduced and the electrochemical treatment repeated in a catholyte (Nowacki et al., 2020b).

2.2. Food applications

Nanochitin can be used to modulate nutrient bioavailability and drug delivery (in particular lipids and fat-soluble nutrients) enhance, saltiness perception, act as surfactant and stabilize complex films (Table 1).

Emulsions are dispersion systems formed by two insoluble liquids. Pickering emulsion is a stable system in which the stabilizing surfactant is replaced by colloidal particles (Skaugrud & Sargent, 1990). Nano crystals produced from chitin are known for their use for encapsulations and Pickering emulsions. Acid hydrolysis, centrifugation, precipitation, dialysis and ultra-sonication of chitin at variable time and temperature combinations were carried out to obtain chitin nano-crystals powder. They were characterized as nano biomaterials, as the SEM analysis of the obtained powder indicated that the fibrous crystals showed length upto several microns and width of few nanometers. The biocompatible nature of chitin had made researchers to work on it for the development of suitable biomaterials as bone regeneration scaffold (Tao et al., 2020). Various methods were employed such as phase separation (thermally induced), electrospinning. The wide use of these scaffolds has been reported in drug delivery, wound dressings as well in other biomedical aspects. In the early 20th century, it has been discovered that protein particles could spontaneously assemble between the air-water interface (Ramsden, 1904). Later, Pickering proved that colloidal particles insoluble in water can be adsorbed to the oil-water interface. Therefore, the resulting emulsion systems has been called Pickering emulsion ever since (Pickering, 1907). Pickering emulsions contain solid particles that act as emulsifiers. These solid particles have a clear size distribution and controllable surface characteristics, so they can produce irreversible adsorption on the oil-water interface, which is more stable than traditional emulsions (McClements, 2015). It has previously been observed that oil-in-water (O/W) Pickering emulsions can be formed with the participation of chitin nanofibrils (Tzoumaki, Moschakis & Biliaderis, 2011a; Zhou et al., 2020). Several studies showed that, due to the ability to generate electrostatic and steric repulsion, CHNF are capable of stabilizing Pickering emulsions against coalescence (Larbi et al., 2018; Zhou et al., 2019). Moreover, coating oil droplets with CHNF has been shown to reduce not only lipid digestion, but also bioaccessibility of vitamin D3 and lipophilic pigment (β-carotene) (Zhou et al., 2020). Due to electrostatic action, nanochitin shows excellent and promising ability in emulsify and saltiness perception enhancing. Besides, recently, nanomaterials have been heated discussed developing food-grade packaging while nanochitin become a powerful potential candidate.

2.2.1. Surfactant and bioavailability

Chitin nanofibrils have been widely demonstrated to effectively absorb lipid droplet and stabilize the emulsion for a long-term storage (at least 30-days storage). Most previous studies were analyzed the impact of particle size, electrical property on oil-water interface when chitin nanofibrils were applied to emulsion systems. Nanochitin are polysaccharide-based nanomaterials isolated from natural sources. Nanochitin is also capable to inhibit lipid digestion as well as lipophilic

Table 1
Key functionalities and nutritional properties of nanochitin.

Functionality	References
Stabilising Pickering emulsions	Larbi et al., 2018; Lv et al, 2021; Zhou et al., 2020
Reducing the absorption rate of lipids (enhanced satiety)	Winuprasith et al., 2018; Zhou et al., 2021
Reducing bioavailability of carotenoids by means of emulsion precipitation	Winuprasith et al., 2018; Zhou et al., 2021
Enhance saltiness by increasing ionic interaction of sodium with taste receptors	Hsueh, Tsai, & Liu, 2017; Jiang et al., 2017
Reinforces food packaging:	
Starch-based	Salaberria et al., 2015
Gelatin-based	Sahraee et al., 2017a
Gelatin nanocomposites	Sahraee et al., 2020; Zheng et al., 2019
Nanocellulose/nanochitin membranes coating	Xu et al., 2020

NANOCHITIN FIBRE (NCF) APPLICATIONS

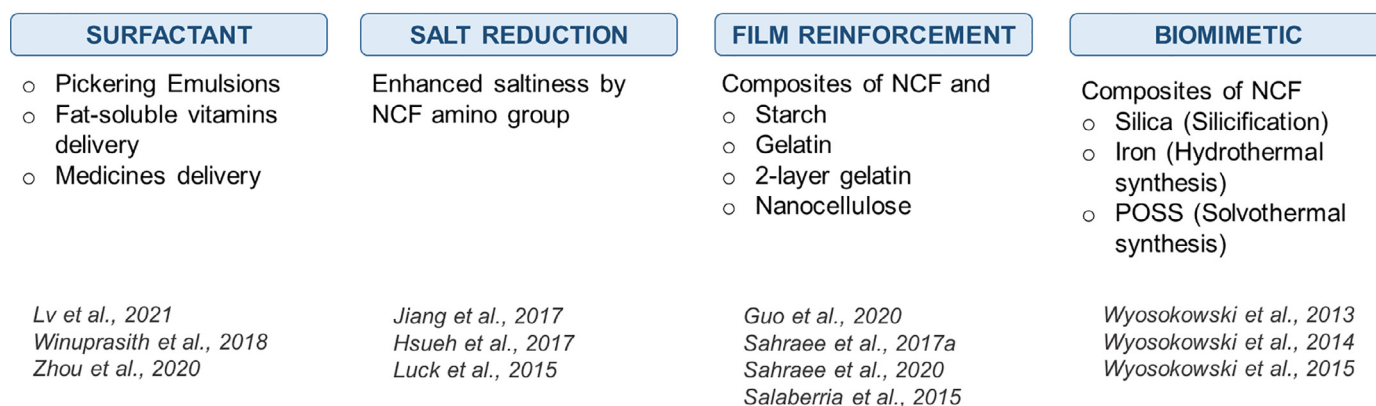| SURFACTANT	SALT REDUCTION	FILM REINFORCEMENT	BIOMIMETIC
○ Pickering Emulsions ○ Fat-soluble vitamins delivery ○ Medicines delivery	Enhanced saltiness by NCF amino group	Composites of NCF and ○ Starch ○ Gelatin ○ 2-layer gelatin ○ Nanocellulose	Composites of NCF ○ Silica (Silicification) ○ Iron (Hydrothermal synthesis) ○ POSS (Solvothermal synthesis)
Lv et al., 2021 *Winuprasith et al., 2018* *Zhou et al., 2020*	*Jiang et al., 2017* *Hsueh et al., 2017* *Luck et al., 2015*	*Guo et al., 2020* *Sahraee et al., 2017a* *Sahraee et al., 2020* *Salaberria et al., 2015*	*Wyosokowski et al., 2013* *Wyosokowski et al., 2014* *Wyosokowski et al., 2015*

Fig. 2. Nanochitin technologies.

components. Experiments on chitin nanofibrils were conducted by Zhou and collaborators in recent years. They have investigated the potential to form food-grade Pickering emulsion by using both nanofibrils of cellulose and chitin. Furthermore, the digestibility of lipid and bioaccessibility of vitamin and β-carotene by using *in vivo* model were also investigated (Fig. 2).

In a recent study of Pickering emulsion (Lv, Zhou, Bai, Rojas & McClements, 2021) the optimal concentration of nanoparticles, the ratio of cellulose nanofibrils (CNF) to CHNF, and the average particle diameter, potential and oil particle size at each stage were determined. The ζ-potential value of the pure CNF was −47.3 mV and that of the pure CHNF was around +36.0 mV. All the mixed systems were very similar to the pure CHNF and had a strong positive charge. This indicated that CHNF plays a key role in electrical surface potential of oil droplets, determining the stability of O/W emulsions. They also adjusted the mean particle diameter and particle size distribution by CNF/ChNF ratio. Interestingly, when CNF was formulated only (1/0), the average diameter of oil particles in the emulsion was larger than that when CHNF was formulated only (0/1), suggesting that the emulsifiers containing individual nanoparticles were more effective than combination emulsifiers. However, the emulsions with a CNF/CHNF ratio of 2/1 contained relatively small droplets observed in the confocal microscopy images. They proposed two possible mechanisms. One was a bridging flocculation caused by the connection of anions on the oil particles to cationic ions on the other oil particles, but subsequent observations did not find flocculants. The other was the entanglement caused by excessive CNF in the continuous phase. The question is, although the mixture of CNF and CHNF can form a stable Pickering emulsion system, since the emulsion formed by CHNF alone can achieve higher effective ability and stability

of binding droplets than the emulsion formed by mixing CNF. Nanocellulose can usually be extracted from plants at a low cost while the extraction methods of nanochitin are more complex. One point to be sure is that the emulsifier has potential to be used in a wide range of emulsified foods, even functional food after considering the impact conducted by the following studies.

CNF have showed the ability of reducing the rate of lipid digestion and decreasing the bioaccessibility of vitamin D (Winuprasith et al., 2018). Recent *in vitro* human studies confirmed this assumption (Zhou et al., 2020, 2021). The reason for the fat absorption rate is well understood and similar to the possible mechanism of emulsifiers. Lipids were coated by nanofibrils and failed to contact with lipase. Compared to the non-ionic surfactant Tween 80 (T80), the bioaccessibility of vitamin D3 and β-carotene was much lower in the emulsions containing nanochitin. The cationic nanochitin may have interfered with the release of vitamin and β-carotene, via two different mechanisms: i) Vitamin and β-carotene were incorporated in the lipid droplet that was not been digest, ii) The molecules released precipitated out of solution (Zhou et al., 2020, 2021). It was confirmed in subsequent experiments that cationic nanochitin can form insoluble complexes with the anionic bile salts. Sediment was observed in the bottom of the test tubes after centrifugation. The amount of sediment increased as the nanochitin concentration increased. Presumably, the positive impact of nanoparticles which reduce lipid absorption can be applied to the production of functional foods. Delivery of drugs can be enhanced via a two-step treatment of chitin: methanol extracts bastadin 25 and araplysillin-I N20 sulfamate, while acetic acid and sodium hydroxide activate the chitin scaffold. Its exposure to the surface confers porosity, while maintaining capillarity, which can enhance bioavailability of drugs in humans (Kovalchuk et al.,

2019). Equally effective is the use of naturally sourced chitin, which provides tridimensional structure for bioactivities, antimicrobial and physicochemical functionality (Muzychka et al., 2021; Tsurkan et al., 2020). Meanwhile, the absorption of lipid-soluble nutrients decreased due to nanoparticles blocking lipid absorption. In the future development of such functional foods or the application of chitin nanofibrils emulsifiers, further research is needed to ensure the absorption of lipid-soluble components.

2.2.2. Salt reduction

The recommended daily intake of sodium reported by the world health organization (WHO) is 3.5–5 g (WHO, 2020). However, according to previous reports, the intake in most countries, like the United States and the United Kingdom ranges from 8.2 to 9.4 g/day, which is above the recommended limits. Consuming too much salt can lead to undesirable physiological reactions and cause diseases. One of the biggest concerns is high blood pressure caused by high salt intake and the possible mechanisms as followed: i) Excess intake of Na+ cause water and sodium retention, resulting in increased blood volume and elevated blood pressure; ii) High salt intake causes cells, especially smooth muscle cells swelling, resulting the narrowing of the lumen of blood vessels; iii) It increases the sensitivity of blood vessels to catecholamines, vasoconstrictive factors. iv) The increase of intracellular sodium will inhibit the Na/Ca exchange and decrease the amount of calcium (Ca) discharged from the cells, which will lead to the increase of calcium concentration in vascular smooth muscle and cause the contraction of the muscle. Whereas, reducing sodium content of food products would likely have decrease in their flavor and lead to lower customer acceptance. Hence, it is prior to reduce the use of salt in food, and it is also a critical topic for food industry to maintain customer acceptance as the reduction of sodium content.

Methods of reducing the content of sodium in food can be roughly categorized into chemical mechanisms, cognitive mechanisms, and product structure design. With chemical mechanisms, saltiness perception can be substituted or enhanced by some flavor additives, for example, potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium sulfate ($MgSO_4$), citric acid, and sodium glutamate. Cognitive mechanisms involve the reduction of table salt use in the diet, which requires a long period for consumers to gradually adjust their dietary habit and attitude. Actions have been taken to raise consumer awareness about reducing sodium, and regulatory policies have forced food manufacturers to label sodium content on products. With product structure design, the size, shape of table salt grains can be modified, grinding them into smaller granules, which enables the modified salt to quickly dissolve. It has been previously reported that the inhomogeneous distribution of table salt can provide taste contrasts and reduce adaptation, which allowing for reduction of salt without loss of saltiness intensity (Noort, Bult, Stieger & Hamer, 2010). Meanwhile, structuring agents can affect the physicochemical nature of food (polyelectrolytic hydrocolloids and osmolality) (Jiang, Tsai & Liu, 2017).

Recent studies investigated the possibility of using chitin nanofiber to enhance saltiness perception (Fig. 2). The amine groups on the CNF molecular chains are protonated, presenting positive charge when pH is below 7 (Jiang et al., 2017). Hence, the dissociated chloride in the NaCl solution (negatively charged) is absorbed by CNF, forming electric double layer, resulting in increasing concentration of free sodium in the solution (Hsueh, Tsai & Liu, 2017). Under the circumstances, CNF increases the possibility that sodium contacts taste receptors on the taste buds, which enhances saltiness perception. The CNF processed with ultrasonication (Hsueh et al., 2017) supports a reduction plan of the use of table salt in curing-solution food products. Saltiness perception can enhance also in producing curing products. The principle of their research is that chloride was adsorbed by protonated CNF and higher content of free sodium in the solution was applied. According to a previous report, the higher the concentration of nanochitosan solution was added to milk, the higher the score of astringency was received (Seo, Chang,

Lee & Kwak, 2011). Astringency is due to the positive charge density of chitosan. If the positive charge density decreases, the astringency also decreases (Luck, Vårum & Foegeding, 2015). Hence, both concentration and charge affect the sensory quality of nano chitosan. On the contrary, it has not been found in nanochitin that those would lead to an increase in astringency.

2.2.3. Reinforcing agent in food-grade film

Nanochitin has excellent physical, chemical and biological properties. It is small in size, light in weight, chemically stable, renewable and biodegradable, non-cytotoxic, and especially high in antibacterial activity. These advantages make this nanomaterial have great potential in food, packaging and biomedical applications (Salaberria, Diaz, Labidi & Fernandes, 2015). However, the question of how to use nanochitin to prepare nanocomposite membranes with high performance and special functions still leaves much room for development in the future. Four food grade composite membranes with these functions are described below: starch-based, gelatin-based, gelatin nanocomposite, nanocellulose/nanochitin membranes coating F-SiO2 suspensions (Fig. 2).

2.2.3.1. Starch-based nanochitin (chitin nanocrystal/nanofibrils) composite film.
Starch has advantages of renewability, availability, low cost, non-cytotoxicity and biodegradability. Meanwhile, starch has chemical similarity with nanochitin. Specifically, the intermolecular hydrogen bonds are formed between the hydroxyl groups of starch and the hydroxyl groups and residual amine groups at the surface of CHNF, which can promote the interaction between them. Therefore, starch has been chosen as the substrate of composite membranes, using chitin as reinforcer for starch-based composites prepared by acid hydrolysis and ultrasound, with nanoparticles compounded with starch (Chang, Jian, Yu & Ma, 2010). Compared with pure starch membranes, the properties of tensile strength and water vapor transmittance are all improved. Other authors further investigated the blocking and antimicrobial properties and the results showed that the composite membranes has the effect of reducing water vapor permeability and oxygen permeability, meanwhile, antibacterial experiment with *Aspergillus Niger* as the strain shows that the composite has good antibacterial properties (Salaberria et al., 2015). Starch nanocomposite films showed better mechanical properties than a starch matrix, displayed better barrier properties than starch matrix. It was found that nanomaterials could not only improve the weak mechanical properties of starch matrix materials, but also further develop antifungal and barrier properties. Nonetheless, the final performance of the thermoplastic starch-based nanoparticles film is affected by the content and type of nanochitin (crystal/fibril) which was compounded into the matrices. Results showed negative effect on the thermal stability of the final starch/chitin nanocrystal (S/CHNC) composite films when CHNC was incorporated into the thermoplastic starch matrices. The main reason for the decrease of thermal stability the composite films may be the decrease of the flexibility of branch chains in the presence of CHNC crystalline. On the other hand, starch/chitin nanofibrils (S/CHNF) composite films showed a positive effect on the thermal stability when the temperature is below 5 °C. The important reason of the better enhanced thermal stability obtained by S/CHNF composite films is that CHNF has a better thermal stability compared to CHNC. Due to the reticular morphology of CHNF, the nanocomposite films prepared with CHNF can induce excellent final properties. This kind of thermoplastic nano starch film is a promising material in food packaging.

2.2.3.2. Gelatin-based nanocomposite films.
Nanochitin can improve physical, thermal, and antifungal properties when it acts as a filler in packaging film (Sahraee, Milani, Ghanbarzadeh & Hamishehkar, 2017a). However, due to its hydrophilicity, nanochitin cannot form a packaging film individually due to poor water vapor resistance. Alternatively, this kind of film can be applied as an interlayer of a packaging polymer to produce functional packaging for foods that suffer from fungal growth like bakery products, fruits, vegetables, and nuts. Moreover,

producing emulsion films by oil incorporation is a good strategy for solving this problem whereas oil has prohibited antifungal properties of nanocomposite gelatin films containing nanochitin. When a gelatin nanocomposite film contains 0.30 g/g oil, it had acceptable overall properties as packaging polymer in food products that are easily susceptible to water vapor or UV-light exposure (Sahraee et al., 2017a).

2.2.3.3. Two layers gelatin nanocomposite and gelatin emulsion. Bread, cakes, cookies, and doughnuts, and other bakery products are an important part of daily diet and often contain complex carbohydrates, proteins, lipids, vitamins, and minerals (Soukoulis et al., 2014). As one of the most popular bakery products, cakes have a longer shelf life than bread, but the growth of mold and lipid oxidation are still the main factors affecting the shelf life of cakes (Lu et al., 201). Biodegradable packaging, a popular material in recent years, has superior environmental characteristics because they are not only made from waste by-products, which are cheap but also have the ability to carry active ingredients in food. Hence, biodegradable packaging has attracted more and more attention (Soukoulis et al., 2014). For the food industry, however, the main challenge is to improve the ability of low barrier properties against water molecules (Zheng et al., 2014).

Numerous nanoparticles have been investigated for their potential properties on biodegradable composite films for sustainability over the years. Compared with polyethene films, the previous report about nanoparticles-composite-gelatin packaging showed excellent barrier and antimicrobial properties as well as the capacity of extending the shelf life. The composite gelatin films can be obtained by compounding nanochitin and nano zinc oxide (nanoZnO) (Sahraee, Milani, Ghanbarzadeh & Hamishehkar, 2020). Nanochitin, the most compatible nanoparticles with the polymer of carbohydrate and protein, is capable to enhance the physical properties as well as the antimicrobial properties of composite films (Sahraee, Milani, Ghanbarzadeh & Hamishehkar, 2017b). On the other hand, nanoZnO, TiO2, MgO, CaO and other metal oxide nanoparticles have attracted great interest in the food industry, due to excellent processing temperature stability, diffusion ability, including packaging, food, safety, animals, humans, and antimicrobial properties. Studies have shown that nanochitin and nanoZnO could improve barrier properties of gelatin films against water vapor due to filling property and the ability to induce a tortuous pathway across the water molecules (Kamnmani & Rhim, 2014). NanoZnO has also shown capacity of UV-light absorption as well as hydrophobic property (Rouhi, Mahmud, Naderi, Ooi & Mahmood, 2013). The addition of preservatives to bakery products may reduce because of the high functionality of biodegradable polymers. Whereas it is not enough for gelatin films to improve the barrier properties by adding nanoparticles. Hence, it might be a feasible solution to reduce the packaging permeability of water vapor that apply gelatin emulsion film as the second layer (Sahraee et al., 2020). Moreover, it is important to be sustainable for the environment and decrease by-product waste pollution. Substituting synthetic polymers with biodegradable packaging may be a sustainable alternative in the production of olefin polymers.

2.2.3.4. Nanocellulose/nanochitin membranes coating F-SiO$_2$ suspensions. At present, there are many types of research on the superhydrophobic phenomenon and its internal structure. In nature, many plants and animals have a special large water-contacting surface, resulting in superhydrophobicity. To have this ability, there are two factors that cannot be ignored: rough and ordered nano or microstructure and low surface free energy (Fu et al., 2020; Sehaqui, Zimmermann & Tingaut, 2014; Zhang et al., 2018). The same properties of the synthetic superhydrophobic interfaces still can be obtained as the natural one (Yao, Bae, Jung & Cho, 2017). Both types of interfaces have large water contact angles, resulting in that water droplets cannot adhere to the interface and slide down quickly, even at a tiny inclination angle. Due to these excellent characteristics, the synthetic superhydrophobic material can apply to self-cleaning coatings, anti-corrosion, anti-icing, oil and water

separation, bioengineering, medical materials, detection and analysis, and water treatment (Guo et al., 2020; Katiyar, Mishra, Srivastava & Prasad, 2020; Lv, Liu, Zhang, Chen & Liu, 2020; Maharjan et al., 2020; Mirzadeh, Dehghani, Rezaei & Mahidashti, 2019; Song, Li, Xu, Liu & Lu, 2019; Xu, Qi, Cheng & He, 2019).

In a study, crosslinked negatively charged 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanofiber (TOCNF) and positively charged partially deacetylated α-chitin nanofiber (α-DECHN), TOCNF/α-DECHN transparent membranes (CCTM) were obtained by suction filtrating, combining the advantages of nanocellulose and nanochitin, expanding future application fields (Xu et al., 2019). NanoSiO$_2$ was modified by heptadecafluoro-1,1,2,2-tetrahydrodecyl dimethylchlorosilane (HFTD), and F-SiO$_2$ with low surface energy was formed (Xu et al., 2020). The F-SiO$_2$ was utilized to manufacture nanostructures on the surfaces, which can help the composite membranes constructing superhydrophobic surfaces. Compared with the pure membrane (nanochitin and nanocellulose composite membrane), the composite ones with F-SiO$_2$ can increase mechanical properties, exhibited super hydrophobicity and transparency properties.

One of the similarities that chitin and cellulose have in their molecular structures and chemical compositions is that the 2-acetamido-2-deoxy-β-D-glucose unit they have in the main component of their backbones. Hydroxyl groups are the only functional unit in cellulose, whereas chitin not only contains hydroxyl groups, but also acetyl groups (CH3CO) and amino groups (NH$_2$) in a small amount. Even though it contains amino and hydroxyl, chitin is highly insoluble in aqueous solutions (Dziril et al., 2015). Those similarity in the structures of chitin and cellulose result in good miscibility. At present, functional materials can be prepared by using the combination of chitin which is dissolved. For example, chitin solution and chitosan solution are mixed to form a composite film, chitin solution and PVC solution are mixed to form a composite hydrogel, chitin solution to recycle natural plastics and so on (Kadokawa, Takegawa, Mine & Prasad, 2011; Sriupayo, Supaphol, Blackwell & Rujiravanit, 2005; Tzoumaki et al., 2011b). Different properties are exhibited by these two polymers. In the presence of moisture, nanochitin membranes are easily broken, whereas nanocellulose membranes still maintain structural integrity due to their hydrophobicity. On the other hand, nanocellulose has higher crystallinity and better physical enhancement ability than nanochitin.

2.2.4. Extreme biomimetic conditions

Biomimetics is the science that replicates biological systems, using a multidisciplinary approach. Biology, chemistry and engineering are combined to synthesize molecules of biological significance. Chitin-silica composites can be prepared *in vitro* by silicification of demosponges (Fig. 2). This process strengthen the polymer structure, allowing further applications of chitin, a bioactive and biodegradable polymer. The technology requires top-down isolation first (washing, alkali and acid treatments) to produce a scaffold. The isolated scaffold is then dispersed in a silica solution and incubated at 120 °C for 24 h. This stimulates silica-chitin interaction via their hydroxyl groups. The result is a two-dimensional chitin-silica composite with α structure (Wysokowski et al., 2013).

Another possibility is hydrothermal synthesis, using iron chloride as precursor, and extremely acidic solution (pH 2) at 90 °C for 48 h (Fig. 2). This hydrolysis process results in the production of iron oxide. This induces chelation of iron oxide to chitin (iron binding hydroxyl group) as well as hydrogen bonding (oxygen binding chitin amino group), producing a two-dimensional α-chitin polymer (Wysokowski et al., 2014).

Three-dimensional chitin composites can be synthesized with methods such as solvothermal synthesis with POSS (silsesquioxane) (Fig. 2). This approach applies to top-down isolates which are subsequently dissolved in POSS solution and treated at 80 °C for 24 h, followed by removal of unbound particles upon ultrasonic bath and drying at 90 °C for 48 h (Wysokowski et al., 2015).

3. Conclusions

Chitin is a biodegradable polysaccharide.. Chitin nanofibres can be extracted from nanofibrils (top-down) or from solutions (bottom-up). Top-down technologies involve either acid and basic solvents (chemical extraction) or enzymes and fermentation (biological extraction). Bottom-up technologies involve solubilisation and electrolysis or microwave treatment.

Two key factors attributed to nanochitin are electrostatic action and the filling. Electrostatic action is expressed when chitin acts as emulsifiers and saltiness enhancing agent. The positive charge of nanofibers can absorb negatively charged particles such as oil droplets, thus reducing lipid digestion, the bioavailability of fat-soluble vitamins, and increasing the release of sodium. Upon static electricity, chloride is adsorbed on the surface of CHNF to form a double layer, which increases the content of free sodium and improves the salty taste. In some composite membranes, such as starch-based membranes and gelatin-based membranes, nanochitin can be used as a filler to improve physical, thermal and antifungal properties. The film can be used as an intermediate layer of packaging polymers for functional packaging of baked goods, fruits, vegetables, nuts and other foods affected by the growth of fungi. The preparation of emulsified liquid film by the oil blending method is an available way to solve this problem. However, the nanocomposite gelatin film containing nanochitin cannot have antifungal properties after the oil blending. Additionally, a large quantity of freely reactive hydroxyl groups and acetamide groups exposed on the surface of nanochitin can be chemically modified and functionalized through chemical derivatization or post-functionalization. Nanochitin and nanoZnO can improve the barrier properties of gelatin film against water vapor by filling characteristics and inducing tortuous paths between water molecules. F-SiO$_2$ can help to build a superhydrophobic surface on the composite membrane. Biomimetics allow further developments of composites with silica, iron and POSS, producing specific functionalities (physical and nutritional).

Overall, nanochitin offers great potential for delivery of bioactives, particularly fat soluble, by enhancing their bioavailability. Numerous technologies are available for their synthesis, with "green" techniques being particularly interesting due to the limited to no use of solvents and impact on native structures. Authors would like to point out the potential of food by-products (seafood waste, mushroom stalk, etc.) as matrix for chitin extraction and nanochitin synthesis. A synergy between circular economy and food engineering is the vision for functional food hydrocolloids: upcycled nanochitin.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

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