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Chitosan: Properties, Modifications and Food Nanobiotechnology

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Abstract

Chitin and chitosan are natural biopolymers produced mainly from crustacean shells of shrimp, crab and lobsters discarded by sea food-processing industries. Chitosan, the deacetylated form of chitin, it is a copolymer of β-(1–4)-2acetamido-D-glucose and β-(1–4)-2-amino-D-glucose units, due to its unique functional properties and distinctive biological activities, chitosan has received great attention and find wide spectrum of biotechnological applications ranging from the environmental, industrial, to agricultural, and medical fields. In the food sector, these biopolymers are best suited, both in their native and chemically modified forms and offer a distinctive application including water purification, juices clarification and deacidification, food shelf-life extension and preservation from microbial deterioration, food quality improvement, food additive, and biodegradable packaging films formation. This review reports chitosan properties and modifications and explores the role of nanotechnology in creating and developing chitosan nanomaterials adapted for food processing, packaging, storage and safety. Furthermore, summarizes their related applications in the food sector.

Keywords: chitosan; properties; modifications;nanotechnology; food biotechnology.

1. Introduction

Chitin is the second most abundant biorenewable and biofunctional polysaccharide in the nature after cellulose. Chitosan is the deacetylated form of its parent polymer chitin [poly- β -(1 → 4)-N-acetyl-D-glucosamine, a major

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component of crustacean shells such as crab, shrimp, and lobsters[1]. The Free amino groups of chitosan that is reflected it's solubility physically, its reactivity chemically and its distinctive bioactivity biologically; attract the attention of chemists and biologists to modify, explore and exploit chitosan potentials ,and owing to its incomparable and remarkable properties, such as biocompatibility and biodegradability, bioactivity, an extensive efforts have been made by multi-disciplinary researchers i.e. chemist, physicist, biologist , engineers , and environmentalists to develop enormous applications ranging from waste water treatment [2], agrochemicals and food [3,4], to biosensor [5] , tissue engineering [6],and drug and gene deliveries [7,8],Since the chitosan food safety (generally recognized as Safe (GRAS)) was improved by the US Food and Drug Administration in 2011[9], chitosan applications extended rapidly with the aid of nanotechnology, chitosan become one of the most exploited polymers of the 21st century in general and in the food industry specially.

In the food sector, nanotechnology advances foods production and functionality via designing, manufacturing, processing and application of chitosan nanomaterials, which have superior physical and chemical properties such as high surface area, porosity, tensile strength, conductivity, photo-luminescent as well as increased mechanical properties as comparison to pure chitosan [10].

The objective of this this review is to outlining chitosan properties, modifications, exploring the role of nanotechnology in the food sector generally, and developing bioactive nanochitosan specially. Furthermore, summarizing reported studies on various applications of chitosan and chitosan-based nanoparticles adapted for food processing, packaging, storage and safety.

2. Chitosan properties and modifications:

Chitosan exhibit a variety of physicochemical and biological properties (Table 1) which enable it for wide range of food applications. It can be applied either in its original form or modified form obtained physically or chemically to generate novel properties and functions (Table 2)

Table 1. Chitosan Properties.

Chitosan properties	Physico- chemical	Molecular weight - degree of polymerization - facile derivatization crystallinity - polycationicity - degree of deacetylation - viscosity, solubility - stability - chemical reactivity - chelating activity - mucoadhesivity -ionic conductivity - processability
	Biological	Biocompatibility - Biodegradability - Bioactivity

Table 2. Chitosan modifications.

Modification methods	Modification techniques	Modifications types	References
Physical	Blending (mechanical mixing)	Chitosan blended with other hydrophilic polymers such as poly (vinyl alcohol)(PVA), poly (vinyl pyrrolidone)(PVP), and poly(ethyl oxide) (PEO)	[11,12]
Chemical	Chemical grafting - photochemical - radiation - plasma induced and enzymatic grafting (tyrosinase)	alkylation - acylation - acetylation - etherification - esterification methylation - N-succinylation - nitration - thiolation - hydroxylation - phosphorylation - fluorination - sulphonation - xanthation - carboxymethylation - hydroxypropylation - N-phthaloylation - silylation - tosylation - Schiff's base formation and co-polymerization	[13-15]

3. Chitosan food Nano-biotechnology:

Since the term "nanotechnology" was coined in 1974 by Norio Taniguchi, Nanotechnology start playing its major roles of fabrication, characterization and manipulation of nano-range (<100 nm) molecules, and pursuit its future discoveries in biology as nanobiotechnology specially in biopolymers involving the design, manufacturing, processing and application of polymer materials filled with nano-particles and/or nano-devices [16-18] . Nanotechnology in the food sector caters several areas such as processing, bioavailability, fortification, packaging, encapsulation, nutraceuticals nanoencapsulation, pathogen detection, food nanosensing and better food quality and safety, etc. [19]. Due to its biocompatibility, high permeability, processability, and excellent film forming ability, chitosan polymer has gained more attention by chemist, physicist, and engineers to develop [20] a wide variety of compositions containing chitosan nanomaterials, nanofibers, films, nanoclay, colloids, composites, gels and other products either alone, in combination with other natural chemical or biological or biochemical compounds [21,22]

(Table 3) summarizes wealth references reporting a wide array of chitosan and chitosan nanomaterials food applications with special emphasizing on nanotechnologies for food processing, packaging, and storage.

Table 3. Chitosan /Nano- chitosan food applications.

No.	Food application	Somme details	Ref.
1	Water purification	-Removal of metal ions, pesticides, phenols, dyes, DTT, PCBs, proteins, amino acids, oil and greases	[23-26]
		- Chitosan based membranes for water purification	
		- Chitosan-based nanocomposites for water de-nitrification	
		- Flocculent/coagulant - Filtration	
2	Clarification	-Juice, tea, beer and beverages clarification	[27-29]
		- β-Chitin and chitosan from squid gladius application as clarifying agent for apple juice	
		- Chitosan-immobilized pectinolytics with novel catalytic features and fruit juice clarification potentialities	
3	Preservation	Papain microencapsulated with chitosan or alginate maintained low minimum inhibitory concentration values after submission to heat treatment, demonstrating its effectiveness and potential application as a biopreservative.	[30]
4	Color stabilization	- Reduction of non-enzymatic browning, color deterioration and retention of nutritional, sensory quality of product during preparation and storage.	[31,32]
		- Addition of chitosan could control the enzymatic browning in apple juice.	
5	Emulsifier agents	- Corn-Bio-fiber gum (C-BFG) were used as an emulsifier with chitosan.	[33-36]
		- The effectiveness of the chitosan particles in forming Pickering emulsions.	
		- Chitosan nanoparticles as particular emulsifier for preparation of novel pH-responsive Pickering emulsions and PLGA microcapsules	
		- Uniform chitosan-coated alginate particles as emulsifiers for preparation of stable Pickering emulsions with stimulus dependence	
		- Oil-in-water emulsions stabilized by chitin nanocrystal particles	
6	Thickening agent	- Increase the viscosity of food	[37-39]
		- Chocolate milk beverage using modified (hydrogel) chitosan as a thickening agent,	
		- Chitosan and alginate are two polyelectrolytes that can be used as thickening agents in the food industry,	
7	Encapsulation	Encapsulation of bioactive compounds (essential oil, terpenes, carotenoids, and anthocyanins polyphenols and probiotics) allowing protection to oxidation	[40]
8	Shelf life extension	- Chitosan/pectin multilayer packaging increases the shelf life of tomato	[41-43]
		- Chitosan coating on mango and papaya slices which helped in increasing their shelf life by retarding water loss and drop in sensory quality	
		- Shelf life extension of white rice cake and wet noodle by the treatment with chitosan	
9	Acidity control	- Chitosan (CS) enriched with salicylic acid (SA) treatment significantly maintained texture and color, inhibited moisture loss and acidity change - Edible coatings (ECs) based on chitosan of fresh-cut pineapple did not affect titratable acidity.	[44,45]
10	Flocculent/coagulant	Preparation of tofu using chitosan as a coagulant for improved shelf-life	[46]
11	Food quality	- Improving the sensory, physicochemical and microbiological quality of pastirma (A	[47]

	improvement	traditional dry cured meat product) using chitosan coating - Enzymatic browning of certain types of juices enhancing the acceptability and appearance	
12	Food texture improvement	- Chitosan effects on the moisture content, pH, color, and texture of flat rice noodles	[48]
		- Effect of chitosan addition on textural properties of sweet potato starch noodle	[49]
13	Active Food Packaging	- Carry additional functional ingredients (such as antioxidants and antimicrobial agents) - Retard microbial growth and potential discoloration - Bactericidal Ag/Chitosan Nanobiocomposites for Active Food Packaging -Colloidal Cu nanoparticles/chitosan composite - Chitosan-sodium phytate nanoparticles as a potent antibacterial agent - Chitosan films and coating incorporated with essential oils on fish, meat products, fruits and vegetables.	[50-52] ,
14	Edible coating	- Reduce moisture transfer, restrict oxygen uptake, lower respiration, retard ethylene production, exhibit resistance to fat diffusion and selective gas permeability, seal in flavor volatiles - Edible films and coatings in seafood preservation	[53]
15	Control fruits postharvest decay	- Chitosan at low molecular weight (LMWC) control postharvest diseases of citrus fruit caused by *Penicillium digitatum, P. italicum, Botrydiplodia lecanidion, and B. cinerea* after 14 days - Effect of chitosan coating on postharvest diseases and fruit quality of mango (*Mangifera indica*)	[54]
16	Antimicrobial	CM and CN, micro- and nanoparticles which have been shown to be effective against E. coli O157: H7, intrauterine pathogenic E. coli (IUPEC), *Vibrio cholerae, S.enterica, Klebsiella pneumoniae, E. col, S. choleraesuis, S. aureus. Streptococcus uberis.*	[55,56]
17	Antioxidant	-DPPH, ABTS, and its protective effects on human erythrocytes - Nitric oxide and Hydrogen peroxide radical scavenging, FIC assay, FARP assay - Anti-lipid Peroxidation	[57,58]
18	Anticholesterol agents	- Reducing low-density lipoprotein (LDL) cholesterol levels and its fat binding capacity - Chitosan dietary supplementation show hypocholesterolemic properties	[59,60]
19	Anti-obesogenic	Dietary prawn shell chitosan exhibits anti-obesogenic potential through alterations to appetite	[61]
20	Food additives	- Chitosan-grafted hydrogels are useful for lactose-intolerant individuals due to controlled released of β-galactosidase - Vinegar products containing chitosan have cholesterol-lowering ability - Nisin-loaded chitosan-monomethyl fumaric acid nanoparticles as a direct food additive	[62-64]
21	Diet supplement	- Dietary supplementation of thiamine and pyridoxine-loaded vanillic acid-grafted chitosan microspheres enhances growth performance, metabolic and immune responses in experimental rats - Dietary chitosan supplementation attenuates isoprenaline-induced oxidative stress in rat myocardium	[65-67]

		- Chitosan and its oligosaccharide derivatives (chito-oligosaccharides) as feed supplements in poultry and swine nutrition	
22	Food Enzymes immobilization	- Immobilization of glucose oxidase on chitosan-based porous composite membranes and their potential use in biosensors - β-galactosidase immobilization in chitosan-grafted hydrogels useful for the production of lactose-free food - Immobilized pullulanase was efficient for continuous starch processing in the food industry.	[68,69]
23	Food biosensors	- Electrochemical chitosan based biosensor: Application to determination of acrylamide in food samples - Encapsulated proteins retain their bioactivity and their biosensing - Bio-nanocomposites xanthine biosensor based on chitosan were tested with fish, beef, and chicken real-sample measurements.	[70-72]

DPPH: 2, 2-diphenyl-1-picryhydrazyl radical scavenging assay, FRAP ferric-reducing antioxidant power assay, ABTS: 2, 2′ -azinobis (3-ethylbenzothiazoline-6-sulphonate) assay.

4. Conclusion

The excellent structural possibilities and unique properties of chitosan accompanied with chemical modifications and nanobiotechnology creativity, permits to develop a wide variety of chitosan nanomaterials and composites with highly functional properties suitable for unlimited versatile of food applications.

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