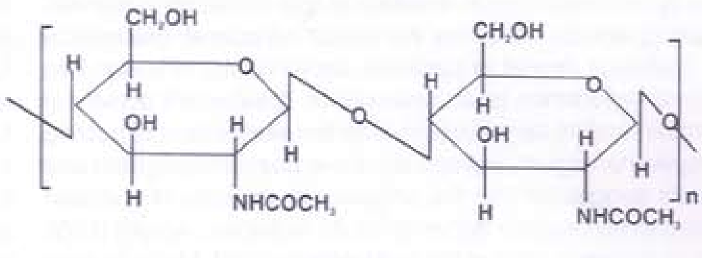
Chitosan – A versatile Biopolymer and its Seafood applications

[2*]U. Parvathy, [2]A. Jeyakumari, [2]A. A. Zynudheen, [2]L.N. Murthy, [2]S. Visnuvinayagam , [1] C. N. Ravishankar
[1]ICAR- Central Institute of Fisheries Technology, Kochi-29 Kerala, [2]Scientist Mumbai Research Centre of ICAR-Central Institute of Fisheries Technology Vashi, Navi Mumbai-400703 (M.S.)
*Email: p.pillai2012@gmail.com

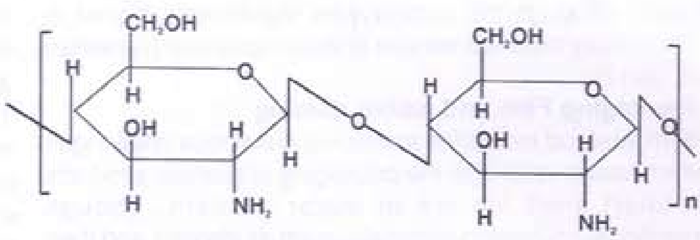
INTRODUCTION

Disposal of seafood processing discards has been a major crisis for most of the seafood producing countries. Of these, shell fish processing scraps contribute to a larger extent. The biodegradation of chitin in the crustacean shell waste is very slow resulting in the accumulation of huge quantities of discards. In this context, conversion of these shell fish processing discards into valuable by-products such as chitin, chitosan and their derivatives as well as their application in different fields is of paramount interest. Chitin, is the second most abundant polysaccharide in nature after cellulose, and is primarily present in the exoskeletons of crustaceans and also in a variety of insects, worms, fungi and mushrooms in varying amount. Chitosan, mainly obtained by deacetylation of chitin, is a high-molecular weight, linear, polycationic heteropolysaccharide made of two monosaccharides viz., N-acetyl-glucosamine and D-glucosamine which are linked by β-(1→4) glycosidic bonds. The relative amounts of these two monosaccharides in chitosan vary considerably, yielding chitosans of varying degrees of deacetylation (75% to 95%), molecular weights (50–2,000 kDa), different viscosities and pKa values. In addition, chitosan has three functional moieties on its backbone: the amino group on the C_2 and the primary and secondary hydroxyl groups on the C_3 and C_6 positions, respectively which play important roles in the various functionalities of chitosan. Chitosan, being biocompatibile, biodegradable, nontoxic and bioadhesive, assures its suitability for pharmaceutical, cosmetics, medical, food, textile, waste water treatment, paper finishing, photographic paper, and agricultural applications (Rinaudo 2006; Kim 2010).

Functional foods are considered to be those enriched or enhanced foods that provide health benefits beyond essential nutrients, when consumed at efficacious levels as part of the varied diet on a regular basis. Recently numerous marine-based functional foods have been identified of which chitin and chitosan has a prominent role. In Seafood Industry, chitosan can be utilized for its various potential applications exploiting its many features, such as antibacterial and antioxidant properties, edible film forming and coating ability, enhanced gelling properties, micro- and nano carrier abilities for bioactive compounds, effluent treatment etc. ICAR-CIFT has conducted numerous studies on the effective extraction of chitin and chitosan from crustacean shell waste as well as its possible applications.



Chitin



Chitosan

As Anti-microbial agent

Chemical preservatives, on account of their negative health effects are being phased out and this has led to the urge to discover new natural anti-microbial agents. Chitosan and its degradation products such as chito-oligomers and low molecular weight chitosans have been studied by several researchers and have gained much attention as a potential food preservative of natural origin due to its anti-microbial activity against a wide range of food borne filamentous fungi, yeast, and bacteria. One feasible mechanism for their anti-microbial activity is a change in cell permeability due to the interaction between positively charged chitosan molecules and negatively charged microbial cell membrane that leads to the leakage of proteinaceous and other intracellular constituents. Other mechanisms include the interaction of diffused hydrolysis products with microbial DNA leading to the inhibition of the mRNA and protein synthesis, chelation of metal ions etc. Chitosan is also known to activate several defence processes in the host tissue, acts as a water binding agent and enzyme inhibitor. The anti-microbial effects of chitosan and its derivatives are reported to be dependent on its molecular weight, degree of deacetylation (DD), and the type of bacterium. Food being of a mixture of different compounds viz., carbohydrate, protein, fat, minerals, vitamins, salts etc and these interact with chitosan leading to the loss or enhancement of anti-microbial activity.

As antioxidant

The health benefits of marine foods are mainly associated with their richness in lipids viz., the long-chain omega-3 PUFAs, such as eicosapentaenoic acid and docosahexaenoic acid. However, these valuable compounds are highly sensitive to oxidation and resultant development of off-odours and off-flavors. Additionally, fish and shellfish muscles contain protein bound iron compounds which also play an important role in initiation of lipid oxidation in marine-based products. With the increased consumer preference for seafoods devoid of synthetic antioxidants, chitosan has gained importance as an antioxidant. Antioxidant activity of chitosan and its derivatives in different seafoods viz., herring (*Clupea harengus*), salmon etc. have been investigated and results suggested that the antioxidant capacity of chitosan added to fish muscle depends on its molecular weight (MW) and its concentration in the food incorporated. Many studies have revealed low or no antioxidant activity of native chitosan, although the activity was significantly higher in the chemically modified version of this biopolymer (Casettari *et al.*, 2012).

As Packaging Film and edible coating

Modern seafood industries are facing numerous challenges of which issues related to the packaging of seafood products with short shelf life are of major concern. Though conventional packaging materials, such as plastics and their derivatives are effective for seafood preservation, they create serious environmental problems. Hence alternative packaging materials considering the economic aspects widens the scope of exploring biopolymer. Edible biopolymer-based films have been investigated for their abilities to avoid moisture or water absorption, reduce oxygen penetration into the food matrix, and their ability to prevent aroma loss and solute transport out of the product (Campos *et al.*, 2011). Chitosan can satisfy these criterias and hence is one of the most promising active biofilm. Chitosan films are tough, long-lasting, flexible and very difficult to tear making their mechanical properties comparable to many medium-strength commercial polymers. But they have lower resistance to water and water vapour transmission due to the strongly hydrophilic nature. Polymer blending or the use of biocomposites and multilayer systems are potential approaches to prepare chitosan-based bioactive coatings or films with desirable characteristics. Chitosan's antimicrobial property makes it a potential candidate for use in the form of active packaging for extending the shelf life of foods.

The use of chitosan as edible films and coatings to extend the shelf life and improve the quality of fresh, frozen and fabricated foods has been investigated widely. The different mechanisms involved include controlled moisture transmission, controlled release of chemical agents (antimicrobial substances and antioxidants), reduction of oxygen partial pressure (decreased rate of metabolism), controlled rate of respiration, high impermeability to certain substances (fats and oils), temperature control, structural reinforcement of food and coat flavour compounds and leavening agents in the form of microcapsules.

As Gel Enhancer

Surimi is a wet concentrate of myofibrillar proteins prepared by washing fish mince free of undesirable components like blood, lipids, enzymes, and sarcoplasmic protein. They form an elastic gel when solubilized with NaCl and heated. The gel-forming properties of the myofibrillar proteins are unstable if not used immediately on account of the degradation by the action of endogenous proteolytic enzymes. Freezing also results in rapid loss of protein functionality due to denaturation. Chitosan is a good option for incorporation into these products to improve their techno-functional quality. Along with chitosan, endogenous transglutaminase (TGase) plays an important role in gel formation. Hydrophobic interactions, hydrogen bonding, and electrostatic interactions during the setting process have been proposed as possible mechanisms by which chitosan can enhance the formation of cross-linked myosin heavy chain components during their polymerization by endogenous enzymes.

As Encapsulating agent

The increased customer health awareness has attracted much attention and demand for functional foods and bioactive compounds. However, most of these compounds are environment sensitive viz., oxygen, light, and temperature as well as vulnerable to harsh in vivo conditions (Alishahi *et al.*, 2011). These problems can be addressed by encapsulation technology wherein active components are entrapped and protected within a stable matrix and released under controlled conditions. Numerous materials are encapsulated for use in the food industry such as oil,

TABLE 1 : ***Seafood Applications of Chitosan***

Application	Mode of Action	References
Anti-microbial Agent	Against various food borne fungi, yeast and bacteria	Sagoo *et al.*, (2002) Tsai *et al.*, (2002) No *et al.*, (2002) Chatterjee *et al.*, (2015)
Anti-oxidant	Reduction/retardation of lipid oxidation in chitosan or their derivative incorporated seafoods	Kamil *et al.*, (2002) Kim and Thomas (2007) Jeyakumari *et al.*, (2016)
Packaging material/ edible coating	Shelf life extension	Remya *et al.*, (2015) Vimaladevi *et al.*, (2015)
Gelling enhancer	Modification of fish protein functionality	Benjakul *et al.*, (2003)
Encapsulating agent	Stable and sustained release of bioactive compounds	Alishahi *et al.*, (2011)
Waste Water Treatment	Precipitation of protein and other suspended solids in the seafood effluents	*Wibowo et al.*, (2007)

vitamins, minerals, antioxidants, colorants, enzymes, and sweeteners. Chitosan can act as an effective encapsulating agent due to its versatile properties (Kumar 2000). Authors have revealed the important implications of utilizing chitosan coatings for the encapsulation, protection and delivery of omega-3 fatty acids. It is suggested that encapsulation with chitosan could be used to protect emulsified polyunsaturated lipids from oxidation during storage while allowing the capsules to release functional lipids on consumption.

As coagulant in Waste water Treatment

Chitosan, with its partial positive charge, can effectively function as a polycationic coagulant in wastewater treatment. It has been widely investigated for the removal of suspended solids from various processing streams and effluents from the processing of poultry and seafood products (Kumar 2000; Shahidi *et al.*, 1999). There are two stages that result in destabilization of a colloidal system; coagulation, the process where the forces holding the particles in suspension are neutralized and flocculation, in which destabilized suspended particles are brought together to form larger aggregates. The most important mechanisms explaining the chitosan effectiveness in seafood plant effluents treatment is mainly attributed to its positive charge and interaction with negatively charged compounds in the effluents such as protein. Furthermore, the hydroxyl groups on the chitosan molecule contribute to increase the precipitation of proteins and other suspended solids in the seafood plant effluents.

CONCLUSION

Chitosan, a highly versatile biopolymer obtained by the deacetylation of chitin, has gained much scope for exploration and application in different fields including food industry. Various researches have revealed its suitability as antimicrobial and antioxidant agent, film-forming ability, gel enhancement, encapsulating ability, in waste water treatment etc. These various applications make it suitable for incorporation in food system for enhancing product stability and improving the nutritional value. More focused studies can reveal further applications of this wonder polymer.

REFERENCES

Alishahi, A., Mirvaghefi, A., Rafie-Tehrani, M., Farahmand, H., Shojaosadati, S.A., Dorkoosh, F.A. and Elsabee, M.Z. 2011. Shelf life and delivery enhancement of vitamin C using chitosan nanoparticles. Food Chemistry 126: 935–940.

Benjakul, S., Visessanguan, W., Phatchrat, S. and Tanaka, M. 2003. Chitosan affects transglutaminase-induced surimi gelation. Journal of Food Biochemistry 27: 53–66.

Campos, C.A., Gerschenson, L.N. and Flores, S.K. 2011. Development of edible films and coatings with antimicrobial activity. Food and Bioprocess Technology 4: 849–875.

Casettari, L., Gennari, L., Angelino, D., Ninfali, P. and Castagnino, E. 2012. ORAC of chitosan and its derivatives. Food Hydrocolloids 28: 243–247.

Chatterjee, N. S., Panda, S. K., Navitha, M., Asha, K. K., Anandan, R. and Mathew, S. 2015. Vanillic acid and coumaric acid grafted chitosan derivatives: improved grafting ratio and potential application in functional food. J. Food Sci. Technol. DOI 10.1007/s13197-015-1874-4.

Jeyakumari, A., George Ninan, Joshy, C. G., Parvathy, U., Zynudheen, A. A. and Lalitha, K. V. 2016. Effect of chitosan on shelf life of restructured fish products from pangasius (Pangasianodon hypophthalmus) surimi during chilled storage. Journal of Food Science and Technology 53(4): 2099-2107.

Kamil, J.Y.V.A., Jeon, Y.J. and Shahidi, F. 2002. Antioxidative activity of chitosans of different viscosity in cooked comminuted flesh of herring (Clupea harengus). Food Chemistry 79: 69–77.

Kim, K.W. and Thomas, R.L. 2007. Antioxidative activity of chitosans with varying molecular weights. Food Chemistry 101: 308–313.

Kim, S-K. 2010. Chitin, Chitosan, Oligosaccharides and Their Derivatives: Biological Activities and Applications, CRC Press, Boca Raton, F. 666.

Kumar, M.N.V. 2000. A review of chitin and chitosan applications. Reactive Functional Polymer. 46: 1-27.

No, H.K., Na, Y.P., Lee, S.H. and Meyers, S.P. 2002. Antibacterial activity of chitosans and chitosan oligomers with different molecular weights. International Journal of Food Microbiology 74: 65-72.

Remya, S., Mohan, C. O., Bindu, J., Sivaraman, G. K., Venkateshwarlu, G. and Ravishankar, C. N. 2015. Effect of chitosan based active packaging film on the keeping quality of chilled stored barracuda fish. Journal of Food Science and Technology DOI 10.1007/s13197-015-2018-6.

Rinaudo, M. 2006. Chitin and chitosan: Properties and applications Progress in Polymer Science. 31(7): 603–632.

Sagoo, S.K., Board, R. and Roller, S. 2002. Chitosan potentiates the antimicrobial action of sodium benzoate on spoilage yeasts. Letters in Applied Microbiology. 34(3): 168–172.

Shahidi, F., Kamil, J.Y.V.A. and Jeon, Y.J. 1999. Food applications of chitin and chitosan. Trends in Food Science & Technology 10: 37-51.

Tsai, G.J., Su, W.H., Chen, H.C. and Pan, C.L. 2002. Antimicrobial activity of shrimp chitin and chitosan from different treatments and applications of fish preservation. Fisheries Science 68:170–177.

Vimaladevi, S., Panda, S. K., Martin Xavier, K.A. and Bindu, J. 2015. Packaging performance of organic acid incorporated chitosan films on dried anchovy (Stolephorus indicus). Carbohydrate Polymers 127 (2015) 189–194.

Wibowo, S., Velazquez, G., Savant, V. and Torres, A. 2007. Effect of chitosan type on protein and water recovery efficiency from surimi wash water treated with chitosan-alginate complexes. Bioresources Technology 98: 539-545.

<u>*Contd. from Page 35*</u>

Industrial applications of Tapioca Starch

Explosives Industry

Tapioca starch is used as wide range binding agent and match-head binder in explosives industry.

Construction Industry

In the construction industry is used as concrete block binder, plywood/chipboard adhesive, gypsum board binder, asbestos, clay/limestone binder, erecting fire-resistant wallboards and paint filler.

Mining Industry

Tapioca starch is used for ore flotation, ore sedimentation and oil well drilling muds.

Other uses

- In metal industries tapioca starch is used in foundry core binder, sintered metal additive and sand casting binder.
- In addition to the above, tapioca starch helps in the preparation of biodegradable plastic film, dry cell batteries, printed circuit boards and leather finishing.

Animal Feed

- Starch is highly economical and therefore extensively used as a filler in the manufacturing of compounded animal feeds.
- Semi-dried leaves of tapioca can be used as safe animal food.
- After harvesting, under sized tubers after grading can be chopped and can be preserved for six months. The cyanide content is reduced up to 80% and can be used for animal food including piggery.