JOURNAL OF ADVANCED MECHANICAL ENGINEERING APPLICATIONS
e-ISSN: 2716-6201

Vol. 5 No. 1 (2024) 8-12
https://publisher.uthm.edu.my/ojs/index.php/jamea

JAMEA

Chitosan Properties: A Preliminary Review

Siti Nur Farahayu Abd Rahman[1], Siti Amira Othman[1]*

[1] *Faculty of Applied Sciences and Technology*
Universiti Tun Hussein Onn Malaysia, Pagoh, 84600, JOHOR.

*Corresponding Author: sitiamira@uthm.edu.my
DOI: https://doi.org/10.30880/jamea.2024.05.01.002

Article Info

Received: 6 November 2023
Accepted: 12 February 2024
Available online: 23 June 2024

Keywords

Chitosan, cholesterol, amino, hydrophobic, chains

Abstract

The content of amino groups in chitosan becomes the main cause of its differences from chitin in the context of structures and properties such as their chelation, flocculation, and biological functions. Furthermore, the random distribution of chitosan makes it easier to generate intra- and inter-molecular hydrogen bonds. Also, the existence of two hydroxyl groups and one primary amine group in chitosan, which can donate a free pair of electrons, make it soluble in diluted aqueous acetic solvents, and allow the formation of the coordination bonds that increase the possibilities for chemical modification. Its modification includes the incorporation of hydrophobic groups. Therefore, this paper reviews the properties of chitosan.

1. Introduction

Chitosan, a natural polysaccharide that can be derived from chitin, a central component of the shells of crustaceans, has received much attention for its commercial applications in various fields, for instance, in the biomedical, agriculture, cosmetic products, food, and chemical industries as well [1]. Chitosan consists of β-(1→4) linked 2-acetamido-2-deoxy-β-D-glucopyranose (GlcNAc) and 2-amino-2-β deoxy-D- glucopyranose (GlcN) units, with the ratio depending on the deacetylation degree as shown in figure 1 [2]. It consists of three reactive functional groups: an amino or acetamido group with primary and secondary hydroxyl groups at the C-2, C-3, and C-6 positions.

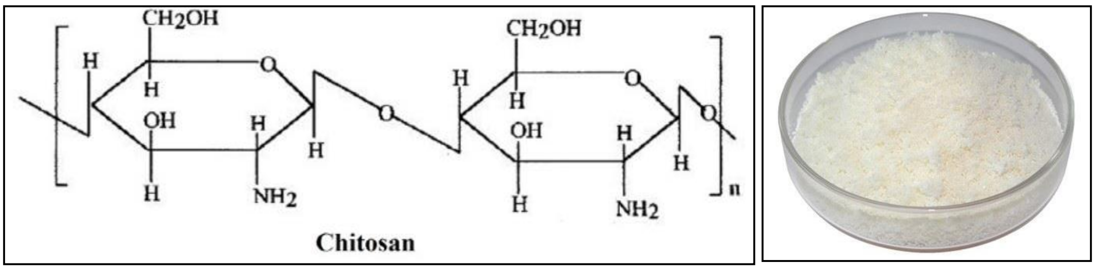

Fig. 1 *The structural formula and powder of chitosan [2]*

1.1 Properties of Chitosan

The properties of chitosan can be divided into two groups, which are chemical and biological properties. Some examples of its chemical properties are linear polyamines, reactive amino acids, and reactive hydroxyl groups. It can also chelate many transitional metal ions. At the same time, chitosan's biological properties include biocompatibility and the ability to bind aggressively to mammalian and microbial cells. The biocompatible properties have introduced chitosan as a natural polymer, biodegradable to normal body constituents, and a safe and non-toxic biopolymer. Besides that, chitosan can bind to mammalian and microbial cells as it is known as an antitumor, anticholesteremic, fungistatic, and hemostatic. It has a regenerative effect on the connective gum tissue. These properties make chitosan vital in various applications nowadays, especially in medical applications [3].

1.2 Hydrophobic Modified Chitosan

Hydrophobic comes from the words "hydro," meaning water, while "phobic" means phobia or fear. Thus, it can be said that hydrophobic is defined as "water-fearing" or any substance that has a phobia of water. The hydrophobic effect is when nonpolar substances tend to stick together in water and keep water molecules from mixing [4]. It describes the segregation and apparent repulsion between water and nonpolar substances. When alkyl chains with at least six carbon atoms are added to chitosan, it interacts hydrophobically with solutions and sticks together on its own's physical and chemical properties change with the presence of hydrophobic interactions between the alkyl chains [5]. This hydrophobic chitosan interaction differs from other interactions, such as hydrogen bonds, electrostatic forces, and Van der Waals bonds.

The difference is due to the cohesive interactions between molecules not directly forming them. Instead, they are caused by the specific structure of water molecules close to the polymer chains. Although no covalent bonds can be observed, the aggregates have been established from the hydrophobic moieties, which behave as crosslinks in a physical network [6]. At present, most researchers agree that the aggregation of chitosan is related to hydrogen bonds and hydrophobic interactions.

Besides that, the hydrophobic behaviour of chitosan can be increased by the attachment of hydrophobic excipients. It is thought that the interactions make substituted chitosan more stable by lowering the matrix's hydration and making it harder for stomach enzymes to break down [7]. The presence of carboxylic acid groups in chitosan makes chitosan pH sensitive. Under acidic conditions, the carboxylic groups exist in non-ionized form and are, therefore, poorly hydrophilic, or known as "water-liking."

1.3 Fat-Binding Capability

Numerous studies have demonstrated the ability of biopolymers, including chitosan, to function as dietary fibres by lowering blood cholesterol concentrations and reducing lipid absorption. A previous study reported that nutritional fibres could alter the breakup and coalescence of lipid droplets in the stomach and small intestine, thus altering the surface area of emulsified lipids exposed to digestive enzymes. The lipid-lowering effects of chitosan have been observed since the 1980s in animal models, and this effect was reported for the first time in humans without any side effects as early as 1993. Then, the increasing evidence of lipid-lowering effects of chitosan has been consistently proven in most literature [8].

Chitosan is claimed to be able to lower total cholesterol levels, as has been observed in many animal studies. Chitosan, which acts as a cationic side, can bind to the surface of anionic lipid droplets, which are stabilised by bile salt or phospholipids, and reduce lipase activity by preventing contact between lipase and emulsified lipid substrates. The electrostatic attraction between positively charged amino groups of chitosan and negatively charged carboxyl groups of fatty acids and bile salts contributes to the strong binding effect of chitosan on both fat and cholesterol. This is influenced by the entrapment of fat droplets in the stomach, which is later followed by precipitation in the small intestine and hydrophobic interactions or hydrogen bonding between lipids and chitosan [9].

Besides that, the fat-binding capability of chitosan is enhanced by the increasing viscosity-average molecular weight, suggesting that during the fat-binding process, the fat molecules are embedded in the long chain of chitosan. This means that a greater molecular weight results in a longer chain, and hence, more fats will be embedded. Therefore, the electrostatic interactions with the entrapment of fat by the viscous polysaccharide chitosan would reduce fat absorption in the diet. It becomes one of the factors in the fat-binding mechanism [10].

Moreover, the chitosan is claimed to entrap the fat droplets formed in the stomach as they are eaten together. As the complex formation between chitosan and fat arrives at the small intestine, chitosan precipitates with the entrapped fat at a neutral pH. This action prevents fat digestion by delaying the related process of removing it, which has been proven in vitro [11].

Chitosan-fat interaction is more convincing through Fourier Transform Infrared (FTIR) analysis and Scanning Electron Microscope (SEM) analysis between chitosan and the chitosan-fat complex. By FTIR test, previous studies showed that there are absorption peaks at 2,924.69 cm^{-1}, 2,854.81 cm^{-1} and 1,744.38 cm^{-1} of the chitosan fat sample spectrum, corresponding to the saturated alkyl and the carbonyl group of a fatty acid, respectively.

Through SEM analysis, a chitosan-oil complex sample shows that instead of the sandlot shape of chitosan alone, the shape of the chitosan-oil complex forms a bulk of blocky particles [12]. This is due to the interaction of chitosan and oil, which causes the chitosan to entrap and surround the fat from the oil as their charges are different from the positively charged amino group in chitosan and the opposite charge of fatty acids in oil. Several parameters have a significant influence on the hydrophobic interactions of chitosan in lowering cholesterol levels, which include: (i) concentration of chitosan; (ii) different pH values; and (iii) different types of vegetable cooking oil.

1.4 Influence of Chitosan Concentration

The behaviour of chitosan, including in entrapping fat from oil, can be influenced by controlling its concentration. From the previous studies, a higher chitosan concentration demonstrated a higher interaction between chitosan and cholesterol, meaning more entrapped fat was obtained. For example, in the pioneering research, the result of the percentage of trapped oil for different oil quantities was discussed and observed. The results suggest that chitosan can effectively reduce lipid absorption and thus lead to weight loss. It was also shown that when the amount of oil content was increased, the entrapped oil percentage decreased. Based on this earlier research, the observed parameter used was the dietary oil concentration. This is different from the experiment that was conducted by changing the oil concentration with the concentration of chitosan powder.

1.5 Influence of pH

The existence of the amino group in the chitosan structure means that the pH substantially alters the properties of chitosan, as follows: At pH > 6.5, chitosan solutions show pH separation, whereas at pH <6.5, they are soluble, carrying a positive charge because of the presence of amino groups. Between pH 6.0 and 6.5 in solution, the free amino groups of chitosan molecules become less protonated, and hydrophobicity along the chitosan chain increases. When the pH is low (less than about 6.0), chitosan can interact with molecules that are negatively charged using electrostatic forces. When the pH is high (above about 6.5), the amino groups in chitosan become deprotonated and can interact hydrophobically with fatty acids and cholesterol [13].

This study claimed that chitosan works best at concentrations above about 6.5 in making hydrophobic interactions with fatty acids and cholesterol. Researchers [7] proposed in their earliest research that at pH 1.0–2.0, the emulsion was formed when chitosan and sunflower oil were mixed, and microscopically, few emulsified oil drops were observed. When the pH value was increased to 5.8, the chitosan emulsion-forming process was improved with a greater number of emulsified droplets. As the pH value increases by about 6.5–7.5, the chitosan precipitates and entraps the lipids, forming the flocculus.

1.6 Influence of Different Types of Cooking Oil

Different cooking oils have other effects on the chitosan properties, especially in analysing their interactions. Different types of vegetable oil were commonly used in most of the studies to investigate the impact of cooking oils on cholesterol. For example, one of the famous vegetable oils chosen is palm oil due to its higher saturated fat content than other vegetable oils. The effects of cooking oil on blood cholesterol are based on its high saturated fat content. Palm oil is claimed to have great potential for raising the LDL cholesterol level in the body. Palm oil consumption promotes a higher increment of LDL cholesterol than other vegetable oils with a low content of saturated fats [14]. Though vegetable oil, including palm oil, has no cholesterol content, its ability to elevate cholesterol levels is similar to or higher than that of most animal fats.

1.7 Dietary Supplement Application of Chitosan

There are many applications of modified chitosan in various fields, for example, biomedical, agriculture, food, and chemical industries, that are beneficial to human beings nowadays. In the medical field, chitosan applications include drug delivery systems, antibacterial activity, tissue engineering, wound healing, and many more. Chitosan is primarily consumed as a dietary supplement. It is often used to prevent dietary fat absorption and control weight.

Interestingly, chitosan has a positively charged tertiary amino group (β-$NH\ 3+$) to which negatively charged molecules like fatty acids and bile acids can strongly attach. Furthermore, it also binds neutral lipids like cholesterol and triglycerides through hydrophobic bonds. In humans, dietary chitosan has been reported to reduce serum total cholesterol levels and low-density lipoprotein (LDL) levels [15]. The result of a previous study that investigated the interaction of chitosan and cooking oil under stomach conditions proposed that dietary chitosan is dissolved at the gastric level and emulsifies the cooking oil before forming a flocculus. This form of flocculus entraps and absorbs the fat oil. It prevents lipid absorption through the intestinal wall by excreting the fat oil with faeces. This unique action of the chitosan mechanism is assumed to reduce weight; hence, it is used as a dietary supplement among us today.

2. Radiation Study Effect on Chitosan

The fat-binding activity of the chitosan was found to improve with irradiation. The previous study shows that irradiation of chitosan with gamma radiation brings about significant changes in the physicochemical and morphological properties of chitosan, providing great potential for various applications. Furthermore, the study claimed that irradiated chitosan's fat-binding capability is higher than that of non-irradiated chitosan [16].

As gamma radiation has a greater penetration rate than other radiations, it can break the chain scission of chitosan molecules at glycosidic linkages. High-energy ionising gamma radiation causes the chains of chitosan to rupture and form irregular arrangements of the molecules. Gamma radiation can produce electronic excitation and ions in an excited state, which leads to possible chemical changes and improves various properties, including fat-binding capability.

Acknowledgement

The authors would like to thank the Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia for the facilities provided that make the research possible.

Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Siti Nur Farahayu Abd Rahman, Siti Amira Othman;* ***data collection:*** *Siti Nur Farahayu Abd Rahman;* ***analysis and interpretation of results:*** *Siti Nur Farahayu Abd Rahman, Siti Amira Othman;* ***draft manuscript preparation:*** *Siti Amira Othman. All authors reviewed the results and approved the final version of the manuscript.*

References

[1] Joyce C. C. Santos, Alexandra A. P. Mansur & Herman S. Mansur (2013) One-Step Biofunctionalizatin of Quantum Dots with Chitosan and N-palmitoyl Chitosan for Potential Biomedical Applications, *Molecules*, 18, 6550-6572, https://doi.org/10.3390/molecules18066550.

[2] Jolanta Kumirska, Mirko X. Weinhold, Jorg Thoming & Piotr Stepnowski (2011) Biomedical Activity of Chitin/Chitosan Based Materials: Influence of Physicochemical Properties from Molecular Weight and Degree of N- Acetylation, *Polymers*, 3, 1875-1901, https://doi.org/10.3390/polym3041875.

[3] Yingzhu Liu, Rongxu Liu, Jingbo Shi, Rui Zhang, Hongjie Tang, Cancan Xie, Fenghui Wang, Jianchun Han & Longwei Jiang (2023) Chitosan/esterified chitin nanofibers nanocomposite films incorporated with rose essential oil: Structure, physicochemical characterisation, antioxidant and antibacterial properties, *Food Chemistry: X*, 18, 100714, https://doi.org/10.1016/j.fochx.2023.100714.

[4] Ke-Xin Huang, Ling-Yue Zhou, Jia-Qi Chen, Na Peng, Hong-Xiang Chen, Hua-Zhi Gu & Tao Zou (2023) Applications and perspectives of quaternized cellulose, chitin and chitosan: A review, *International Journal of Biological Macromolecules* 242 (3), 124990, https://doi.org/10.1016/j.ijbiomac.2023.124990.

[5] Zhen Wu, Hong Li, Xiaowan Zhao, Fayin Ye & Guohua Zhao (2022) Hydrophobically modified polysaccharides and their self-assembled systems: A review on structures and .food applications, *Carbohydrate Polymers*, 284, 119182, https://doi.org/10.1016/j.carbpol.2022.119182.

[6] Munirah M. Al-Rooqi, M. Masudul Hassan, Ziad Moussa, Rami J. Obaid, Nahid Hasan Suman, Manfred H. Wagner, Sameer S.A. Natto & Saleh A. Ahmed (2022) Advancement of chitin and chitosan as promising biomaterials, *Journal of Saudi Chemical Society* 26 (6), 101561, https://doi.org/10.1016/j.jscs.2022.101561.

[7] Abbas Mehraie, Saied Khanzadi, Mohammad Hashemi & Mohammad Azizzadeh (2023) The new coating contains chitosan and Hyssopus officinalis essential oil (emulsion and nanoemulsion) to protect shrimp (Litopenaeus vannamei) against chemical, microbial and sensory changes, *Food Chemistry: X* 19,100801, https://doi.org/10.1016/j.fochx.2023.100801.

[8] Mohammad Mukarram, M. Naeem, Tariq Aftab & M. Masroor A. Khan (2022) Chapter Fourteen - Chitin, chitosan, and chitooligosaccharides: Recent advances and future perspectives, Editor(s): M. Naeem, Tariq Aftab, M. Masroor A. Khan. *Radiation-Processed Polysaccharides*, Academic Press, Pages 339-353, https://doi.org/10.1016/B978-0-323-85672-0.00012-X.

[9] Jie Yu, Hongping Quan, Zhiyu Huang, Junbang Shi, Shihao Chang, Lilong Zhang, Xuewen Chen & Yuling Hu (2023) Interaction between hydrophobic chitosan derivative and asphaltene in heavy oil to reduce the viscosity of heavy oil, *International Journal of Biological Macromolecules* 247, 125573, https://doi.org/10.1016/j.ijbiomac.2023.125573.

[10] Zhihua Pang, Mengya Sun, Borui Li, Imane Bourouis, Cunshe Chen, Yating Huang, Xinqi Liu & Pengjie Wang (2024) Morphology, surface characteristics and tribological properties of whey protein/chitosan composite particles and their fat replacing effect in O/W emulsion. *International Journal of Biological Macromolecules*, 259(2),129301, https://doi.org/10.1016/j.ijbiomac.2024.129301.

[11] Subham Rakshit, Kalyanbrata Pal, Subhadeep Mondal, Arijit Jana, Keshab Chandra Mondal & Suman Kumar Halder (2023) The extraction of chitosan from biologically derived chitin by bacterial chitin deacetylase is a process optimisation and product quality assessment. *International Journal of Biological Macromolecules*, 244, 125389, https://doi.org/10.1016/j.ijbiomac.2023.125389.

[12] Amol D. Gholap, Satish Rojekar, Harshad S. Kapare, Nikhar Vishwakarma, Sarjana Raikwar, Atul Garkal, Tejal A. Mehta, Harsh Jadhav, Mahendra Kumar Prajapati & Uday Annapure (2024) Chitosan scaffolds: Expanding horizons in biomedical applications: carbohydrate *Polymers*, 323, 121394, https://doi.org/10.1016/j.carbpol.2023.121394.

[13] Kumara B.N., N.G. Gurudatt & K.Sudhakara Prasad (2023) Carboxymethyl-hexanoyl chitosan: A promising candidate for hydrophobic and hydrophilic drug delivery. *Carbohydrate Polymer Technologies and Applications*, 6,100401, https://doi.org/10.1016/j.carpta.2023.100401.

[14] Shiv Shankar, Diako Khodaei & Monique Lacroix (2021) Effect of chitosan/essential oils/silver nanoparticles composite films packaging and gamma irradiation on shelf life of strawberries, *Food Hydrocolloids*, 117,106750, https://doi.org/10.1016/j.foodhyd.2021.106750.

[15] Sun, Y., Neelakantan, N., Wu, Y., Lote-Oke, R., Pan, A., & van Dam, R. M. (2015). Palm Oil Consumption Increases LDL Cholesterol Compared with Vegetable Oils Low in Saturated Fat in a Meta-Analysis of Clinical Trials. *The Journal of nutrition*, 145(7), 1549–1558, https://doi.org/10.3945/jn.115.210575.

[16] Firzanah Hisham, M.H. Maziati Akmal, Farah Ahmad, Kartini Ahmad & Noorasikin Samat (2024) Biopolymer chitosan: Potential sources, extraction methods, and emerging applications. *Ain Shams Engineering Journal*, 15 (2), 102424, https://doi.org/10.1016/j.asej.2023.102424.