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Research Progress on Water-Soluble Chitosan

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Abstract：

Chitosan has good film-forming property, adsorption, biocompatibility, biodegradability and antimicrobial properties, but it can only be dissolved in weak acidic aqueous solution and cannot be directly dissolved in water, which greatly limits its application. In order to increase its solubility in water, chitosan is modified, the research on the water-soluble derivatives of chitosan is reviewed in this paper, and its application in the protection of paper relics is briefly introduced.

Key words：Chitosan, Water-solubility, Protection of cultural relics

Chitin is a kind of natural polysaccharide macromolecular polymer synthesized by biology in animals and plants, which mainly come from shrimp shells, crab shells, insect shells and so on. Chitosan (CS) is obtained by deacetylation of chitin. The chitin is deacetylated under homogeneous conditions, and water-soluble product can be obtained by controlling the degree of deacetylation at about 50%[1]. The primary hydroxyl group secondary hydroxyl group and amino group on the glucosamine unit in the chitosan molecular chain, with strong reactivity, which can be modified and embellished by functionalization to improve its solubility. not good and it need rewriting

1. Chemical Modifications of Chitosan

1.1 Acylation

Acylation refers to a reaction in which an acyl group is introduced into a molecule. Generally, a reactant reacts with an acid anhydride or an acid halide to introduce an acyl group into a product molecule. The amino or hydroxyl groups in the chitosan molecules have the reactive activity, and the aliphatic or aromatic acyl chloride of different molecular weights can be introduced.

The O- acylation reaction of chitosan is difficult to carry out. Because the reaction activity of C6-OH in chitosan is much smaller than that of the amino group, the amino group is more easily acylated than C6-OH. Wang C *et al*. use the N, N, N- trimethyl chitosan and methanosulfonic acid dropping the carbonyl chlorid under the ice bath. After freeze-drying, a water-soluble N, N, N- three methyl -O- self acyl chitosan is obtained[2].

N- acylation modification mainly improves the water solubility of chitosan by introducing hydrophilic groups. Zheng G S *et al*. prepare water-soluble chitosan by N-acetylation under acetic acid-methanol homogeneous conditions, and the degree of deacetylation is about 56% calculated by FT-IR, which could be completely dissolved in the pH (7.0-7.4) physiological buffer system, such as pure water, physiological saline and so on[3].

Chen H J *et al*. prepare water-soluble butanedioic anhydrid acylated chitosan at room temperature using water as medium and sodium carbonate as catalyst. The results show that the acylation reaction basically occurs in the C-2 amino group of chitosan, and water-solubility of product is best when the mole ratio of butanedioic anhydrid to chitosan is 2.0 and sodium carbonate to succinic anhydride is 0.80[4].

Cui Wenhui *et al.* produce chitosan-citric acid from acylated modified chitosan, and measure the average molecular weight and water-solubility. As a result, it is confirmed that the acylation reaction occurred, and the average molecular weight and water-solubility of chitosan-citric acid are significantly increased[5].needs rewriting

1.2 Alkylation

There are lone electron pairs on the amino group in chitosan molecules, which have nucleophilic properties, so alkylation mainly occurs on the amino group. According to the reaction mechanism, alkylation can be divided into three categories: Michael addition reaction, Schiff base reaction and quaternylation reaction.

The Michael addition reaction is the conjugate addition of an electrophilic conjugated system with a nucleophilic reagent. Sashiwa uses chitosan to react with hydroxyethyl acrylate, hydroxypropyl acrylate and polyethylene glycol acrylate. Acrylic acid was successfully attached to chitosan molecules, and the solubility is improved[6,7].

The amino groups of chitosan molecules and the active carbonyl groups can be condensed to form the Schiff base. Wang H D *et al.* use chitosan to react with aromatic aldehyde to obtain chitosan Schiff base, and then the Schiff base is reacted with chloroacetic acid, after the final reaction, O-carboxymethyl chitosan is obtained by removing amino protection after reaction products, which has good water-solubility[8].

The introduction of quaternary ammonium group, with large steric resistance and strong hydration ability, which can greatly weaken the hydrogen bond between chitosan molecules and increase the water-solubility of chitosan derivatives. Sang-Hoon Lim *et al.* prepare a chitosan quaternized derivative with good water-solubility by introducing 2,3-epoxypropyl trimethyl ammonium chloride (GTA) onto the chitosan molecule [9]. needs rewriting

Song Y P *et al.* use different molecular weight chitosan to carry out quaternylation and determine the water-solubility of the products. The results show that all the three TMCs obtained after modification which are soluble in water, and the solubility order is TMC (700,000)>TMC (40,000)>TMC (100,000) [10].

Yang Longqiang *et al.* use GTA reacted with chitosan to prepare water-soluble chitosan quaternary ammonium salt (HTCC). Then, HTCC is used to react with chloracetyl chlorid to obtain chloroacetyl chitosan quaternary ammonium salt (CAHTCC). Finally, pyridine instead of active chlorine in CAHTCC, which is used to obtain water-soluble chitosan bi-quaternary ammonium salt (PAHTCC) [11].

N,N-dimethyl chitosan quaternary ammonium salt was synthesized with formaldehyde as catalyst under acidic conditions, then the Hoffman reaction is carried out with the bromo alkane under the action of catalyst, thus producing the N- long alkyl chitosan quaternary ammonium salt, which is found that it has high synthesis yield and water-solubility[12]. needs rewriting

1.3 Esterification

The hydroxyl groupat C-6 position of chitosan molecule can react with acid or anhydride to form an ester, which is usually sulfated and phosphated.Sulfated reagents are generally concentrated in H_2SO_4, SO_3 and $ClSO_2OH$, and P_2O_5 is commonly used for phosphorylation.The esterification reaction is mainly carried out by a hydroxyl group reaction, and the amino group is also partly reacted. Yu Peipei *et al.* use chitosan to react with benzoyl chloride to synthesize chitosan benzoate. The results show that the C_6-OH and C_3-OH of chitosan are acylated when the reaction temperature is 0℃, the time is 3h, and the monomer ratio is 6:1, and the ester has good solubility in various organic solvents [13].

1.4 Carboxylation

In order to improve the hydrophilicity of polysaccharides, one of the commonly used methods is carboxyalkylation. The most common carboxylic modification of chitosan is carboxymethylation and carboxybutylation, which can simultaneously react at the hydroxyl and amino active sites, finally, an N,O-carboxyalkylated chitosan derivative is obtained.

Wang X Q *et al.* use chitosan (CTS) and reactive brilliant blue KN-R dyes as raw materials to prepare novel N,O-carboxymethyl chitosan dyes by a two-step reaction. The results show that the substitution of carboxymethyl group and the grafting of sulfonic acid groups destroy the strong intramolecular and intermolecular hydrogen bonding, which leads to the decrease of crystallinity. The water-solubility of N,O-CMCS-D is obviously improved, which is suitable for in weak acid and weak alkaline environment[14].

1.5 Etherification

Hydroxyethyl chitosan (HECTS) is a chitosan derivative which is produced by the active H group in the molecular structure of natural polymer chitosan , such as the amino or hydroxyl group, reacting with hydroxyethyl reagent. HECTS can be classified into N,O-hydroxyethyl chitosan (N, O-HECTS), N-hydroxyethyl chitosan (N-HECTS) and O-hydroxyl according to the difference in the position at which hydroxyethyl groups are introduced, in which N,O-HECTS is widely used due to its relatively simple preparation process. Wang Ting *et al.* modifies the alkalized chitosan with bromoethanol to form N,O-hydroxyethyl chitosan (N, O-HECTS). The results show that the higher the substituting degree of hydroxyethyl, the better the water-solubility of product. When the substituting degree of hydroxyethyl is more than 82.42%, the corresponding hydroxyethyl chitosan can dissolve well in the water under the neutral condition[15].

1.6 Graft

The active groups in chitosan molecule provide possibility for graft reaction. There are two ways to graft: promoting the generation of free radicals on the chitosan skeleton, further stimulating them to polymerize with other monomers in the reaction system; another grafting route relies on the characteristics of chitosan itself, in which reactive groups in the molecule are coupled to other molecular chains that can react.

Luo Q Q *et al.* use reactive polyglycol to modify natural macromolecular chitosan, and the polyglycol graft chitosan polymer (PEG-g-CS) is synthesized by acylation. The results show that the chitosan modified by PEG has good water-solubility, which can be used as waterborne coating to finish the antibacterial finishing of leather surface[16].

Tao Feng synthesizes O-polyethylene glycol monomethyl ether-N-maleic anhydride polyethyleneimine chitosan derivative. The final product of the synthesis not only improves the water-solubility and stability of chitosan, but also facilitates further modification of chitosan due to the introduction of a large amount of active amino groups [17].

Sun Zhimin *et al.* synthesize pyridine-chitosan by grafting small pyridine groups onto chitosan, determining the substituting degree and water-solubility of product, finally, pyridine-chitosan, with good water-solubility and substituting degree of 0.66, is obtained[18].

1.7 Oxidative degradation

Decreasing the molecular weight of chitosan can improve the solubility of chitosan. Since the number of intramolecular hydrogen bonds decreases as the molecular weight decreases, the hydrogen bonding action is weakened, so that it can interact with water molecules, thus the solubility property is improved.

Yao Bangtao *et al.* use hydrogen peroxide degradation to prepare water-soluble chitosan. The viscosity average molecular weight of oligochitosan is 4566.9 by extrapolation. The structure of water-soluble chitosan is consistent with the structure of raw chitosan by infrared spectroscopy[19].

Shen W T *et al.* use H_2O_2 as oxidant to oxidize and degrade chitosan into water-soluble oligosaccharide in neutral medium. The results show that the yield of water-soluble oligosaccharide can reach about 90% when the dosage of H_2O_2 is 3.0-3.5 mL (30%H2O2) /g (CTS) and the reaction temperature is 60℃ and the reaction time is 7-8 h, respectively [20].

Huang H B *et al.* use microwave-assisted H_2O_2/UV system to rapidly oxidize and degrade chitosan to prepare water-soluble oligosaccharides with different low molecular masses. The experimental results show that the natural chitosan is degraded rapidly within 5min in the system, and the obtained chitosan has good water-solubility in the wide range of pH. The chemical structure of degradation products is characterized by FTIR and XRD. The results show that the oligosaccharides still retain the structure of sugar ring, and the oxidative degradation mainly leads to cleavage of β-glycosidic bond on the main chain, and the product still maintains the basic chemical structure and functional groups[21].

2. Application of chitosan derivatives in protection of paper relics

Since chitosan is similar to plant cellulose in structure, and it is a polyelectrolyte, which has significant affinity for paper fiber, which can be used as reinforcing agent, surface sizing agent, sizing agent, flocculant and retention aid. The chitosan derivatives after chemical modification are widely used, for example, which can be used to protect cultural relics[22].

Sun Z Q *et al.* use propylene oxide as an etherifying agent to obtain hydroxypropyl chitosan with good water-solubility under alkaline conditions. It is sprayed on the surface of the paper with a proper concentration of glue, which has obvious effect on the strengthening and protecting the paper relics[23]. Cao Yuhong *et al.* study the graft modification of cellulose-chitosan, making a certain concentration of glue with an appropriate amount of cross-linking agent, after spraying on the surface of the paper, which is found that the tensile strength and the folding resistance are significantly improved. It is thus proved that the protective glue using the cellulose-chitosan graft product as the main component has obvious protective effect on paper cultural relics[24]. Duan D C uses natural organic macromolecules (bacterial cellulose, chitosan) to study the fiber structure reinforcement of paper and the antibacterial treatment of paper. The experimental data proves that the tensile strength of the paper is significantly improved [25].

3. Conclusion

Chitosan is the only alkaline amino polysaccharide in nature. Its main chain is rich in hydroxyl and amino groups, with active chemical properties, which can be modified by chemical methods to improve its solubility and be imparted functional properties at the same time, so as to prepare and develop a novel chitosan derivatives with excellent properties.

References

1. Sun D F,Zhu C L, Zhang W M, *et al.*Study on the preparation of water-soluble chitosan by N-acetylation[J]. Chinese Wild Plant Resources,2010, 29(06): 48-50+56.

2. WangC, Xin M H, Li M C, *et al.* Synthesis and Antibacterial Activity of O-hexanoylated Chitosan Quaternary Ammonium Salt [J]. Functional Material, 2013,44(15): 2148-2151.

3. Zheng G S, Zheng H Z, Xie H G, *et al.* Preparation of a water-soluble chitosan and its application in microencapsulated cell culture [J], 2015,46(20):20078-20082.

4. Chen H J, Jiang X, Jiang F R, *et al.* Preparation and pH response of water-soluble butanedioic anhydrid acylated chitosan [J]. Chemical and Biological Engineering, 2015, 32(06): 50-53.

5. Cui W H, Guo Q, Li Q P, *et al.* Comparison of structural and functional properties of chitosan and Chitosan-Citric Acid Complex [J]. Food Science, 2017,38(05): 134-141.

6. Sashiwa H, Yamamori N, Ichinose Y, *et al.*Chemical modification of Chitosan, 17 michael reaction of chitosan with acrylic acid in water [J]. MacromoleculeBioscience, 2003(3):231-233.

7. Sashiwa H, Yamamori N, Ichinose Y, *et al.*Michael Reaction of Chitosanwith Various Acryl Reagents in Water[J]. Biomacromolecules,2003(6):1250-1254.

8. Wang H D, Wang J T. Preparation of Chitosan Derivative by SchiffBase and its Antibacterial Activity [J]. Journal of Chemical Engineering of Chinese Universities, 2012,26(06): 1048-1053.

9. Lim S H, Hudson S M.Synthesis and antimicrobial activity of a water-soluble chitosan derivative with a fiber-reactive group[J]. CarbohydrateResearch,2004, 339(2):313-319.

10. Song Y P, Chen X X, Zhang H D. The Modification of Chitosan and Preparation of Nanoparticles [J]. Journal of Shijiazhuang University, 2017, 19(06): 9-14.

11. Yang L Q, Li R C, Liang S P. Preparation and Antioxidant ActiVity of NoVel Double Quaternary Ammonium Salt DeriVative of Chitosan [J]. Chinese Journal of Applied Chemistry, 2015, 32(03): 322-326.

12. Xie C F. Study on the synthesis of N- long alkyl chitosan quaternary ammonium salt [J]. Shandong chemical industry, 2016, 45(04): 23-24.

13. Yu P P, Xia W S. Study on synthesis and antibacterial property of benzoylation chitosan [J]. Food and Machinery, 2011, 27(5): 115-119.

14. Wang X Q, Zhang Y, Yu Z M. Study on the preparation of N,O- carboxymethyl chitosan antibacterial dye [J]. Journal of Beijing Forestry University, 2016, 38(11):104-110.

15. Wang T, Cai Z S, Zhang T T, *et al.* Synthesis of water-soluble N,O-hydroxyethyl chitosan and optimization of its synthetic condition [J]. Chemical Research and Application, 2018, 30(03): 395-399.

16. Luo Q Q, Li K J, Liu G Y, *et al.* Preparation and characterization of polyethylene glycol modified chitosan as antibacterial coating for leather [J]. Leather Science and Engineering, 2016, 26(01): 28-32.

17. Tao F. Synthesis of water-soluble PEI chitosan [J]. China New Technologies and Products, 2016(09): 48-49.

18. Sun Z M, Chen Q C, Huang J Y, *et al.* Preparation, characterization and antioxidant activity in vitro of pyridine chitosan [J]. Journal of Nuclear Agricultural Sciences, 2016, 30(02): 295-303.

19. Yao B T, Chen J W. Preparation of water-soluble chitosan by hydrogen peroxide oxidation degradation [J]. Paper Science & Technology, 2015, 34(06): 60-62+97.

20. Shen W T. Preparation and Characterization of Water-Soluble Chito-Oligosaccharides [J]. Chemical Industry Times, 2017, 31(04): 18-21.

21. Huang H B, Zeng G S, Chen Y, *et al.* Preparation and Characterization of Water-Soluble Chitooligosaccharides Produced by a Facile Method [J]. Packaging Journal, 2018, 10(02): 1-7+50.

22. Wang X M, Qi Y P, *et al.* Modified natural polymer materials for paper protection [J]. To Chemistry Journal, 2018(01): 82-87.

23. Sun Z Q, Qiu J H, Xu F Y, *et al.* Study on the Conservation of Paper Relic by O-(Hydroxyl Isopropyl)Chitosan [J]. Chemistry&Bioengineering, 2005(01): 39-41.

24. Cao Y H, Qiu J H, Zhu Z Z, *et al.* Study on the Conservation of Paper Based Historic Relics by Cellulose-chitosan Graft Product [J]. China Pup &Paper, 2008(03): 32-35.

25. Duan D C. Application of bacterial cellulose and chitosan in repairing and strengthening of paper relics and mildew resistance [D]. Liaoning University, 2017.