

STRUCTURAL IDENTIFICATION OF AMINOPOLYSACCHARIDE CHITOSAN APIS MELLIFERA WITH GLUTARALDEHYDE

¹Ikhtiyarova G.A., ²Ulashov Sh.M.

^{1,2}Tashkent State Technical University

<https://doi.org/10.5281/zenodo.11178170>

Abstract. *The article contains the synthesis of chitosan aminopolysaccharide Apis mellifera in liquid nitrogen and the preparation of Schiff bases based on glutaraldehyde with chitosan, electron microscopy of chitosan synthesized by a cryogenic method, and IR spectroscopy of the resulting chitosan and glutaraldehyde. The presence of intermolecular hydrogen bonds between the polymer and the aldehyde allows us to conclude that the mechanism of interaction between glutaraldehyde and chitosan is valid.*

Keywords: *chitosan, kriogen method, glutar aldehyde, Schiff bases, chitin, synthesis, IR spectra, modification, , organic compound.*

The unique structure of chitosan aminopolysaccharide and the presence of a positive charge determines its introduction into practice, as well as the expansion of their areas of application. Ideally, chitin is a linear polymer based on N-acetyl glucosamine units. Chitin, poly (β -(1-4)-N-acetyl-D-glucose-2-amine), is a natural polysaccharide of great importance [1]. Chitosan is an aminopolysaccharide consisting of β -(1 \rightarrow 4)-linked D-glucosamine residues, as well as N-acetyl-D-glucosamine.

As a rule, chitosan is isolated from chitin, which is part of the shells of crustaceans, but can also be isolated from chitin of other origins (chitin from mushrooms, crabs, mollusks, insects and others).



**Figure 1. Natural sources of chitosan a) crabs b) mushrooms c) chafer
c) honey bees e) flies**

The method for producing chitosan by the cryogenic method [2] using liquid nitrogen from dead bees is carried out as follows: dried bee dead is pre-crushed to a size of 350 Mesh for 2-3 minutes (cryogenic method), then demineralization is also carried out in a liquid nitrogen

environment of crushed bee dead in 4% hydrochloric acid simultaneously for 30 minutes and left for 2 hours at room temperature, followed by washing with water to pH 7, then the crushed demineralized bee dead is deprotenized at a ratio of T:L = 1:10 in sodium hydroxide solution concentration 1H for 30 minutes at a temperature of 60-70 °C, followed by washing with water to pH 7, then demineralized and deprotenized bee dead meat is deacetylated in a 35% NaOH solution at 90 °C for 60 minutes at a ratio T:L = 1:10 s for the purpose of chitosan synthesis.

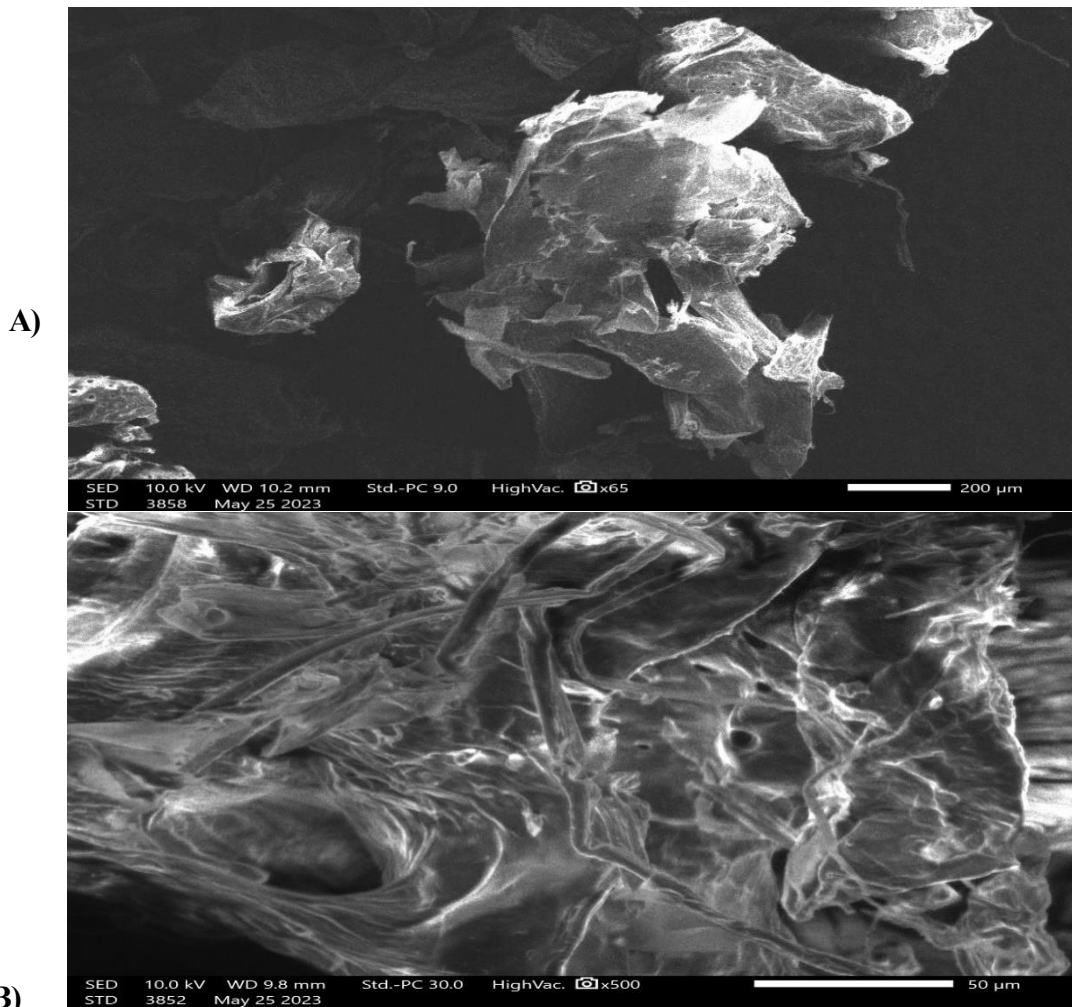
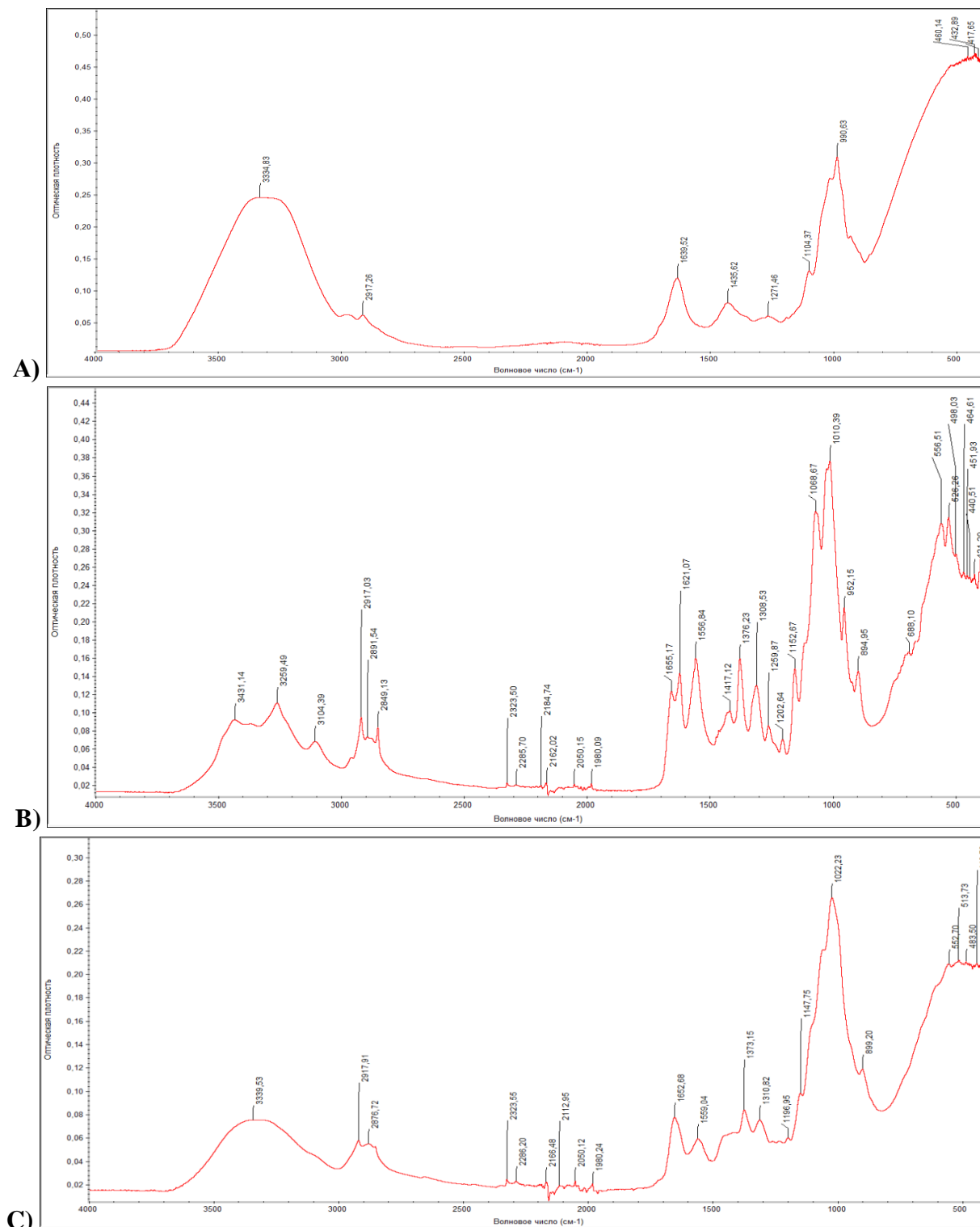


Figure 2. Scanning electron microscopy images of A) chitosan obtained in a liquid nitrogen environment B) chitosan obtained without nitrogen

Scanning electron micrographs of the resulting chitosan in liquid nitrogen are shown in Fig. 2. The figure shows the difference between chitosan obtained in liquid nitrogen, since after cryogenic grinding the chitosan particles are much smaller and it becomes light and airy.

The addition of nucleophilic reagents to the carbon atom of the carbonyl group is one of the fundamental reactions and is of significant interest, since it plays a certain role in chemical reactions and biochemical processes. Schiff bases have a multifactorial effect, exhibiting antioxidant, anti-inflammatory, hepatoprotective, analgesic [3], bactericidal [4–8], antitumor [1, 9], and antiviral [10] activity. Glutaraldehyde - (glutaric dialdehyde, pentandial) is an organic compound, aldehyde with the chemical formula $C_5H_8O_2$. Transparent and colorless liquid, easily soluble in water, irritating to the eyes and lungs. It is used as a tanning agent in leather production, and is also used in the textile industry [11]. In the study, we obtained Schiff bases, that is, based on chitosan and glutaraldehyde.

IR spectroscopic studies were carried out on a Spekord-75UR spectrophotometer in the wavelength range 4000-500 cm⁻¹. The assignment of characteristic absorption bands was interpreted according to the procedure. In the spectra of glutaraldehyde (Fig. 3a) there is an intense stretching vibration band in the range of 1775-1645 cm⁻¹; another band of moderate or low intensity at 2830-2690 cm⁻¹, characteristic only of the spectra of aldehydes, often has the form of a doublet.



**Figure 3. Fourier transform IR spectrum of a) glutaraldehyde
b) Chitosan Apis Mellifera c) Chitosan-glutaraldehyde**

In the IR spectra of glutaraldehyde, the first overtone of the ν C=O absorption bands is observed in the region of 3400 cm⁻¹. High intensity band in the region of 2720 cm⁻¹. There is a

very broad high-intensity band of the bound hydroxyl group ν O-H in the frequency range 1800–1700 cm^{-1} . C-H bonds and groups are less strongly absorbed in the frequency range of 1400 cm^{-1} . Two weak vibrations of the nC-O group were also found in the frequency range of 1010 and 900 cm^{-1} related to alcohol compounds. Apparently, the stretching vibrations of C=O alkyl-CHO bonds in the region of the absorption band 750–400 cm^{-1} are not very informative [12].

The IR spectrum of chitosan (Fig. 3 (b)) shows peaks in the region of 3272 cm^{-1} and 1377–1028 cm^{-1} , which indicate the presence of an NH_2 group. With this absorption, absorption bands appear in the region of 1360–1000 cm^{-1} for all types of amines, caused by the participation of the C–N bond in the skeletal vibrations of the molecule. In the sample of chitin and chitosan, bands with maxima at 1446 cm^{-1} of the bending vibration of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups and 1373 cm^{-1} (inflection) of the bending vibration of the OH bond were also recorded. In the chitosan sample, a broad band of average intensity is observed in the region of 1320–1387 cm^{-1} , corresponding to the vibration of the OH bond. When studying the spectra of the third sample, one can observe the presence of intermolecular hydrogen bonds between chitosan and aldehyde. The results of IR spectroscopic studies, clearly defining the types of chemical bonds, allow us to conclude that the mechanism of interaction of glutaraldehyde with chitosan is valid. Thus, the occurrence of mainly hydrogen bonds between the amine groups of chitosan on the one hand and hydroxyl groups and due to the carbonyl group of glutaraldehyde has been established.

REFERENCES

1. Wu, T. Physicochemical Properties and Bioactivity of Fungal Chitin and Chitosan / T. Wu, S. Zivanovic, F. A. Draughon [et al.] // Journal of Agricultural and Food Chemistry. - 2005. – C. 3888-3894.
2. Ikhtiyarova G.A., Mengliev A.S., Ulashev Sh.M. Selection of chitosan by cryogenic method from bee deaths and synthesis of schiff base based on salicylaldehyde and its use in fabric dyeing // Proceeding X International Conference «Industrial Technologies and Engineering» ICITE – 2023, Volume I. P. 280-284.
3. Меркович Е.Л., Карпуэт М.Л., Бабак В.Г., Ким В.Е., Вихорева Г.Л. / Вискозиметрическое исследование кинетики начальной стадии гелеобразования в растворах хитозана в присутствии глутарового альдегида // Коллоидный журнал. 2001. Т. 63, № 3. С. 383-388.
4. *Glutaraldehyde as a fixative in bioprostheses and drug delivery matrices*// *Biomaterials*. 1996. V 17. P. 471-484.
5. Duatti, A. Synthesis and structure of an amino sugar Schiff base complex of technetium (V) containing salicylaldehyde in an unusual coordination mode // *Inorg Chem*. - 1987. – Vol. 13., № 26. – P. 2182-2186
6. Yang, C. / Enzymatic modification of chitosan by cinnamic acids: Antibacterial activity against *Ralstonia solanacearum* // *International journal of biological macromolecules*. – 2016. – Т. 87. – С. 577-585.
7. Игнатьева П.Е., Жаворонок Е.С. и др. Композиции на основе водных растворов хитозана и глутарового альдегида для эмболизации кровеносных сосудов // Тонкие химические технологии / *Fine Chemical Technologies* 2019 том 14 № 1. С 25-30.

8. Чернышова Е.Б., Тужиков О.И., Невестенко М.А., Березин А.С., Юдин В.Е., Добровольская И.П. Исследование модификации хитозана низкомолекулярными и полимерными альдегидами // Известия ВолгГТУ, серия Химия и технология элементоорганических мономеров и полимерных материалов. 2015. № 7 (164). С. 125–129.
9. Вихорева Г.А., Шаблыкова Е.А., Кильдеева Н.Р. Модификация хитозановых пленок глутаровым альдегидом с целью регулирования их растворимости и набухания // Хим. волокна. 2001. - № 3. - с. 38-42.
10. Кильдеева Н.Р., Перминов П.А., Владимиров Л.В., Новиков В.В., Михайлов С.Н. О механизме реакции глутарового альдегида с хитозаном // Биоорганическая химия. 2009. Т. 35. № 3. С. 397–407.
11. J.Azimov, T.Kodrov, Sh.Shoyimov. Study of the Effect of Aldehydes on Lightfastness and Physical and Mechanical Properties of Karakul Skins. International Journal of Advanced Research in Science, Engineering and Technology Vol .8,Issue 9,September 2021 18232-18236 pp.
12. Ихтиярова Г.А. Изучение взаимодействия аминополисахарида хитозана *Apis Mellifera* с глутаровым альдегидом // Композицион материаллар илмий-техникавий ва амалий журнали. Тошкент-2024. № 1/2024. С. 30-33.