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Oxidized starch/CMC based biofilm: Synthesis and characterization

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Starch-based biopolymers derived from renewable resources offer a sustainable alternative to plastic packaging. One of the main advantages of starch-based biopolymers is their ability to biodegrade, as well as being economical due to the availability and low cost of starch. This makes them more economically attractive for producers and consumers. Although there are still problems with improving their properties. This research centered on developing a biodegradable biofilm from oxidized corn starch and carboxymethylcellulose, using succinic anhydride as a crosslinker. The biofilm's mechanical strength, water absorption, and biodegradability were evaluated and compared to a commercial biopolymer. The biofilm exhibited a strength of 0.78 MPa, absorbed 0.21% water, and had a biodegradability rate of 0.008%. These findings suggest that the biofilm has significant potential for industrial applications, particularly in the biofilms and bioplastics sector. This study contributes to the ongoing global efforts to create sustainable alternatives to conventional plastic packaging, a critical aspect of environmental preservation. The promising characteristics of the synthesized biofilm indicate its potential to significantly influence the future of packaging materials. This research marks a progressive step in the pursuit of sustainable packaging solutions.

Key words: starch, biofilm, cellulose, biodegradable, composite film.
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1 Introduction

Plastic is a product with wide potential, which is obtained from petroleum raw materials. Currently, due to the low mechanical properties and moisture permeability of plastic products, the largest area of consumption is the production of packaging materials. In addition, more than 42% of all plastic materials are used in this industry [1-3]. This has led to the excessive accumulation of household plastic waste and the creation of an island of plastic waste. Because of plastic is chemically and mechanically stable, the process of its decomposition in the environment is very slow. As a result, the soil layer, atmosphere and hydrosphere are in great danger [4, 5]. In this regard, the last ten years, the development and production of biodegradable films based on biopolymers: starch, cellulose, pectin and chitosan has started to develop rapidly. In particular, the scope of starch-based biofilms is increasing everyday [6, 7]. However, due to the special hydrophilicity and mechanical properties of starch, it becomes brittle and therefore requires starch modification. [8, 9].

In the study [10], a starch-chitosan-based packaging for food products with antibacterial properties was developed, which can reduce the amount of Escherichia coli up to 23.8%, and Staphylococcus aureus up to 25.6%. Also, in research [11], a package for storing lamb was developed by modifying the starch-pectin composite with broccoli leaf polyphenols. In addition, by oxidizing starch with a strong oxidation agent, increasing the carboxyl and carbonyl groups in its molecule, it is possible to obtain thermoplastic starch for film production which was reported by researchers [12]. This, in turn, proves that it is possible to modify starch with other monomers.

Based on the research of scientists related to biofilms, it can be seen that the biodegradation, physical and chemical properties of materials obtained by modifying oxidized starch with biomonomers are effective.

In this regard, current study investigated the possibility of obtaining biodegradable biofilm by modifying oxidized corn starch with a cellulose ester derivative in the presence of a crosslinking agent.

2 Materials and methods

2.1 Materials

H_2O_2 (STST 177-88, 30%), starch (STST 32159-2013), carboxyl methylcellulose (STST 5.588-70), succinic anhydride (Sigma Aldrich), glycerin (STST 6259-75) and distilled water. All reagents were used without preliminary purification.

2.2 Oxidation of starch

A suspension of corn starch and distilled water in a ratio of 1:10 g/ml was intensively stirred continuously in a flask with a rotary cooler at a temperature of 80±2°C for 1 hour until a stable solution was formed. The resulting thick solution was cooled to a temperature of 25±2°C. Then, 100 ml of 8% hydrogen peroxide solution was added dropwise to the prepared starch thick solution. The resulting mixture was continuously stirred at room temperature for 24 hours, and the prepared suspension was neutralized with distilled water until pH=7 using a centrifuge. The neutralized suspension was dried to a constant mass in a vacuum cabinet (Grodtorgmash DC-80, Belarus) at a temperature of 50±2°C. The dried mass was ground to obtain a film.

2.3 Starch/carboxyl methylcellulose (CMC) biofilm preparation

In order to develop a biodegradable film, 0.875 g of oxidized starch was weighed into 50 ml of a pre-prepared 5% carboxymethyl cellulose (CMC) solution and continuously stirred in a magnetic stirrer until a homogeneous solution was formed. Further, 0.75 g of succinic anhydride and 7.5 ml of glycerol were added to the prepared solution and stirred for another 30 minutes until a homogeneous mixture was formed. The resulting mixture was poured into a disk-shaped plate and placed in a vacuum cabinet at a temperature of 60±2°C for 16 hours. As a result, a film was obtained Figure 1.

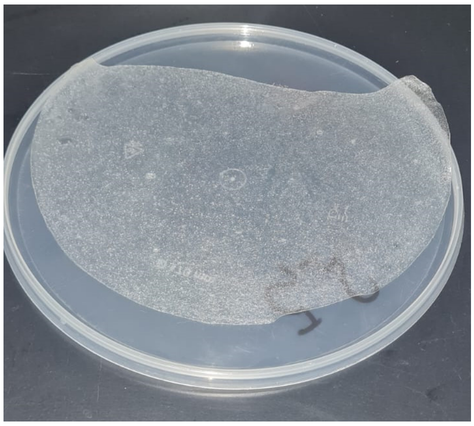

Figure 1 – Obtained biofilm from $Starch_{oxd}$/CMC

2.4 FTIR analysis

The analysis was performed using an FT-801 FTIR spectrometer (Simex, Russia), with a resolution of 1 cm^{-1} at a range of 300-4700 cm^{-1}, at a temperature of 25±10ºC, in accordance with the standard method. An accessory was used to measure attenuated total reflection (ATR) and specular-diffuse reflection (SDR).

2.5 Mechanical Characterization

The mechanical characteristics of the biofilm was studied using a texture analyzer (TA-3000, LabSol, China) with a measured load range of 0.01–60N and a loading speed range of 0.0005–500 mm/min. The data registration was performed automatically using a computer. During the testing of the samples under a load of 0.01 N, the movement speed was 0.1 mm/min. The samples were tested until the maximum tensile force was reached or before the sample became deformed.

2.6 Water absorption and biodegradation properties

The film sample was prepared and dried at 50°C for 24 hours. The dried film was placed in a buffer solution with a pH of 5.5 for 3 days, removed from the water and dried using a filter paper, and its weight was measured with an accuracy of 0.0001 g.

3 Results and disscussion

3.1 FTIR analysis of oxidized starch

Figure 2 shows the result of FTIR analysis of oxidized starch compared to the original starch. In the figure 2a represented spectra region between 3500-

3000 cm^{-1} indicates the presence of OH groups and signal on 1653 cm^{-1} is characterized by the absorption of the C-O bond [13,14]. Corresponding absorption of all CH_2 groups was identified on 2868 cm^{-1}. The absorption at 1147 cm^{-1}, 1078 cm^{-1} and 990 cm^{-1}, respectively, reflects the valence oscillations of the C-O bond, C-O-H and C-O-C groups in the glucose ring. The absorption signals 855 cm^{-1}, 856 cm^{-1} and 867 cm^{-1} indicate a β-glycosidic bond [15,16]. In Figure 2b, absorption of C=O bond in carboxyl and carbonyl groups formed in oxidized starch was observed in the range of 2100-2150 cm^{-1} [17].

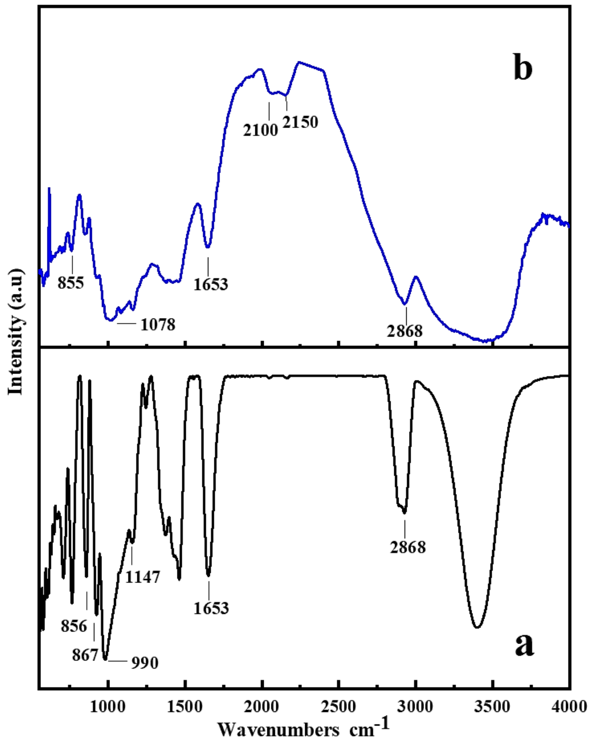

Figure 2 – FTIR spectrum of a-initial starch; b- oxidized starch

3.2 FTIR analysis of biofilm

Figure 3 shows the relative FTIR spectrum of the starch/CMC biofilm with the original monomers. The intensity of the signal can be noticed in the absorption region of 1710 cm^{-1}, characteristic of the carboxyl groups in the molecule of oxidized starch and CMC, is maximally reduced in the spectrum of the biofilm. This may be due to the fact that during the synthesis, the bonding agent succinic anhydride leads to low intensity by cross-linking the carboxyl groups in the monomer molecule [18-20].

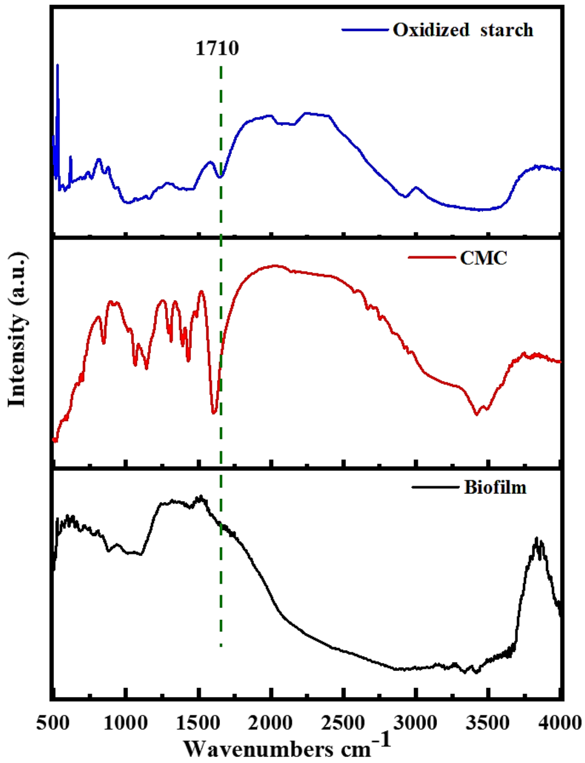

Figure 3 – FTIR spectrum of biofilm $Starch_{oxd}$/CMC

3.3 Mechanical Characterization

During the study, the mechanical properties and water absorption properties of the biofilm were compared with the polyester-based biodegradable commercial product TAPIOPLAST (SMS Corporation, Thailand). The result of studying the mechanical properties of the biofilm is shown in Figure 4. The commercial product TAPIOPLAST has been found to have a mechanical strength of 2.5 MPa. The mechanical strength limit was to be found, of starch/CMC biofilm is equal to 0.78 MPa, that is, 3 times smaller than that of TAPIOPLAST. This is because the main composition of the TAPIOPLAST film can be synthetic polyester in addition to the biodegradable component.

In the studies [21, 22], it was determined that the mechanical strength limits of films based on oat starch and topaca starch are equal to 0.36 and 0.78 MPa. It shows that the result obtained in this study corresponds to the indicators of the previous study.

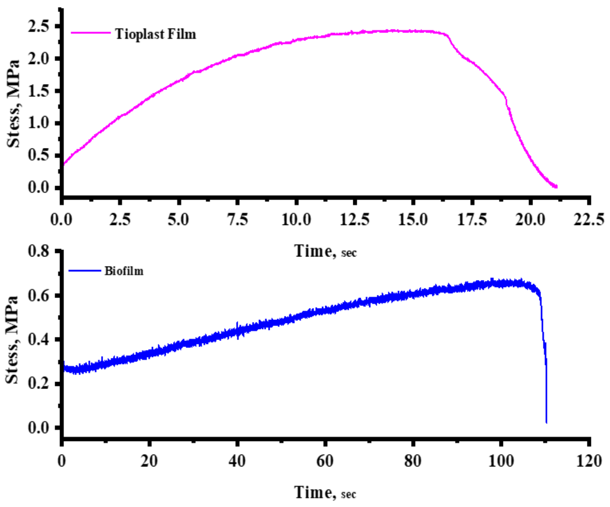

Figure 4 – Plot of mechanical strength of Starch$_{oxd}$/CMC biofilm compared to commercial film

3.4 Water absorption and biodegradation properties

Short-term biodegradability of Starch$_{oxd}$/CMC-based biofilm compared with commercial product TAPIOPLAST (Table 1). Since the pH of the surface layer of the soil is between 5.5 and 6.5, the biodegradation properties of biofilms were studied over a period of 3 days using a weak acid buffer solution with a pH of 5.5 as a soil model. In addition, the property of water absorption in this environment was also determined. According to the obtained results, the degree of water absorption of polyester-based biodegradable commercial product TAPIOPLAST was 0.19%, and the degree of biodegradation was 0.0001%. Starch$_{oxd}$/CMC biofilm had a water absorption degree of 0.21% and a biodegradation degree of 0.008%. The values of the degree of water absorption of both obtained samples were insignificant and showed that the Starch$_{oxd}$/CMC film was exposed to biodegradation for a longer time [23,24].

Table 1 – Starch$_{oxd}$/CMC comparative values of the short-term biodegradation rate of the biofilm based on the commercial product TAPIOPLAST

Sample	Water absorption degree, %	Biodegradability, %
TAPIOPLAST	0,19%	0,0001
Biofilm	0,21%	0,008

4 Conclusions

The chemical structure of the Starch$_{oxd}$/CMC biofilm obtained during the study revealed that the cross-linking agent succinic anhydride binds the carboxyl groups in the starch and CMC molecules. In addition, the biodegradation, mechanical and water-swelling properties of the obtained biofilm were compared with the commercial film TAPIOPLAST. As a result, the mechanical strength limit of Starch$_{oxd}$/CMC biofilm was 0.78 MPa. The degree of water absorption was to be determined in a short period of time was 0.21%, and the degree of biodegradation was equal to 0.008%. The Starch$_{oxd}$/CMC biofilm obtained within the framework of this study has the potential to be used in the development of food packaging, mulching coatings in agriculture, and drug-carrying capsules in pharmaceuticals.

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References

1. Hosseini S.N., Pirsa S., & Farzi J. Biodegradable nano composite film based on modified starch-albumin/MgO; antibacterial, antioxidant and structural properties // Polymer Testing. – 2021. – Vol. 97. – P. 107182. https://doi.org/10.1016/j.polymertesting.2021.107182
2. Sganzerla W.G., Rosa G.B., Ferreira A.L.A., et al. Bioactive food packaging based on starch, citric pectin and functionalized with Acca sellowiana waste by-product: Characterization and application in the postharvest conservation of apple//International Journal of Biological Macromolecules. – 2020. – Vol. 147. – P. 295-303. https://doi.org/10.1016/j.ijbiomac.2020.01.074
3. Resano-Goizueta B.K., Ashokan T.A., & Trezza Padua, G.W. Effect of nano-fillers on tensile properties of biopolymer films // Journal of Polymer Environment. – 2018. – Vol. 26. – P. 3817–3823.
4. Shankar S., & Rhim J-W. Bionanocomposite films for food packaging applications. Reference module in food science. – 2018 https://doi.org/10.1016/B978-0-08-100596-5.21875-1

5. Biduski B., do Evangelho J.A., da Silva F.T., de Mello S.L., Halal E., Takimi A.S., Carreno N.L.V., Dias A.R.G., & da Rossa E. Physicochemical properties of nanocomposite films made from sorghum-oxidized starch and nanoclay. Starch Biosynthesis, Nutrition, and Biomedicine. – 2017. – Vol. 69. – P. 1700079.

6. Bandopadhyay S., Martin-Closas L., Pelacho A. M., & DeBruyn J. M. Biodegradable Plastic Mulch Films: Impacts on Soil Microbial Communities and Ecosystem Functions // Frontiers in Microbiology. – 2018. – Vol. 9. – P. 819. https://doi.org/10.3389/fmicb.2018.00819

7. Wang B., Sui J., Yu B., Yuan C., Guo L., Abd El-Aty A. M., & Cui B. Physicochemical properties and antibacterial activity of corn starch-based films incorporated with Zanthoxylum bungeanum essential oil // Carbohydrate Polymers. – 2021. – Vol. 254. – P. 117314. https://doi.org/10.1016/j.carbpol.2020.117314

8. Kaur P., Alam T., Singh H., Jain J., Singh G., & Broadway A. A. Organic acids modified starch–CMC based biodegradable film: antibacterial activity, morphological, structural, thermal, and crystalline properties // Journal of Pure and Applied Microbiology. – 2023. – Vol. 17(1). – P. 241-257. https://doi.org/10.22207/JPAM.17.1.14

9. Vu H.P.N., & Lumdubwong N. Starch behaviors and mechanical properties of starch blend films with different plasticizers // Carbohydrate Polymers. – 2016. – Vol. 154. – P. 112–120. http://dx.doi.org/10.1016/j.carbpol.2016.08.034

10. Wu L., Lev S., Wei D., Zhang S., Zhang S., Li Z., Liu L., & He T. Structure and properties of starch/chitosan food packaging film containing ultra-low dosage GO with barrier and antibacterial // Food Hydrocolloids. – 2023. – Vol. 137. – P. 108329. https://doi.org/10.1016/j.foodhyd.2022.108329

11. El Halal S.L.M., Colussi R., Deon V.G., Pinto V.Z., Villanova F.A., Carre˜no, N.L.V., Dias A.R.G., & da Rosa Zavarezea E. Films based on oxidized starch and cellulose from barley // Carbohydrate Polymers. – 2015. – Vol. 133. – P. 644–653. http://dx.doi.org/10.1016/j.carbpol.2015.07.024

12. Kaiyrbekov N., Akatan, K., Kabdrakhmanova S., Kuanyshbekov T., Imasheva A., & Battalova A. Modification of nanostarch by citric acid // Physical Sciences and Technology. – 2021. – Vol. 8(1-2). – P. 66-70. https://doi.org/10.26577/phst.2021.v8.i1.09

13. Da Rosa Zavareze E., Pinto V.Z., Klein B., El Halal S.L.M., Elias M.C., Prentice-Hernández C., & Dias A.R.G. Development of oxidised and heat–moisture treated potato starch film // Food Chemistry. – 2012. – Vol. 132. – P. 344–350.

14. Liewchirakorn P., Ngamchuea K. Benign electrolytic modifications of starch: effects on functional groups and physical properties // RSC Advances. – 2023. – Vol. 13. – P. 30040-30051. https://doi.org/10.1039/D3RA06382H

15. Prabhu S.V., Hemalatha P., Tizazu B.Z., & Gosu A. Development of teff-starch based edible film: mechanical and optical properties // IOP Conference Series: Materials Science and Engineering. – 2021. – Vol. 1091. – P. 012050.

16. Subramanian S., Natarajan K. A., & Sathyanarayana D. N. FTIR spectroscopic studies on the adsorption of an oxidized starch on some oxide minerals // Mining, Metallurgy & Exploration. – 1989. – Vol. 6. – P. 152–158. https://doi.org/10.1007/BF03402707

17. Wilpiszewska K. Hydrophilic films based on starch and carboxymethyl starch // Polish Journal of Chemical Technology. – 2019. – Vol. 21(2). – P. 26-30. https://doi.org/10.2478/pjct-2019-0016

18. Vu H. P. N., & Lumdubwong N. Starch behaviors and mechanical properties of starch blend films with different plasticizers // Carbohydrate Polymers. – 2016. – Vol. 154. – P. 112–120.

19. Wang Y., Liu H., Geng F., Yang P., Lü J., Li X. Label-free analysis of biofilm phenotypes by infrared micro- and correlation spectroscopy // Analytical and Bioanalytical Chemistry. – 2023. – Vol. 415. – P. 3515–3523. https://doi.org/10.1007/s00216-023-04741-4

20. Ortega-Toro R., Jimenez A., Talens P., & Chiralt A. Properties of starch-hydroxypropyl methylcellulose based films obtained by compression molding // Carbohydrate Polymers. – 2014. – Vol. 109. – P. 155–165.

21. Saberi B., Thakur R., Vuong Q.V., Chockchaisawasdee S., Golding J.B., Scarlett C. J., & Stathopoulos C.E. Optimization of physical and optical properties of biodegradable edible films based on pea starch and guar gum // Industrial Crops and Products. – 2016. – Vol. 86. – P. 342–352.

22. Żołek-Tryznowska Z., & Kałuża A. The influence of starch origin on the properties of starch films: Packaging Performance // Materials. – 2021. – Vol. 14. – P. 1146.

23. Zainuddin, S., Hasan, S. M. K., Loeven, D., Hosur, M. Mechanical, fire retardant, water absorption and soil biodegradation properties of poly (3-hydroxy-butyrate-co-3-valerate) nanofilms // Journal of Polymers and the Environment. – 2019. – Vol. 27. – P. 2292–2304. https://doi.org/10.1007/s10924-019-01517-9

24. Santos Cotta A. A. R., Ferreira L. F., Borges S. V., Nascimento B. D. S., Dias M. V. Biodegradation, water sorption isotherms and thermodynamic properties of extruded packaging composed of cassava starch with tomato peel // Journal of Polymers and the Environment. – 2023. https://doi.org/10.1007/s10924-023-03094-4

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