

OXIDATION OF CORN STARCH WITH PERIODIC ACID WITH PURPOSE OF USE IT AS HIGHER ADHESIVE COMPONENT

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Abstract: *In this work, chemical modification of starch using periodic acid was carried out to oxidize it. Samples of the original and oxidized starch were analyzed using chemical analysis, spectrophotometry, thermogravimetry, and IR spectroscopy. Morphological changes were studied using scanning electron microscopy. Thus, in this part of the investigation, samples containing aldehyde groups in the macromolecular chain of starch were synthesized using the periodate oxidation reaction.*

Keywords: *starch, oxidation, periodate, chemical modification, morphology, specters, dialdehyde*

Introduction.

Starch is regarded as one of the most valuable and cost-effective biopolymers, widely available for industrial applications. From natural starch, various commercial products such as thickeners, stabilizers, emulsifiers, bioethanol, and biodegradable plastics can be obtained. In papermaking, starch is extensively utilized as a sizing material to enhance the paper's mechanical strength and film-forming abilities by binding fibers, pigments, and fillers within the paper web structure [1–5]. Numerous studies have demonstrated that incorporating starch can significantly influence the mechanical, thermal, structural, morphological, and barrier features of different rubber-based films [5, 6]. Oxidation of starch is considered an efficient modification technique for generating value-added materials with wide practical applications in both food and technological industries. Oxidized starches belong to the class of degraded or chemically modified polysaccharides and are distinguished from their

native counterparts by reduced molecular mass and the introduction of additional functional groups such as carbonyl and carboxyl within the monomer units [3, 6].

Among the oxidized starch derivatives, starch dialdehyde (SDA) is one of the most promising and versatile compounds, drawing attention for its role in developing biodegradable packaging materials, super absorbents, and heavy-metal sorbents for wastewater treatment. Recent research has revealed that SDA can form stable coordination complexes with metal ions, allowing it to function as an eco-friendly and biodegradable adsorbent for removing toxic metals from industrial effluents and contaminated soils [7–8]. The synthesis of SDA can be carried out via chemical oxidation employing agents such as sodium hypochlorite (NaClO), hydrogen peroxide (H_2O_2), periodic acid (KIO_4), or hydrochloric acid (HCl). Among these, periodate oxidation is particularly selective in cleaving vicinal diols, leading to the formation of two aldehyde groups on each glucose unit (Fig. 1), which gives the product its distinct physicochemical properties [9]. Nonetheless, the application of stoichiometric oxidants in such processes generates considerable quantities of inorganic residues, posing environmental concerns inconsistent with the principles of green chemistry [10].

Materials and Methods

During the oxidation of polysaccharides, depending on the nature of the selected oxidant, derivatives containing functional fragments such as carboxyl, aldehyde, and ketone in the polymer chain can be obtained. For example, one of the widespread oxidants of polysaccharides is periodate. Typically, as a result of periodate oxidation, the chemical bond between the C_2 and C_3 carbon atoms is broken, forming two aldehyde groups in the monomer ring. These polysaccharide derivatives are called dialdehydes and are widely used in industry to obtain various composite materials [11-12]. It is worth noting that the periodate oxidation process can be carried out in a homogeneous or heterogeneous environment, depending on the solubility of polysaccharides in water. Dialdehyde polysaccharides are easily

amenable to various chemical modifications due to their high reactivity. There is also the possibility of modifying their chemical structure to create new functional materials [13].

After periodate oxidation, polysaccharides are easily reacted with various nucleophilic compounds due to the electrophilic nature of the aldehyde groups present in the monomer residue. For example, periodate-oxidized cellulose, pectin, dextran and other polysaccharides are currently widely used in practice as polymer carriers for low-molecular compounds [14-16].

Results of Studies

In this work a chemical modification of starch using periodic acid was carried out to oxidize it. This reaction can be represented by the following scheme:

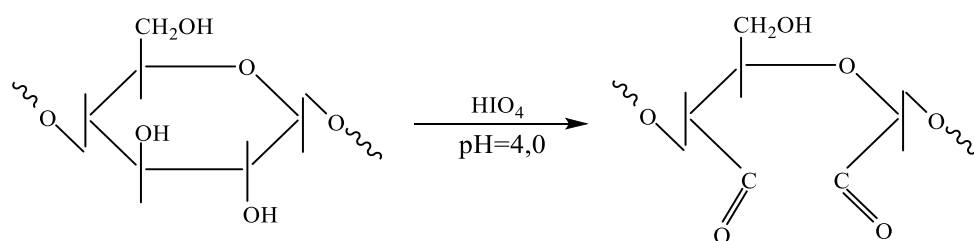


Table 1 shows the effect of time on the degree of periodate oxidation of starch. As can be seen from the table, when the periodate oxidation time was increased from 1 to 8 hours, the amount of aldehyde groups in the starch increased. Increasing the oxidation time from 8 to 12 hours led to a decrease in the amount of aldehyde groups in the starch [17]. In turn, the decrease in aldehyde groups indicates that they are oxidized to -COOH functional groups under the influence of IO_4^- ions. At the same time, increasing the periodate oxidation time leads to a decrease in the yield of reaction products due to the hydrolysis process.

Table 1

Effect of periodate oxidation time on the degree of starch oxidation

(t=20 ° C; starch:HIO₄ =1:1)

No.	Oxidation time, hours	Oxidation level	-CHO, %	Yield, %
1	1	8	2.9	95.2
3	2	14	5.0	91.5
4	3	25	9.0	85.0
5	5	27	9.7	81.6
6	8	30	10.8	78.2
7	10	28	10.0	74.5
8	12	26	9.4	70.0

In order to determine the effect of periodate concentration on the degree of starch oxidation, we also carried out the reaction in the molar ratio starch:HIO₄=1:2. As can be seen from Table 2, with an increase in the molar ratio of the oxidizing agent, the formation of aldehydes in the starch composition accelerates [18-20]. At the same time, the chemical transformation of the formed -CHO groups to -COOH also accelerates, and the resulting products undergo more rapid hydrolysis.

Table 2

Effect of periodate oxidation time on the degree of starch oxidation

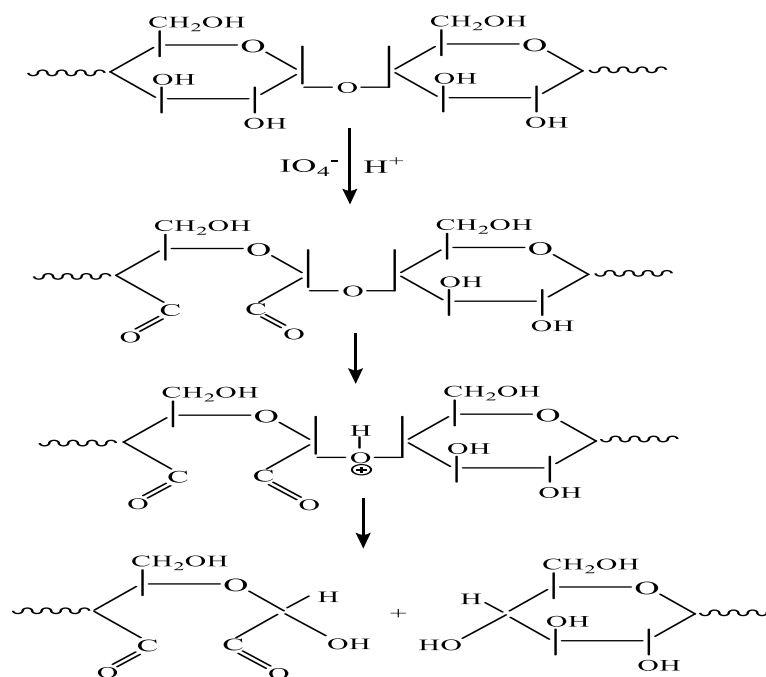
(t=20 ° C; starch:HIO₄ =1:2)

No.	Oxidation time, hours	Oxidation level	-CHO, %	Yield, %
1	1	12	4.3	93.7
2	1.5	18	6.5	88.0
3	2	23	8.3	83.3
4	2.5	25	9.0	79.4
5	3	21	7.6	75.0

We assume that as a result of periodate oxidation of starch, the C₂ and C₃ chemical bonds are broken, forming two aldehyde groups in one monomer residue.

The resulting dialdehyde starch is resistant to acidic environments and begins to be destroyed through the C₁ and C₄ chemical bonds. As the number of aldehyde groups in the macromolecule increases, the resistance of the polymer chain to acidic environments begins to decrease [21-23].

The chemical hydrolysis of a starch macromolecule as a result of the periodate oxidation reaction can be represented by the following scheme:



Analysis and Discussion

Analysis of the IR spectrum of dialdehyde starch revealed the presence of absorptions characteristic of primary -OH groups in the range of 3230-3376 cm^{-1} . The absorption at 1160 cm^{-1} belongs to the -C-O-C- bond. It was proven that the absorption characteristic of aldehyde groups is present in the region of 1725 cm^{-1} .

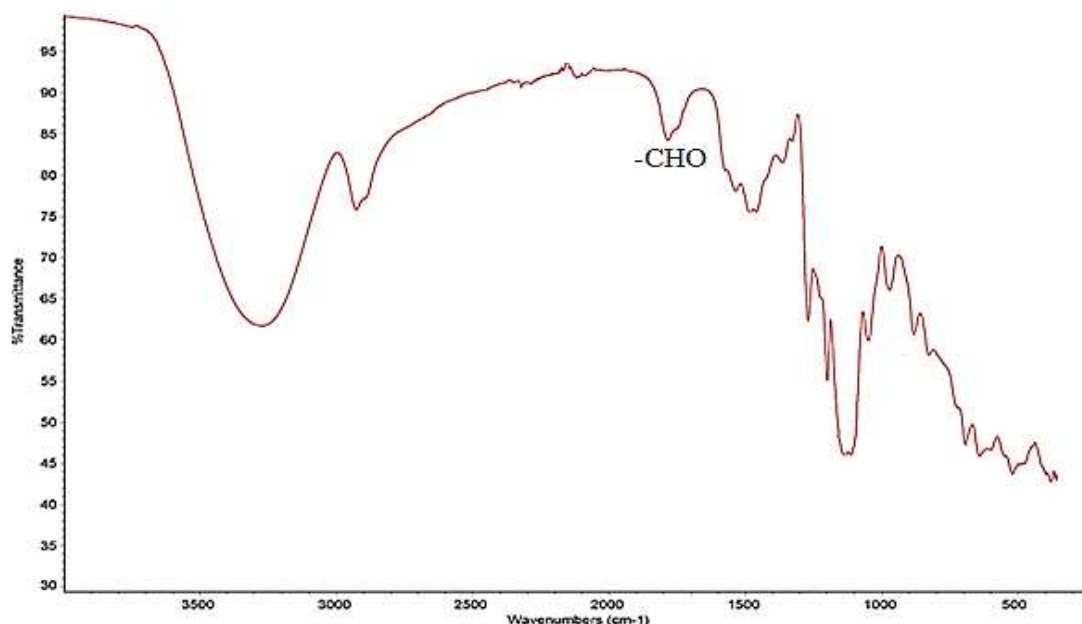


Figure 1. IR spectrum of dialdehyde starch (-CHO content 10.8%)

As can be seen from table 3, the molecular weight of starch decreases as a result of periodate oxidation. This, in turn, leads to an increase in the polydispersity index of the destruction products formed as a result of the hydrolysis of the starch polymer chain from 2.75 to 3.38 and can affect the adhesive properties of the sizing product.

Table 3

Molecular parameters of dialdehyde starch

No.	-CH O content, %	Mw, Da	Yes, yes.	Polydispersity coefficient
1	2.9	118 5 0 0	43 0 0 0	2, 75
2	5.0	11 23 0 0	376 0 0	2.98
3	9.0	9 0 0 0 0	29 7 0 0	3, 10
4	9.7	882 0 0	27 3 0 0	3, 23
5	10.8	8 50 0 0	251 0 0	3.38

Electron microscopy analysis of the synthesized dialdehyde starch derivatives revealed dramatic morphological changes in the molecular structure. In particular, as the amount of aldehyde groups in the starch increases, the degree of surface tension on the starch increases and the shape of the particles changes.

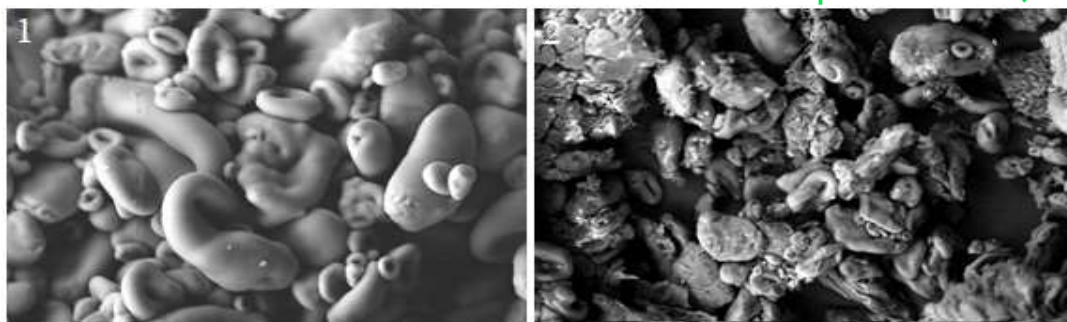


Fig.2. Dialdehyde with aldehyde group content of 5.0 and 10.8%. electron microscope images of starch samples

the $\pi \rightarrow \pi^*$ transition of C=O bonds in -CHO groups occurs in the region of 230-250 nm, the region of 254-270 nm corresponds to the absorption of -CHO groups introduced

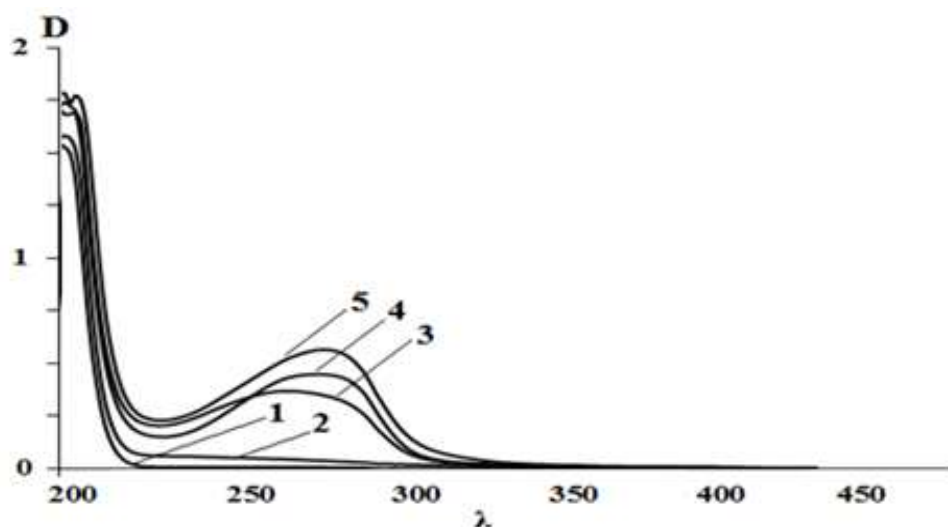


Fig. 3. UV spectra of starch (1) and oxidized starch samples with aldehyde contents of 2.9% (2), 5.0% (3), 9.0% (4) and 10.8% (5)

It is known that starch macromolecules form many hydrogen bonds due to the interaction of hydroxyl groups [24]. This, in turn, ensures that starch exhibits the necessary physical and mechanical properties. In starch oxidized with periodate, the initial properties may change due to the reduction of hydroxyl groups. One of these

is its temperature stability. In order to study the thermal stability of the synthesized samples, we performed thermal analysis.

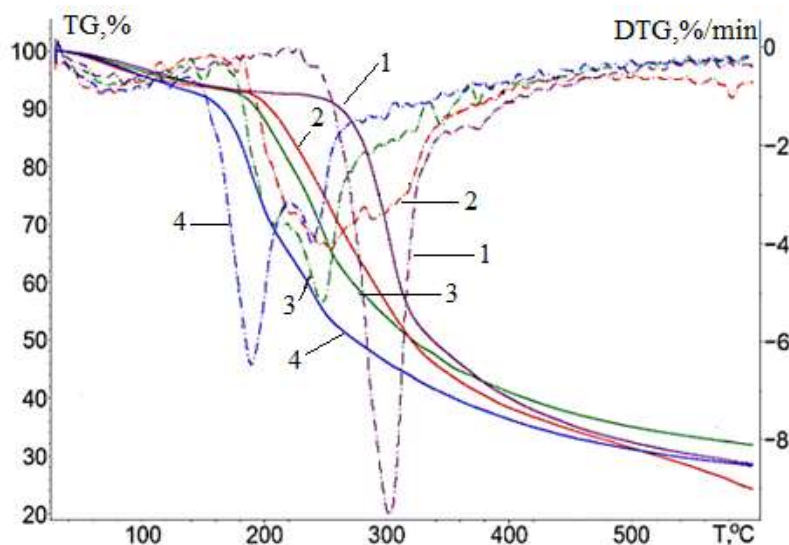


Figure 4 . Thermal analysis of starch (1) and oxidized starch samples with aldehyde contents of 2.9 % (2), 5.0 % (3), 9.0 % (4) and 10.8 %

The results of thermal analysis of starch and periodate-oxidized starch samples are shown in Figure 4. It can be seen from this figure that the introduction of aldehyde groups into the starch macromolecule dramatically changes its thermal stability. According to the results of the thermal analysis, the tested samples undergo thermal destruction in three stages: the first stage corresponds to the range of 64-168°C. In this case, water adsorbed on the polysaccharide macromolecule begins to be released, in the second stage, the starch polymer chain begins to be destroyed in the range of 168-385°C. Finally, in the third stage, the polysaccharide carbonization process ends at 385-590°C. From the results of the thermal analysis, it is worth noting that the weight loss of all samples in the second stage is approximately 50-52%. From the DTG curves it can be seen that the thermal destruction of the dialdehyde starch samples consists of two parts ($t=187-216^{\circ}\text{C}$ and $t=216-230^{\circ}\text{C}$). In contrast, the thermal destruction of the starch polymer chain occurs at $t=295^{\circ}\text{C}$. It can be seen from the figure that the carbonization temperature of the oxidized starch derivatives corresponds to a lower thermal range than that of starch.

Conclusion.

Thus, in this part of the investigation, samples containing aldehyde groups in the macromolecular chain of starch were synthesized using the periodate oxidation reaction. The effect of the molar ratio of HIO_4 and the reaction time on the oxidation degree of the synthesized dialdehyde starch samples was determined. The chemical structure, morphology, molecular parameters and thermal stability of the dialdehyde starch samples obtained as a result of the periodate oxidation reaction were studied.

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