Section 2. Chemistry

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INVESTIGATION OF THE STRUCTURE OF DIALDEHYDE POLYSACCHARIDES WITH VARIOUS DEGREES OF OXIDATION

Abstract. Chemical modification of starch and cellulose was carried out using the periodate oxidation reaction. The structure of oxidized polysaccharides with different aldehyde group contents was studied by titrimetric analysis, X-ray diffraction analysis, and electron microscopy. According to the X-ray diffraction analysis data, amorphization of the structure of polysaccharides occurs in the process of periodate oxidation. Electron microscopy substantiated that as aldehyde groups grow in the macromolecular chain of starch and cellulose, there is a significant change in the morphology of polysaccharides.

Keywords: polysaccharides, starch, cellulose, periodate oxidation, structure, morphology.

Introduction. Due to their unique physical and chemical properties, biocompatibility, and high availability, polysaccharides, as well as their various derivatives, find a variety of practical applications. To date, to obtain new derivatives of polysaccharides with valuable properties, preference is given to the preliminary modification of the macromolecular chain of biopolymers, in which alcohol groups are replaced by more reactive groups. In turn, the presence of new functional groups in the main macrochain of natural polymers makes it possible to synthesize derivatives of polysaccharides [1–3]. For example, dialdehyde derivatives of polysaccharides are of great interest as intermediates. They can be used for various chemical transformations involving electrophilic aldehyde groups [4–6]. The synthesis of aldehyde-containing polysaccharide derivatives can be carried out in several ways, the most common of which is the periodate oxidation reaction [7; 8]. The formation of -CHO groups in the monosaccharide units of polysaccharides occurs as a result of the nucleophilic attack of oxygen atoms of IO_4^- ions at the vicinal hydroxyl groups, usually located at C_2 and C_3, contributing to the rupture of -C–C- and leading to the formation of two aldehydes simultaneously. Depending on the reaction conditions and the structure of the oxidized polysaccharide, the rate-limiting step can be the formation of a cyclic intermediate or its decomposition [9].

Usually, the periodate oxidation reaction is carried out at a temperature not higher than room temperature, since with an increase in temperature, reoxidation of -CHO to -COOH is observed. The duration of the reaction for each polysaccharide may be different from several minutes to several days and mainly depends on the physicochemical characteristics of the initial biopolymers. During the periodate oxidation of polysaccharides under heterogeneous conditions, products are obtained that differ greatly in supramolecular and morphological structure.

Since there is practically no information in the literature devoted to the direct observation of the structural features of dialdehyde polysaccharides synthesized under heterogeneous conditions, we set the task of studying the nature of changes in the structure of starch and cellulose after their chemical modification by periodate oxidation. The availability of such data will allow a deeper understanding of the relationship between the structure and physicochemical properties of oxidized polysaccharide derivatives.

Materials and methods. The following were used in the work: Sodium periodate (AR) was obtained from the GuangFu of Tianjin Fine Chemical Industry Research Institute; cotton cellulose (CC) with a degree of polymerization of 1400 and a molecular weight of 226.8 kDa; potato starch was purchased from Potato Industrial Enterprise "Nowamyl" S.A., Nowogard, Poland.

Periodate oxidation of starch and CC. Starch was modified as follows: 0.02 mol of dried starch was placed in a 500 ml dark glass flask, and 200 ml of acetate buffer pH 4.25 and 0.2 N $NaIO_4$ solution were added at a molar ratio of starch: IO_4^- = 1:1.5. The reaction of periodate oxidation of starch lasted 1–8 hours at t =20 °C. The target products of the periodate oxidation reaction were considered to be the insoluble fraction of modified starch. The obtained samples of starch dialdehyde (DAS) were filtered on a Shotta filter and successively washed with 0.5–1 L of water with the addition of a hydrochloric acid solution to pH 1, then with 1 L of acetone/water, and finally with 0.2–0.25 L of acetone until a negative reaction to IO_4^- and IO_3^- (control by reaction with a solution of silver nitrate). The reaction products were dried in the dark under a vacuum over P_2O_5. The degree of oxidation of the samples was calculated by back iodometric titration [10].

Periodic oxidation and purification of CC were carried out similarly to starch modification. The duration of cellulose oxidation was 1–7 days. The obtained samples of cellulose dialdehyde (DAC) after completion of oxidation were filtered on a linen filter, dried in the dark under vacuum over P_2O_5, and analyzed.

Comparative X-ray diffraction analysis of the initial polysaccharides, DAS, and DAC samples with different oxidation states was carried out on an XRD-6100 powder diffractometer (Shimadzu, Japan). The morphological structure of the samples was studied by scanning electron microscopy (SEM). To obtain electronic images, the presented samples were covered with a 15 mm thick carbon layer in a vacuum using a Q 150 RES device (QUORUM, USA) and then analyzed using an EVOMA10 scanning electron microscope (Zeiss, Germany).

Results and discussions. In the chemical modification of starch and CC with sodium periodate, oxidation occurs under heterogeneous conditions.

Table 1.– Influence of the reaction time on the degree of oxidation and the yield of DAS (starch: IO_4^- =1:1.5; t=20 °C; pH 4.25)

Duration of starch oxidation, hour	Iodine number	*Degree of starch oxidation, mol%	Content of aldehyde groups,%	The yield of DAS from the initial mass of starch,%
1	31.4	12	4.3	92.6
3	93.5	36	12.9	90.0
5	116.7	45	16.2	85.4
8	156.0	60	21.6	82.5

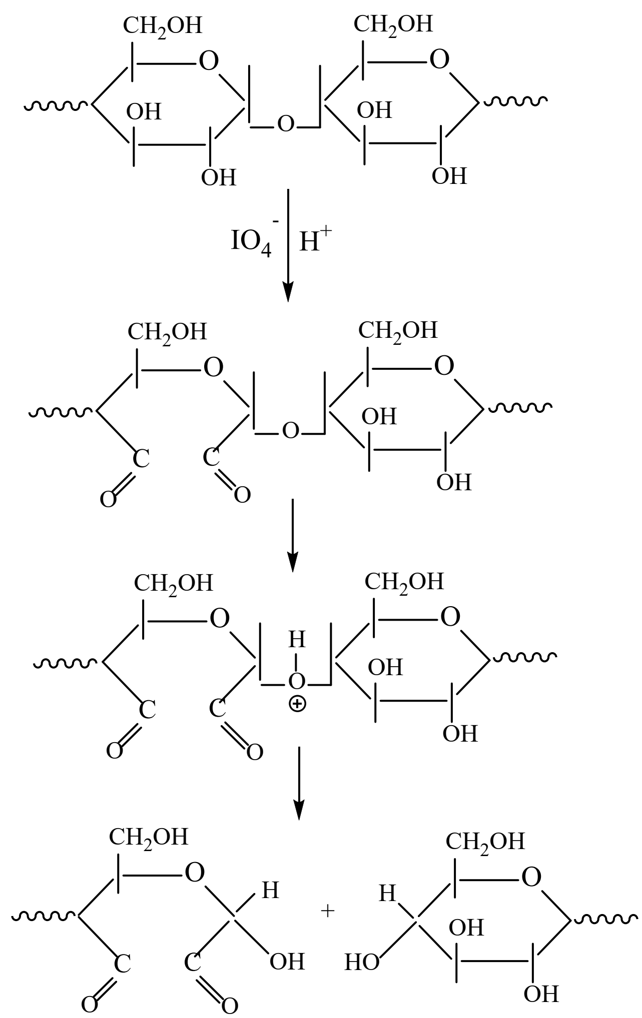
** The degree of oxidation – the number of oxidized units for every 100 units of the polysaccharide*

Table 2.– Influence of the reaction time on the degree of oxidation and the yield of DAC (starch: IO_4^- =1:1.5; t=20 °C; pH 4.25)

Duration of CC oxidation, days	Iodine number	*Degree of CC oxidation, mol%	Content of aldehyde groups,%	Yield of DAC from the initial mass of CC,%
1	42.0	16	5.8	98.2
2	98.7	38	13.7	97.6
3	131.2	50	18.0	94.5
5	175.8	67	24.2	92.0

Therefore, the total rate of this reaction depends on the rate of penetration of the reagent from the external environment into the accessible regions of polysaccharide macromolecules. During the oxidation of polysaccharides, it was revealed that each is characterized by a different rate of oxidation. The different kinetics of the periodate oxidation of polysaccharides are associated with their supramolecular structure and physicochemical properties. Tables 1 and 2 present comparative data on the effect of periodate oxidation time on the content of aldehyde groups and the yield of reaction products.

The data presented in (Tables 1 and 2) show that with an increase in the time of periodate oxidation, a regular increase in the number of aldehyde groups in the composition of the reaction products occurs. However, along with an increase in the degree of oxidation of polysaccharides, a decrease in the yield of DAS and DAC was observed. This is explained by the fact that during the modification of starch and CC in the presence of IO_4^- in an acidic medium, polysaccharide macromolecules are hydrolyzed according to the following scheme:



The results of X-ray diffraction analysis indicate the occurrence of the reaction of periodic oxidation in a heterogeneous medium. Figures 1 and 2 show that with an increase in the number of aldehyde groups in the modified starch and CC, there is a gradual disappearance of crystalline regions in the original polysaccharides, which is caused by the oxidation of -OH groups involved in the formation of inter- and intramolecular hydrogen bonds. On X-ray patterns of DAS and DAC, a smoothing of the peak is observed in the range of angles from 15 to 25°.

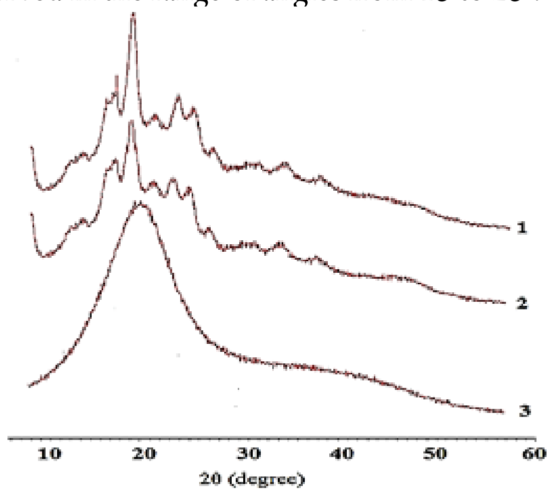


Figure 1. X-ray patterns of starch (1) and DAS with oxidation states of 12 mol% (2) and 60 mol%

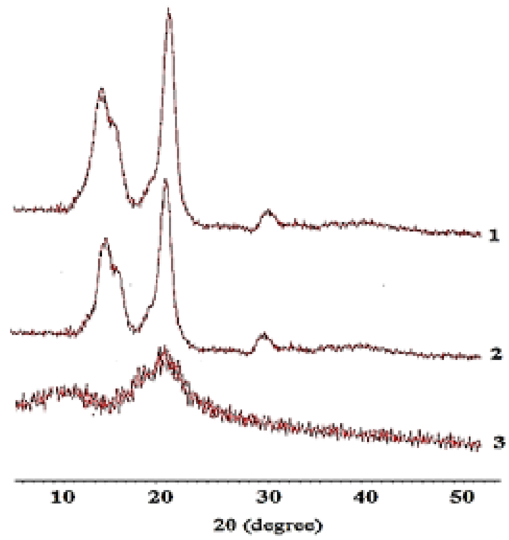


Figure 2. X-ray patterns of CC (1) and DAC with oxidation states of 16 mol% (2) and 82 mol%

The resulting DAS with different degrees of oxidation were studied by SEM (Fig. 3). It was found that after periodate oxidation, DAS samples with different aldehyde group contents consist of inhomogeneous particles differing in shape. At the same time, with an increase in the degree of oxidation of the modified starch, pores and microcracks expanded, and the shape and geometry of the particles changed.

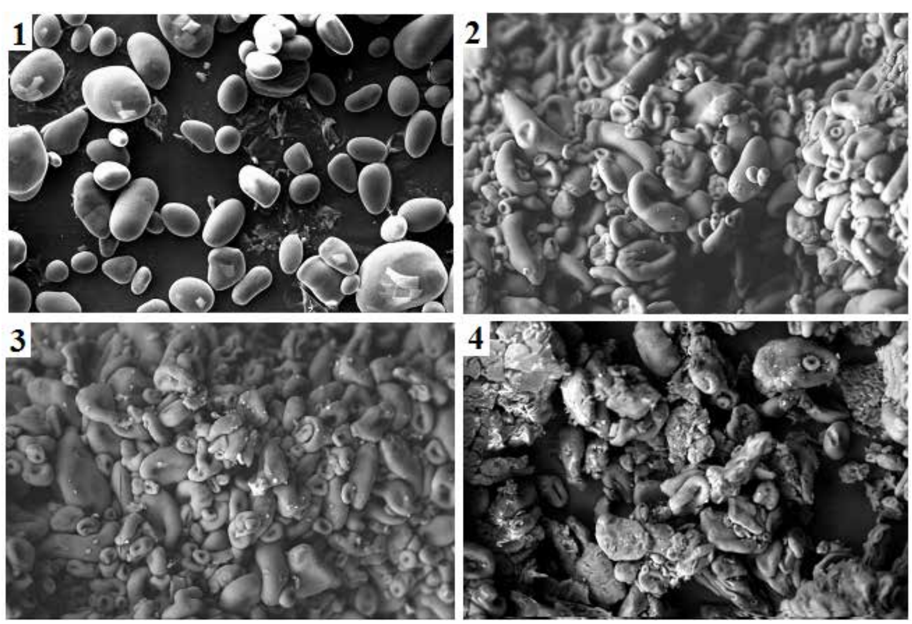


Figure 3. SEM images of (1) starch and DAS samples with (2) 12, (3) 36, and (4) 60 mol% oxidation states

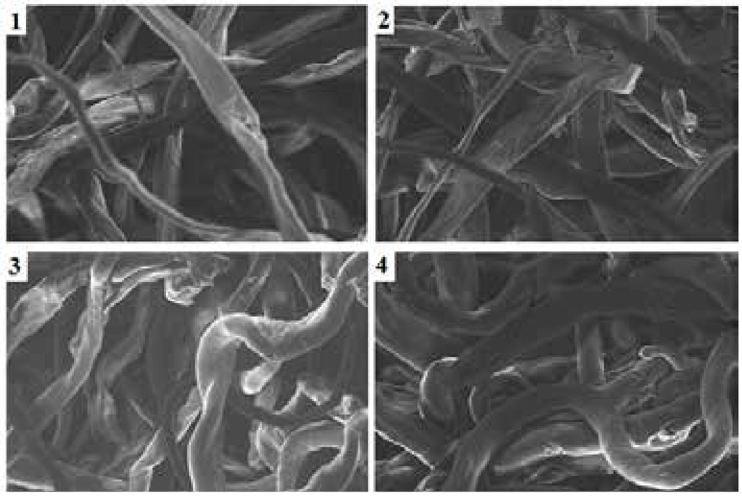


Figure 4. SEM images of (1) CC and DAC samples with (2) 16, (3) 50, and (4) 82 mol% oxidation states

The SEM images (Fig. 4) show that the original cellulose is characterized by straightened and mostly crimped fibers. After the periodate oxidation of CC under heterogeneous conditions, the initial state of the fibers begins to change and is characterized by the formation of loose areas. These changes directly correlate with the degree of oxidation of the resulting DAC samples.

Conclusion. The studies performed have shown that the inclusion of aldehyde groups in the polymer molecules of starch and cellulose leads to a change in the structure of the initial polysaccharides. With an increase in the degree of oxidation of polysaccharides, their amorphization increases and profound changes are observed in the morphology of the studied samples.

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