

Oxidizing Effect of Corn Starch by Oxidizing with Hydrogen Peroxide Purpose Obtaining its Basis Adhesive Materials

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Abstract. Currently, native starch as a binder and sizing component is used extremely rarely due to its inherent disadvantages. It has been replaced everywhere with modified starches of various kinds. Studies have shown that polyelectrolyte flocculants can be created on the basis of starch if ionizable groups are introduced into the macromolecules of amylose and amylopectin. At the same time, it was found that the treatment of starch with oxidizing agents (of various natures and activities) can significantly improve the functional properties of native starch when gluing, used for surface sizing, and as a binder for corrugated cardboard. In this work, also obtained oxidized starch in order to create an adhesive binder on its basis, and only local raw materials were used. It is shown that this method makes it possible to regulate the number of functional groups (oxidizing effect - OE) in oxidized starch and its paste viscosity within a wide range. This is achieved by changing the molar ratio of the catalyst and oxidizer. During the oxidation process, it is possible to vary the concentration ratios of the oxidizer, catalyst, and conditions. Using FeSO₄ as a catalyzer, the oxidized starch pastes show a less pronounced pseudoplasticity and are characterized by reduced viscosity. The analysis showed that during the oxidation of corn starch with hydrogen peroxide, changes in the supramolecular structure of starch are insignificant: a certain repeated decrease in the level of crystallinity takes place, which leads to a decrease in the gelatinization temperature and also the viscosity of starch pastes.

1. Introduction

It is known that surface sizing requires starch, which has a reduced viscosity in comparison with natural, high stability, and a high degree of stickiness. This is important to ensure that the starch systems in the sizing process are large enough and good in terms of performance and stability [1, 2]. For starch, it is customary to use the term dispersion rather than solution since most of the modified starches do not form true solutions after cooking in water due to incomplete solubility; therefore, it is customary to use the more general term “dispersion” for both modified and natural starches [3, 4].

Today, in production, when obtaining modified starches suitable as a component of adhesives for the paper and cardboard industries, two technologies are most widely used: 1) starch oxidation; 2) enzymatic hydrolysis [5]. The technology of starch oxidation is based on the process of treating a starch system or paste with oxidizing agents (hypochlorite or peroxide) [6]. The wide spread use of sodium hypochlorite is due to its high efficiency. However, the oxidation process produces toxic by products that pollute the environment. Although oxidized starch prepared by hydrogen peroxide has already been investigated, most researchers [7] focus on the preparation of oxidized starch with a low degree of oxidation, usually below 10%. However, the cost of oxidants is very high, and the decomposed reaction products would pollute the environment. Based on oxidized maize starch (OMS) with good hydrophilicity, was prepared and OMS-based hydrogels by HE-3DP (3D-OMS) were constructed [8].

During the oxidation reaction, two fundamentally important processes take place: a decrease in the molar mass of polysaccharide due to the separation of glycosidic bonds, and the formation of oxidized groups from the hydroxyl groups of starch-carboxyl and carbonyl. With environmental concern as a priority, the oxidant hydrogen peroxide has drawn researchers' great interest because of its low cost and green water decomposition product [9]. Generally, an accessible and inexpensive transition metal catalyst is added so as to speed up the reaction.

In works [10, 11] it is proposed to use ferrous tetrasulfophthalocyanine as an alternative to ferrous sulfate in the preparation of starch oxidized with hydrogen peroxide. However, when using this compound, it is possible to synthesize more than 12 functional groups per 100 glucose units. The disadvantage of this method is also the impossibility of selectively producing of modified starches with the given number of these groups. A scheme of oxidation with H_2O_2 is indicated in figure 1 below.

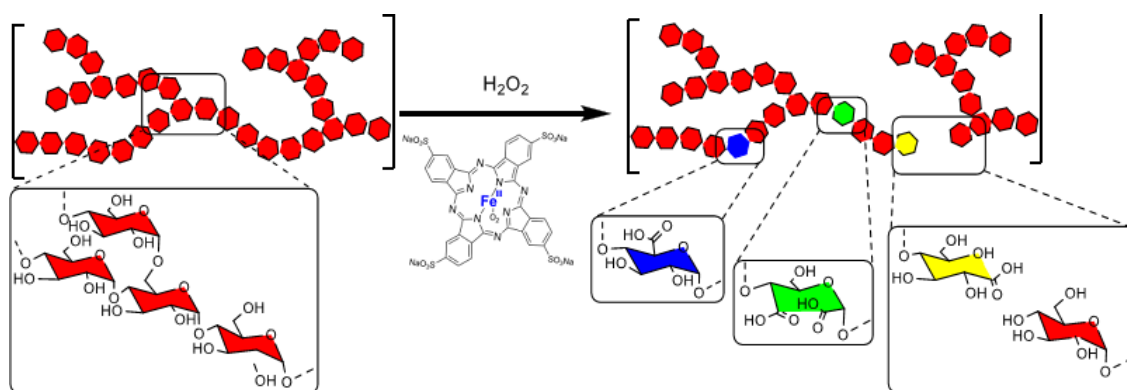


Fig. 1. Scheme of selective oxidation of starch with H_2O_2 in the catalyst of iron complexes.

A decrease in molal mass will result in a decrease in the viscosity of the modified starch system. As a result of the formation of functional groups, the solubility and stability of starch pastes increase. This is due to the fact that these groups in the macromolecule interact better with water than hydroxyl groups (of which some are substituted), which increases the effect of the interaction of amylose units with hydrates, increases its solubility, and reduces the rate of reverse degradation the formation of crystallites and hydrogels [12, 13]. The course of processing is realized as well as the presence of a low temperature, a further increase in the temperature of starch paste formation (in some cases up to $60^\circ C$), which usually occurs in starch factories, thus, as well as the presence of a high temperature ($120-140^\circ C$), the presence of such functions in reactor furnaces.

Since solid starch granules do not interact with solid catalyst particles, the starch needs to be gelatinized before oxidation [14]. Starch gelatinization is achieved in twin screw extruders or jet cookers, where the granules are broken and solubilized by a combination of shear stress and temperature [15]. The goal is to simplify the well-known technique by changing the temperature as well as the amount of catalyst and oxidizing agent to obtain oxidized starch, on the basis of which it would be possible to create adhesive compositions for corrugated cardboard. For this purpose used local raw materials and reagents that are commercially produced and available.

Highlights and Innovation

Oxidized starches with high OE values were prepared using $FeSO_4$ and H_2O_2 , respectively, as a catalysts and oxidants. The oxidation time was reduced to 2 hours when 0.35% H_2O_2 was added. The oxidation reduced the intrinsic viscosity and crystallinity of starch. The transmittance in the IR spectra of the oxidized starch solution increased when temperature and OE were enhanced.

Nevertheless, it should be pointed out that an experimental investigation is very important in understanding the origin of the characteristic variation so as to conclude the regular reasons. Unfortunately, to the best of knowledge, no theoretical study has reported the oxidized derivatives with different properties so far. Thus, this paper would complete a detailed investigation to analyze the properties of oxidized modified starch, aiming at the origin and differences in structural stability and shearing viscosity. Note that investigation should be very reasonable for this studied system

because of the existence of some small glucopyranose residues derived from the partial breakage of starch molecular chains by oxidant modification.

2. Materials and Methods

2.1. Raw materials and reagents. Native corn starch was supplied from Golden Corn Starch Company in Tashkent, Republic of Uzbekistan. Hydrogen peroxide (H_2O_2 , 34.5–36.5%) analytical grade (99.5%) was purchased from Uzbekistan Hydrogen Peroxide JV LLC (Navoi, Uzbekistan). Ferrous sulfate (2) is obtained by purifying the technical crystallization water of ferrous vitriol (TS 07621395-338:2015) produced by SE "Navoi Mining and Metallurgical Combine" (Navoi, Uzbekistan). Sodium hydroxide and hydrochloric acid are products of JSC "Navoiyazot" (Navoi, Uzbekistan). Other chemicals were used as received without further purification in the laboratory.

2.2. Oxidation process and research methods. The reaction of corn starch modification with hydrogen peroxide was carried out using a ferrous (2) sulfate catalyst. The concentration of functional groups was studied by a known method [16]. Viscosity measurements (η) of aqueous oxidized starch pastes were carried out on a rotational viscometer, Thermo Scientific HAAKE Viscotester 2 Plus (Germany) (γ). X-ray diffraction patterns (XRD) for the powders were obtained using XRD-6100 equipment from Shimadzu (Japan). The study of infrared spectroscopy was carried out on the instrument Affinity-1S Fourier Transform Infrared Spectrophotometer (Shimadzu, Japan).

3. Results and Discussion

3.1. Oxidation reaction kinetics

The reaction of the polysaccharide and H_2O_2 mainly takes place with a catalyst (Fe^{2+} , Cu^{2+} , etc.), and in no way to the radicalion direction, when a redox potential mixture is formed in this medium between Fe^{2+} and H_2O_2 , and after that it results is: $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}\cdot$ with the formation of hydroxyl radicals occurring [17]. However, the schematic mechanism is described as shown in Figure 2 [18]:

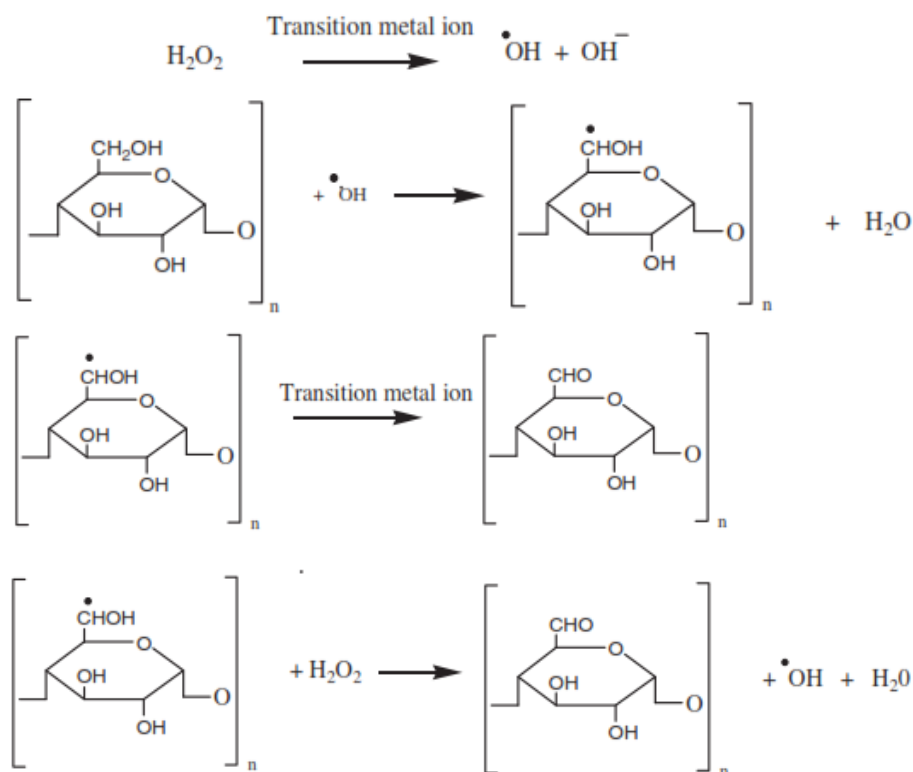


Fig. 2. Radical-ion mechanism of hydrogen peroxide oxidation of the starch.

It is clear that in the absence of Fe^{2+} ions, starch mal reacts with hydrogen peroxide, eventually forming free radicals (OH) [19]. The resulting free radicals take away a hydrogen atom from starch, generating the corresponding macroradical that reacts with dissolved oxygen to give the corresponding oxidized product. It is likely that the rate of reaction and the degree of change of starch during the interaction with hydrogen peroxide without a catalyst are perceptibly small. Initial studies revealed that the effect of hydrogen peroxide in the absence of a catalyst, as well as the effect of FeSO_4 in the absence of an oxidizing agent, did not oxidize the polysaccharide in any way.

Oxidative modification of starch is observed only when they are used together. To prove the appearance of new functional groups in the fraction units of the molecule, the content of functional groups in modified and native starch was determined by titration with sodium hydroxide (to determine carboxyl groups) and hydrochloric acid (to determine carbonyl groups).

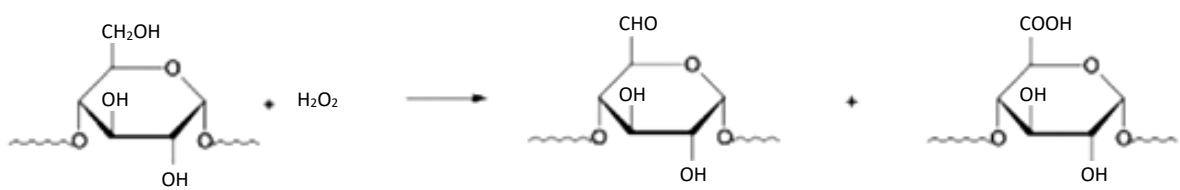


Fig. 3. Oxidizing reaction scheme of starch by the oxidant H_2O_2 .

To determine the influence of the ratio $[\text{FeSO}_4]/[\text{H}_2\text{O}_2]$ on the degree of starch modification (number of functional groups), a series of experiments were carried out, during which the amount of their sulfate was varied at a constant amount of hydrogen peroxide [20]. According to the completion of the oxidative change of the starch, the nature of the carbonyl and carboxyl groups in the acquired starch was established (Fig. 4).

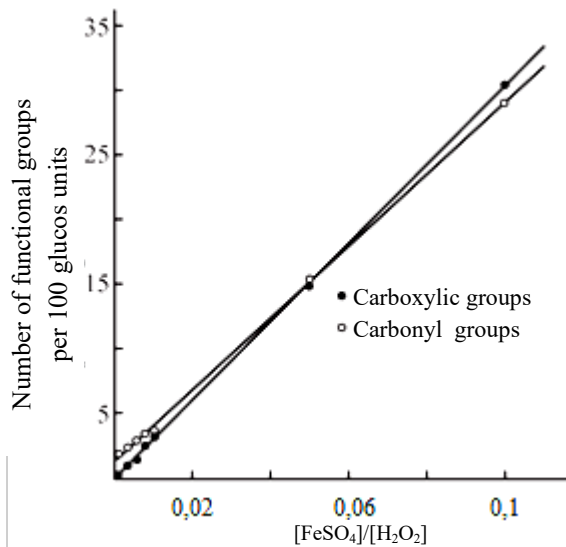


Fig. 4. The dependence of the content of functional groups on the modified starch from $[\text{FeSO}_4]/[\text{H}_2\text{O}_2]$.

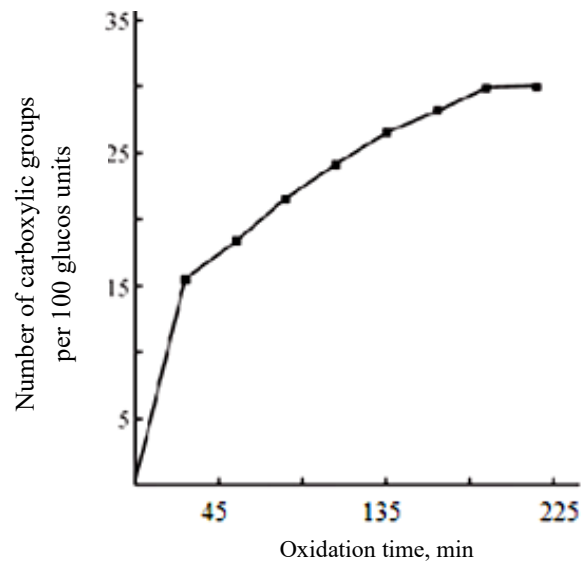


Fig. 5. Dependence of the content of carboxyl groups in modified starch from processing time at a molar ratio of iron sulfate and hydrogen peroxide 1:10.

As follows from the data presented, the number of functional groups linearly depends on $[\text{FeSO}_4]/[\text{H}_2\text{O}_2]$, which makes it possible to obtain oxidized starch with a given number of carboxyl and carbonyl groups. As shown in Figure 5, at 40°C , the reaction proceeds very quickly and is almost completed in 2–3 hours. When using iron tetrasulfophthalocyanine, it takes 5–6 hours to complete the process [21].

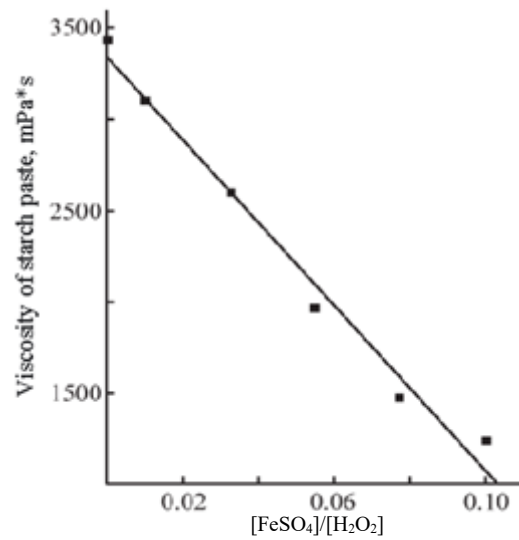


Fig. 6. The dependence of the viscosity of the paste prepared from modified starch on the paint relationship.

Along with the increasing oxidizing effect of starch, its viscosity decreased. The degree of oxidation and destruction of polysaccharide can be increased simultaneously with the concentration of hydrogen peroxide and FeSO₄ solution, while the reaction time of oxidation, to a lesser extent, affects the content of the introduced carboxyl and carbonyl groups as well as the dynamic viscosity samples [22]. Therefore, in this work, the viscosity of a paste prepared from oxidized starch. The research results are shown in the form of a graphic in Figure 6.

In the graph, the viscosity is linear and decreases with an increasing number of functional groups. When using FeSO₄, the oxidized starch paste does not show pronounced signs of pseudoplasticity and is characterized by a decrease in viscosity.

3.2. X-ray diffraction analysis and infrared specters.

A cursory review of the literature on the development of modifications with oxidizing agents makes it possible to learn about the change in the rheology of starch systems in which the splitting of polysaccharide macromolecules is affected by the interaction with hydrogen peroxide and the concentration ratio of the oxidizing agent and catalyst. It is clear that with increasing oxidation state, dynamic viscosity of modified water paste starches decreases, which should be observed with a decrease in the degree of polymerization of branched starch and an increase in the proportion of linear chains with a lower molecular weight.

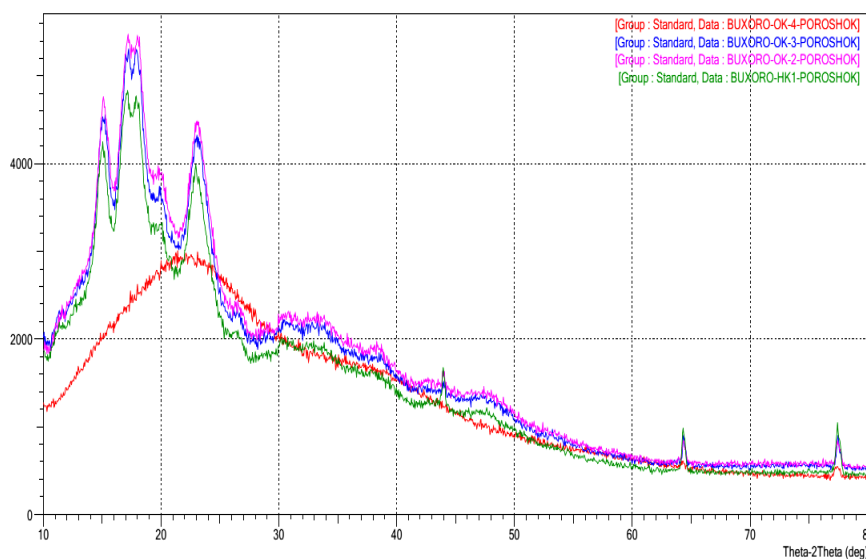


Fig. 7. X-ray patterns of corn starch native (green) and product of its oxidation by different concentrations of H₂O₂ (violet (0,25%), blue (0,35%), and red (0,45%)) to dry mass of the starch.

X-ray diffraction analysis showed that during the oxidation of corn starch with hydrogen peroxide, changes in the supramolecular structure of starch are significant: a slight decrease in the degree of crystallinity is observed in starch after its oxidation, manifested in a decrease in the intensity of reflexes at angles 15, 17, 18, and 23°. These values indicate that A-type crystallization did not change after oxidation and that the oxidation occurred in the amorphous region [23]. However, the crystallinity decreased slightly with the increase in oxidation degree, indicating the partial depolymerization of the amylopectin chain [24]. Red line indicates a decrease in the degree of crystallinity of starch after its oxidation, and these changes are more significant the higher the concentration of the oxidizing agent. This is evidence of a decrease in crystallinity after the end of the reaction.

To study the changes that occurred in the starch molecule after modification, used infrared spectroscopy. The study of infrared spectra makes it possible to monitor structural changes in starch polymers, such as changes in functional groups, helical chain conformation, crystallinity, retrogradation, and water content [25]. In the IR spectra of untreated starches (potatoes, wheat, common, and waxy corn), different bands are observed: bands in the range of 2900–3000 cm^{-1} correspond to C-H stretching, bands in the range of 1160–1100 cm^{-1} correspond to C-O and C-C stretching, with little influence of C-OH stretching, while the region 1077–928 cm^{-1} shows asymmetric deformation of C-OH and CH_2 [26–28].

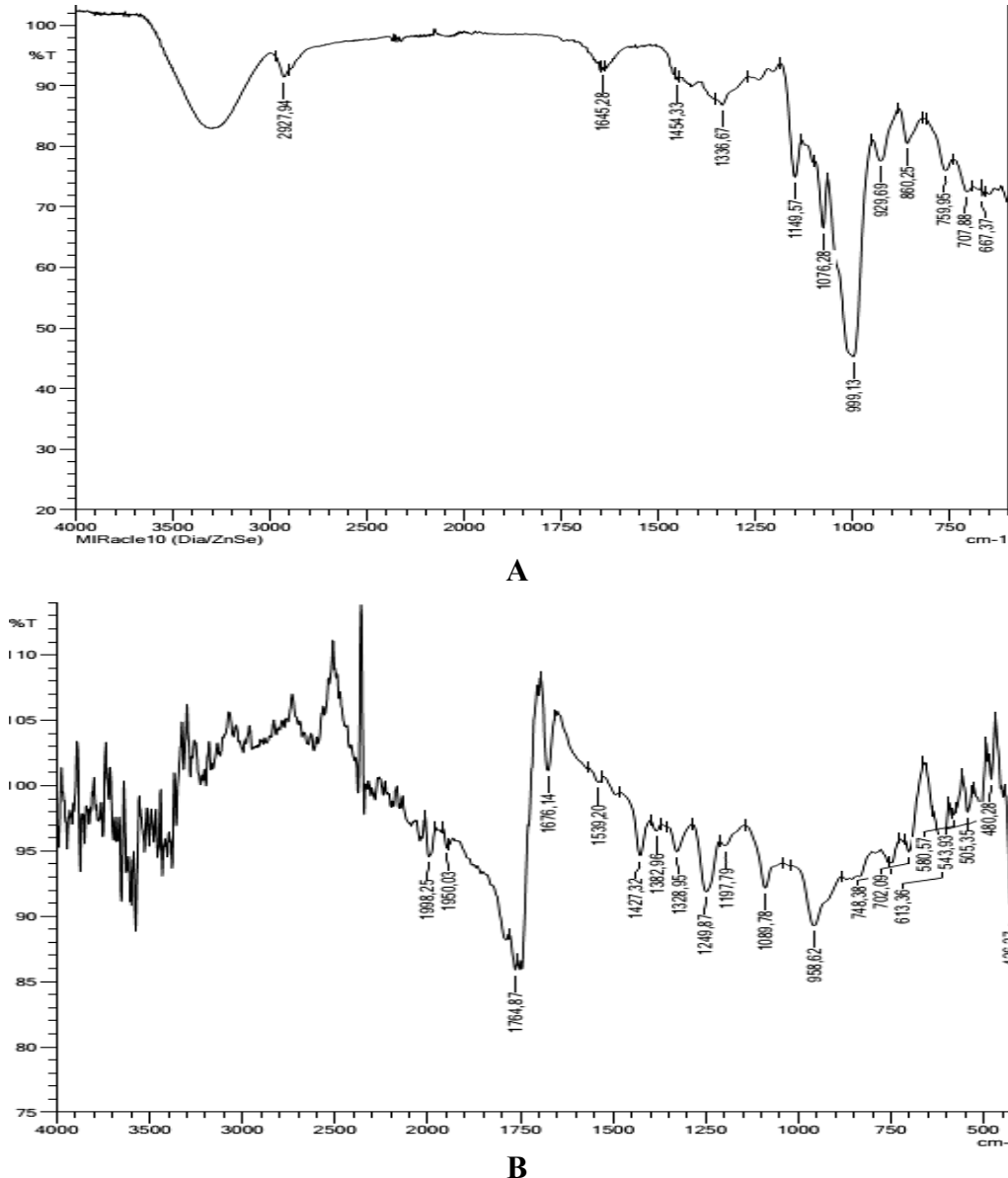


Fig. 8. Infrared specters of the native starch (a) and oxidized starch (b) by hydrogen peroxide.

In Fig. 8, one can see the characteristic signals of the native (a) and corn starch oxidized with hydrogen peroxide at a concentration of 0.35% by dry weight of starch (b), except for the occurrence of a more strong absorption tension at 1764 cm^{-1} , corresponds to the reeling of the carbonyl group. The wobbles of the carbonyl group usually have strong tension. However, in the IR spectra of corn, the pulsation of the carbonyl group illustrates that a small peak in the IR spectrum of corn starch was oxidized, while this absorption in the IR spectrum of native starch gave only a tiny peak. A part of this is that, absorption at 1676 cm^{-1} (corresponding to an intramolecular hydrogen bond) and wobble at 3577 cm^{-1} (corresponding to hydroxyl) had a somewhat different shape and intensity.

4. Conclusions

Thus, the results let us conclude that during the oxidation of corn starch, the molecular and supramolecular structure of its granule is in significant. The most significant changes in starch macromolecules under the action of hydrogen peroxide were a decrease in molecular mass, which was found in a strong reduction in the viscosity of aqueous pastes of oxidized starch. By improving this technology, it is possible to control not only the concentrations of C=O and COOH groups but also the rheology of oxidized starch solutions. An increase in the oxidation and breakdown of starch is carried out by a proportional change in the concentration of the oxidizing agent and catalyst in the system. At the same time, it has been found that the duration of oxidation reactions to a lesser extent affects the content of carboxyl and carbonyl groups, as well as the dynamic viscosity of oxidized starch pastes.

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