Starch oxidation and study of changing its properties for use as an adhesive component for the production of corrugated cardboard

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Abstract. It is known that for sizing papers and cardboards, starch is required, which has a lower viscosity compared to natural, increased stability and increased binding capacity. This is necessary so that the starch dispersions in the size press have a sufficient high concentration, are processable and remain stable. The choice of an oxidizing agent and the conditions for the method of oxidizing corn starch are theoretically substantiated. The mechanism and regularities of the process of starch oxidation have been studied. Changes in the gel-forming and sorption properties of starch during its oxidation were revealed. The intervals of quantitative parameters of the components for the modification process are determined. The dependence of the surface tension of starch pastes on its concentration in solution has been obtained.

1 Introduction

Starch is one of the most large-tonnage chemicals used since ancient times, and to this day remains the main one in the production of paper and cardboard products [1-2]. Its application is diverse - additives in paper pulp for strengthening, a binder for surface sizing and coating of paper, adhesives for gluing corrugated cardboard, paper bags and paper-coiled containers, coagulants in the treatment of industrial and domestic wastewater. Multiple derivatives of native starch are obtained by methods modifications. Modified, or altered, starches that have new properties, are finding more and more diverse applications in various industries. Modified starches generally have the same appearance as native starches. However, by influencing it with various physical, chemical and biological methods that change directionally its properties such as solubility, viscosity, transparency, stability of pastes and other physicochemical parameters, starches with new properties are obtained.

The main transformations that starches undergo in the modification processes are: 1. Cleavage (depolymerization) of starch polysaccharide components with or without preservation of the granular structure. 2. An increase in the number of existing or the emergence of new functional groups, rearrangement of the structure of polysaccharide chains as a result of trans-glycolysis. 3. Loss of the original structure of starch grains and their acquisition after dehydration of the new structure. 4. Interaction of hydroxyl groups of

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starch with various chemicals with the formation of ester bonds and the addition of their residues. 5. Simultaneous polymerization of blocks of partial hydrolysis of starch and other monomers (copolymerization) with the formation of new compounds [3-4].

Being a natural plant polymer, starch consists of a linear polysaccharide - amylase, built from α-D-glucopyranose residues with 1-4-α-glycosidic bonds, and branched amylpectin, built from amylase fragments (from 12 to 25 α-D-glucopyranose residues). Linked by 1-6-α-glycosidic bonds (fig.1).

Fig.1. Amylose structure and Amylopectin structure

The degree of polymerization of amylase is 200-3000, amylpectin is 600-3000000, and the ratio by weight is approximately 1:3. Native starch is a white powder consisting of small hard granules (grains). Depending on the natural starch supplier (potatoes, cereals, corn, maize, rice, tapioca, etc.), the shape and size of the granules are very different. The average size is in the range of 5-50 microns. Humidity ranges from 12–21%[5-6].

Native starch granules are not soluble in cold water, but form unstable suspensions. When heated in water, starch granules hydrate, swell, greatly increase in size and then collapse with the formation of a colloidal solution (gel), due to its high viscosity and stickiness, it is mainly called "paste". The temperature at which starch grains begin to break down is called the "gelatinization temperature". It depends on the origin of starch and is in the range of 56-82 0C. The resulting paste is unstable [7].

These shortcomings greatly complicate the use of native starch in the technology of surface sizing of paper. However, despite the difficulties and problems, so far, native starch has been used for this purpose. This is explained by the low cost and wide choice on the market. At the same time, native starch has a chemical nature, easily amenable to change under the influence of various physical and chemical factors to obtain modified products. These products are not only largely devoid of the disadvantages of native starch, but also acquire new properties that are valuable for use in paper technology. Therefore, in the overwhelming majority of cases, native starch is used in a modified form [8-9].

It is known that in practice for the preparation of modified starches for sizing of paper and cardboards. Two technologies have been widely used: 1) starch oxidation; 2) enzymatic hydrolysis. Starch oxidation technology is based on the processing starch suspension or dispersion with oxidizing agents (for example, sodium hypochlorite or hydrogen peroxide). During the oxidation reaction, there are two fundamentally important processes - reducing the molecular weight of starch due to the gap glycoside bonds and the second - the formation of hydroxyl groups starch of oxidized groups - carboxyl and carbonyl [10-11].

Decline molecular weight leads to a decrease in the viscosity of gelatinized starch dispersions. The formation of carboxyl and carbonyl groups leads to improved solubility and stability of starch dispersions. This is due to the fact that the carboxyl and carbonyl groups in starch interact better with water in comparison with hydroxyl (which they partially replaced) and due to this, the force of interaction of molecules amylase with water increases, the solubility of amylose increases, and the processes of retrogradation, crystallization and gel formation decrease. The oxidation process can be carried out both at
low temperature temperature below the starch gelatinization temperature (up to 60 °C), which usually made in starch factories [12].

2 Experimental part

**Raw Materials and Reagents.** Corn starch According to Gost-7698-93 (acceptance rules and methods of analysis [13]), hydrogen peroxide (30%), 10% sodium hydrogen sulfite solution, 0.4% of the iron sulfate solution, 4% sodium hydroxide solution, 3% hydrochloric acid solution, 0.1 mol/L hydrochloric acid solution, 0.11 mol/L sodium hydroxide solution are used for solution preparation.

**Preparation Process.** A portion of pea starch with a known moisture content is placed in warm \(40-45 \, ^\circ\)C distilled water (the concentration of the suspension should be 38-40% dry matter) and placed in a thermostat, heated to a temperature of 44 +1º C with constant stirring. Upon reaching a predetermined temperature (44+1ºC), a catalyst is introduced into the suspension in the form of a 1% solution of FeSO\(_4\). The catalyst solution is added in two steps; first, half the solution is added and the suspension is mixed for 15 minutes, then the rest. 15 minutes after adding the second half of the solution and stir the suspension for 15 minutes then the rest. 15 minutes after the introduction of the second half of the catalyst solution, the required amount of hydrogen peroxide is introduced into the suspension. The oxidation reaction is carried out by varying the amount of hydrogen peroxide of iron sulfate and temperature. Samples of samples are taken at regular intervals. The selected samples of the starch suspension are neutralized with an alkali solution and filtered on a Buchner funnel. The oxidized starch thus obtained is washed by stirring the precipitate in two times the amount of distilled water, filtered again on a Buchner funnel and dried in air or in an oven.

**Rheology of starch pastes.** From a starch sample passed through a sieve with holes of 1 mm, a paste of a certain concentration is prepared that meets the conditions of the experiment. The paste is placed in a cylinder with a diameter and height of 5 cm and placed in a desiccator saturated with water vapor for a day for structure formation. A day later, using a Rebinder conical plastometer, the limiting shear stress is determined under gradual loading, starting from the smallest loads and up to the maximum, to the full height of the cone. The plastometer is characterized as an instrument with a uniform stress field, a penetration instrument. The principle of operation of this instrument is based on measurement of the penetration depth of a cone into the compound under a fixed external load. Given an external load \(F\) and measuring the penetration depth \(h\) of a cone it is possible to calculate the plastic strength \(P_m\) of the compound being tested \(P_m=K_\alpha *F/h^2\), where \(K_\alpha\) is a dimensionless coefficient that depends on the vertex angle of the cone.

**Carboxyl Content Determination.** Determination of carboxyl groups using potentiometric titration is based on changes in the pH of solutions of the test substance [14]. A weighed portion of the polymer from 0.1-0.3 g was poured with an excess of 0.01 N NaOH, then titrated with 0.01 N HCl, 0.5 ml each. The pH value of the titrated solution was determined on a potentiometer. The method is applicable even at low COOH concentrations. Based on the obtained titration data, plots of pH=f(VHCl) dependence were plotted. Based on the graphs, the percentage of carboxyl groups was calculated using the formula: \(C_{COOH} = \frac{V_{NaOH} - V_{HCl}}{45/10^3} \times 100\), % where 45 is m.v. COOH groups; \(V\) is the volume of hydrochloric acid corresponding to the potential jump point, is determined graphically.

**Electron microscopic studies.** Structural morphologysorbent and its elemental composition were studied with using a scanning electron microscopeEVO MA 10 (Carle
Zeiss, Germany), equipped with micro analytical system for energy dispersive x-ray (EDX) microanalysis INCAEnergy 300 (Oxford Instruments, UK).

**X-ray Analysis.** X-ray diffraction (XRD) patterns of the samples were characterized by an XRD-6100 instrument (Shimadzu) over the scanning range (2θ) of 10–85° (scanning rate: 10° min\(^{-1}\), monochromatic Cu K\(\alpha\) radiation). The relative crystallinity (RC) of the starch granules was calculated using the following equation: RC (%) = \(\frac{Ac}{Ac + Aa}\) * 100, where Ac is the crystalline area; and Aa is the amorphous area on the X-ray diffractograms.

### 3 Results and Discussion

**The Utilization Rate of Hydrogen Peroxide.** In the process of starch oxidation, the destruction of its macromolecules occurs simultaneously with oxidation. Under the action of an oxidizing agent, hydroxyl groups are converted into aldehyde groups, and with further exposure to an oxidizing agent, the latter are oxidized to carboxylic acid groups. Oxidant amount is an important part in the oxidant preparation of starch program. For it directly influence the molecular structure change of carboxyl content and oxidation starch. It has been established that the content of carbonyl (-CHO-) and carboxyl (-COOH-) groups characterizes the degree of oxidation and degradation of starch macromolecules.

**Fig. 2.** Oxidation of starch with hydrogen peroxide.

In this regard, the content of carbonyl and carboxyl groups in starch samples isolated with different degrees of oxidation was changed. Analysis of the content of carbonyl and carboxyl groups is carried out according to the methods described. The results of the study are presented in the Table 1.

**Table 1.** The content of carbonyl and carboxyl groups in samples of corn starch subjected to different degrees of oxidation.

<table>
<thead>
<tr>
<th>No.- sample</th>
<th>Oxidation conditions</th>
<th>Content in starch, %</th>
<th>Jelly strength grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{H}_2\text{O}_2) concentration % to dry matter</td>
<td>(\text{FeSO}_4) concentration % to dry matter</td>
<td>Carbonyl groups mg/g starch</td>
</tr>
<tr>
<td>1</td>
<td>0,25</td>
<td>0,12</td>
<td>0,26</td>
</tr>
<tr>
<td>2</td>
<td>0,25</td>
<td>0,16</td>
<td>0,49</td>
</tr>
<tr>
<td>3</td>
<td>0,35</td>
<td>0,12</td>
<td>0,82</td>
</tr>
<tr>
<td>4</td>
<td>0,35</td>
<td>0,16</td>
<td>1,01</td>
</tr>
</tbody>
</table>

Analysis of the content of the above carbonyl and carboxyl groups was carried out according to the methods described in the literature [15]. The results obtained indicate that with an increase in the concentration of hydrogen peroxide and the concentration of iron sulfate in the liquid phase of the starch suspension, an increase in the content of carbonyl and carboxyl groups is observed.

It should also be noted that the increase in the content of - COOH - groups in starch is insignificant and does not exceed 0.39% of the dry matter of starch. At the same time, the
relationship between the strength of starch-sugar jelly samples of oxidized corn starch and the content of -CHO- and -COOH- groups in them is not observed.

Fig. 3. The dependence of the concentration of the oxidizing agent on time: for oxidized starch slurry (25%)

Fig. 3. shows the curves of the decrease in the concentration of the oxidizing agent depending on the treatment time for starch oxidized with hydrogen peroxide for 1.5 hours at different temperatures (curves 2-25°C, 3-30°C). In order to estimate the proportion of the decrease in the concentration of the oxidizing agent due to the reaction of interaction with native starch, the treated starch suspension was subjected to centrifugation, the oxidizing agent was introduced into the separated centrifuge, and the rate of decrease in its concentration was measured.

If we compare the concentrations of the oxidizing agent achieved in the same time for all three cases, we get that, for example, in 15 min. reaction, the consumption of the oxidizer was 22.5% at 25°C, 53.75% at 35°C, and 65.31% at 40°C. Thus, a certain contribution to the overall acceleration of the loss of the oxidizer for a mechanically processed suspension is made by the fact that some of the starch impurities are in an extracted dissolved or colloid-dispersed state and are oxidized faster.

As can be seen from Fig. 3, the reaction rate for oxidized starch suspension at 30-40 °C is higher than at 25 °C. Thus, the same degree of conversion of the oxidant is achieved at 30°C in 60 minutes, and at 40°C in the treated one - in 30 minutes. After 30 min. reaction, the rate of loss of the oxidant in both cases decreases sharply, and curves 2 and 3 converge significantly. This is due to the fact that the difference in reactivity in pre-treated starches manifests itself mainly as long as surface processes are taking place, i.e. before the onset of the oxidation stage in the bulk of the grain, which is limited by diffusion, and this is reproduced at almost equal temperatures [16].

In order to study the changes in starch grains during the oxidation process, photographs were taken by the scanning electron microscopic method. Native rice and starch modified with an oxidizing agent are photographed (Fig. 4). Micrographs taken with an electron microscope show large differentiations in the starch granules.
Fig. 4. Electron micrographs of granules (native (A) and oxidized (B-C) corn starch (c = 6%) (with the introduction of an oxidizing 0.012% (B-20° and D-40°C), 0.015 % (D-40°C) to the dry weight of starch).

The purpose of this step is to have information on the morphology of native corn starch granule and starch nanoparticles prepared by the oxidation-sonication method. The granules of oxidized starches were more delicate in appearance, which is probably due to the lower viscosity and hence the low molecular weight of oxidized starches [17]. Micrograph analysis of oxidized starches does not explain differences in digestibility. These changes on the surface of the starch granule are undesirable due to the larger contact surface of the starch with the reagent. SEM obtained the morphology of starch nanoparticle.

The SEM data show that native maize starch granules had irregular or truncated shapes. Surface of unmodified maize starch granules was smooth without observable pores. After oxidation-sonication in varied process parameters, the starch particle size was much smaller with more than 1000 times size reduction. However, the corn starch nanoparticle in this work was a slight difference with the corn starch nanoparticle produced by similar combination method oxidation and sonication in previous work by [18]. The differences in particle size could be caused by crop resource, the arrangement of starch component, and preparation method [19].

The activating effect of the oxidizing agent is confirmed by microscopic observations, it can be seen that as the concentration of the oxidizing agent in the solution and the temperature of the reaction mixture increase, the starch grains undergo more and more changes, they gradually lose their spherical shape, depressions, folds, and kinks appear and develop in them. The spherical shape of starch nanoparticles may be related to starch blocklet’s presented in starch granules [20].

In the process of starch oxidation, changes occur both in the amorphous and in the crystalline regions of the starch grain. In this case, an increase in the degree of crystallinity of oxidized starch is observed [21]. In order to identify changes that increase with the absorption of corn starch, the structure of starch grains of different degrees of oxidation was studied. In this case, the X-ray angular scattering method. Investigation of the susceptibility of the phenomenon of native and oxidation of starch, unusual values of the relative viscosity of the dispersions.
According to the accepted classification, according to which the type of structure of starch grains is characterized by the type of diffraction pattern obtained during their X-ray diffraction analysis, grains of corn starch are of type C in structure [22, 23]. The resulting diffraction patterns of native and oxidized corn starch are shown in Fig. 5.

![Diffraction Patterns](image)

**Fig. 5.** X-ray diffraction patterns of native and oxidized corn starches: 1-native starch; 2-oxidized starch with $\eta_{rel}=2.6$; 3-oxidized starch with $\eta_{rel}=1.8$

An analysis of the diffraction patterns shows that in the grain structure of both native and oxidized starch there are regions with an amorphous and crystalline structure. The diffraction patterns of the original and oxidized samples have a similar appearance, but differ in area, which characterizes the content of the amorphous and crystalline parts of starch.

It is known that the degree of crystallinity can be determined from the ratio of the total scattering of crystallites to the total scattering from amorphous and crystalline regions [24]. The degree of crystallinity thus established for native corn starch was 27%, for oxidized starches: sample 2-29.8%; sample 3-29.8%. As can be seen, the oxidized starch samples have a higher degree of crystallinity than the native starch sample, which can obviously be explained as follows. During the reaction, under the action of an oxidizing agent, starch macromolecules are destroyed. Probably, this process occurs at a higher rate in the amorphous regions of starch grains, which leads to an increase in the proportion of scattering per crystalline part of the starch. In connection with this mode of oxidation, an increase in the relative crystallinity of starch is observed. Thus, as a result of the studies, the dependence of the content of -CHO- and -COOH- groups on the concentrations of the oxidizing agent and catalyst in the liquid phase of the starch suspension was revealed, and it was also found that under these oxidation modes, the relationship between the strength of oxidized starch jelly and the content of carbonyl and carboxyl groups are missing. These data led to the study of the process of jelly formation of starch during oxidation.

Aqueous starch dispersions have the ability to form jelly, which is associated with the structure and chemical nature of its polysaccharides. Diluted starch pastes are less likely to gel, but at higher solids concentrations, a gel is readily formed even from dispersible starch. The properties of starch jelly depend on the content of the linear polysaccharide component in them, the size of the molecules, the concentration of the dispersion, the duration of gelation, and other factors [25]. It is known that the strength of jellies depends on the interweaving of starch molecules, especially molecules with straight amylose chains. It is believed that the strength properties of structured starch dispersions are characterized by maximum shear stress [26].

In this regard, the change in the maximum shear stress of oxidized corn starch jelly depending on the concentration of dispersions and the duration of gelation was studied. The
samples of oxidized corn starch with relative dispersion viscosity $\eta = 1.8$ were subjected to the study. The determination of the limiting shear stress was carried out using a conical plastometer according to the well-known method described in the literature [27]. The research results are presented in the form of dependence curves in the coordinates "maximum shear stress - duration", "maximum shear stress - concentration" in Figures 6 and 7.

![Fig.6](image1)  ![Fig.7](image2)

**Fig.6.** Dependence of the maximum shear stress (Pm) of oxidized corn starch jelly on the duration of gel formation ($t$)  
**Fig.7.** Dependence of the maximum shear stress (Pm) of oxidized corn starch jelly on the concentration of solids in dispersions

The obtained data on the maximum shear stress of jelly depending on the duration of gelation (Fig.6.) indicate the occurrence of elastic-plastic deformations. The figure shows that an increase in the duration of exposure of jelly leads to an increase in their strength. A particularly intense increase in strength is observed in the first 4 hours, which is due to the increased content of linear polysaccharide in corn starch [28-29]. An increase in the concentration of dry substances in oxidized starch dispersions also leads to an increase in the strength of jelly (Fig.7). The results of the experiments indicate that oxidized corn starch jelly has great strength. An increase in the concentration of solids and the duration of exposure of the jelly leads to an increase in their strength. A significant increase in strength is observed in the first 24 hours. Further, the strength of the jelly changes slightly.

### 4 Conclusion

As a result of the research, the properties of native and oxidized corn starch were studied. It was revealed that in the process of oxidation of pea starch, its structure and physico-chemical properties change. It has been established that during the oxidation of starch, the strength of its grains decreases, which can be explained by the destruction or weakening of intra and intermolecular bonds. This leads to an increase in solubility and a decrease in the water-holding capacity of starch.

### References


