

Research Article

Modification of Potato Starch by Acetylmalic Acid Chloroanhydride and Physicochemical Research of the New Product

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The article presents the research results of the product's properties of potato starch modification by acetylmalic acid chloroanhydride. Modification of potato starch has been carried out and has been confirmed by elemental analysis. In the infrared spectra, changes in the frequency oscillations of native starch in the noncharacteristic region have occurred: the frequency of oscillations at 981.81 cm^{-1} has increased and in the spectrum of modified starch has been at 1024.82 cm^{-1} ; the band with frequency of oscillations of 923.07 cm^{-1} has shifted to 866.66 cm^{-1} , and the band with frequency of oscillations of 609.79 cm^{-1} has shifted to 672.22 cm^{-1} , indicating the change in noncharacteristic region of the native starch sample after acylation. The properties of obtained modified product have been studied and this modification has appeared to change the shape of moisture and starch bonds, along with decreasing appearance of grains and reduced degree of crystallinity from 12 to 4%.

1. Introduction

Modified starch is used in various sectors of food industry: confectionery, baking, brewing, meat and dairy, and food-concentrate, for sale through the trading network, in the catering system, and for technical purposes (in the textile, in paper industry, and for drilling wells). Modified starches refer to nutritional supplements with the indices E1400–E1451. Among chemically modified starches, acetylated [1] oxyalkylated, phosphate and succinate are known. Chloric, phosphoric, and sulphuric acids; potassium hydroxide; ammonium persulphate; phosphorus chloroxide; acetic anhydride or acetic acid; vinyl acetate; derivatives of amber acid are considered to be modifiers.

Starch has been recently used more often for production of biodegradable packaging materials. However, there are some restrictions on its use in this field: low moisture resistance and low mechanical properties. Modification of starch changes the structure of starch, as a result of which its properties change, which allows expanding the possibilities of practical application. That is why work in the direction

of modification of starch for demands in various sectors of economy is needed and is still going on. Thus, the authors [2] have made cassava starch modification by propionic acid anhydride to improve interfacial adhesion of polyurethane. The authors [3] propose corn and amaranth starch modification from octane succinyl derivatives in order to improve the emulsification properties and to use in encapsulation. Scientists [4] have made chemical modification of sago starch by reacting esterification with fatty acid chlorides in the absence of organic solvent to produce nonpolar sago ether.

Corn starch esters synthesis with fatty acids has been carried out using vinyl laurate and stearate as reagents [5].

Some authors propose a method for synthesizing starch esters by fatty acids without organic solvents as the most effective [6].

Scientists [7] propose starch esterification by octanol, lauryl, and palmitoyl chloride.

In order to obtain hydrophobically modified starch, esterification of starch was carried out by chlorides with long-chain fatty acids (C_8 , C_{12} , and C_{16}) [8].

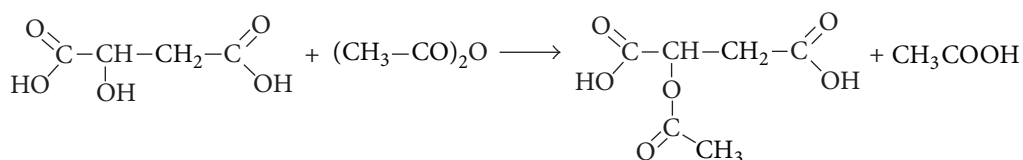
The properties of corn starch fatty acids higher esters have been studied by the authors [9].

The authors [10] modified potato starch by butyryl chlorides, capryloyl, lauryl, palmitoyl, and oleyl.

Thus, this work in the field of starch modification is considered to be relevant and is going on in order to obtain starch with set technological properties. The problem of improving modification method, which should be noncomplicated and cost-effective, is also relevant.

2. Materials and Methods

2.1. Materials. Potato starch produced by LLC "August-Kyi" and malic acid (E 296) were used along with the following solvents: DMSO, DMF, methanol, ethanol.



Into a 100 cm³ reactor equipped with a magnetic stirrer, a heater, a thermometer, and a refrigerator with a gas meter, 26.8 g (0.2 M) of malic acid was added, adding 24.5 g (0.24 M) of acetic anhydride and 1 drop of sulphuric acid, while stirring the mixture stood during 1.5 hours at the temperature of 50–60°C. Then the temperature was raised to 90°C and the

Starch was prepared as follows: 100.02 g of potato starch was placed into a 500 cm³ flask, connected to a water jet pump and heated on a boiling water bath for 8 hours. Product yield was 88.00 g (loss due to drying is 12%).

2.2. Purification of DMSO. 300 cm³ of DMSO was maintained over CaO at the temperature of 400°C for 2 days. Then DMSO was moved to a flask of 500 cm³ adding 30 cm³ of dry benzene. Water remains were discharged at atmospheric pressure in the form of azeotrope with benzene; then DMSO was distilled in vacuum of a water jet pump.

2.3. Acidification of Malic Acid by Acetic Anhydride

mixture was stirred for 0.5 hours. Acetic anhydride and acetic acid excess was discharged into water jet pump vacuum.

28 g of product was obtained, which was used without further purification.

2.4. Synthesis of Acetylmalic Acid Chloroanhydride



28.0 g (0.13 M) of acetylmalic acid was placed into a 100 cm³ reactor equipped with a magnetic stirrer with a heater, a dropping funnel, a thermometer, and a reflux condenser with a gas meter and a gas transfer tube. When stirring through a dropping funnel, 34.0 g (0.286 M) of SOCl₂ was added in small portions. We observed calm gas release and slight heating of reaction mass. In 1 h a drop of DMF was added, with the temperature being maintained at 50–60°C for the next 5 hours. SOCl₂ excess remained in water jet pump vacuum; 32 g of product has been obtained which was used without further purification.

2.5. Esterification of Starch by Acetylmalic Acid Chloride. 9 g (0.05 M per glucose) of dried starch and 300 cm³ of dried DMSO were placed in a three-speed 500 cm³ reactor equipped with a magnetic stirrer with a heater, a dropping funnel, a thermometer, and a reflux condenser with a gas meter and a gas transfer tube. The mixture was stirred for 3 h

at the temperature of 70°C to form a clear, colorless jelly. Then they stopped heating and added 0.5 g of K₂CO₃ (about 2% of the starch weight). When stirred, 32 g (0.15 M) of acetylmalic acid chlorohydride was added dropwise. Reaction mass became thicker and, in 1 hour, it turned into a very dense, light yellow color. Then mixture was heated again while being stirred for further 2 h at the temperature of 50–60°C. Reaction mixture was left at the room temperature overnight. Then, 200 cm³ of methanol was added and vigorously stirred for 1 hour. A dropped white precipitate was filtered off in water jet pump vacuum and washed with distilled water (2 × 50 cm³), ethanol (2 × 50 cm³). The resulting product was dried in the air at the room temperature.

3. Research Methods

An infrared test was performed by the Nexus-475, Nicolet, a KBr tablet.

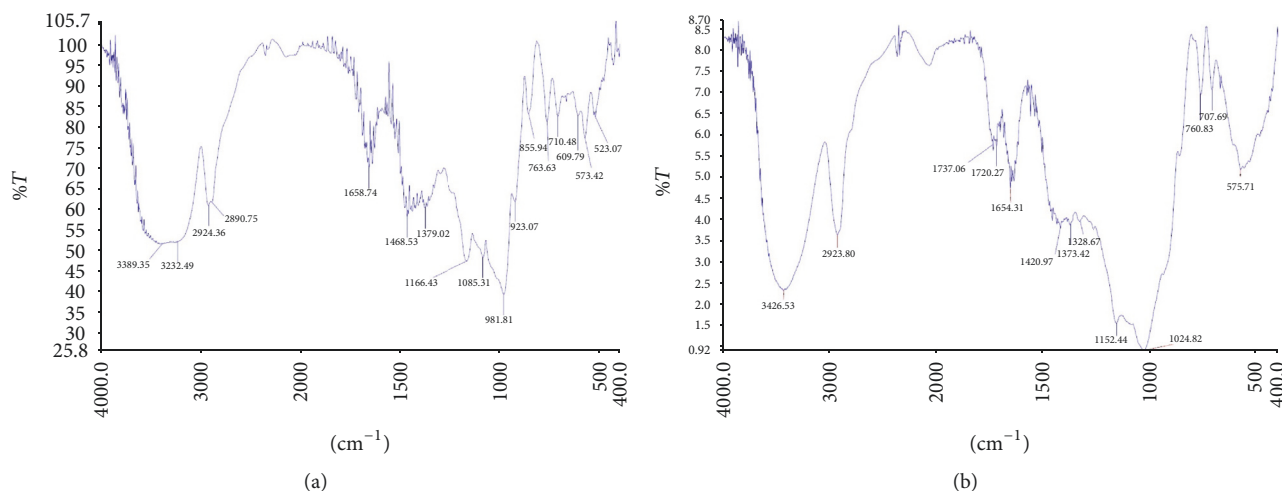


FIGURE 1: IR spectra of native (a) and modified (b) potato starch.

X-ray diffraction analysis was carried out by the DRON-3M device in $\text{CuK}\alpha$ emission with Ni filter; $U = 35$ kV, $I = 20$ mA; counterdisplacement angle $\Delta 2\theta$ is $0,04^\circ$; time of intensity reckoning is 3 s.

Thermogravimetric research was carried out by the Q-1500B device.

NMR spectra were recorded by the Mercury NMR spectrometer, Varian, 400 MHz in DMSO-d_6 .

4. Results and Discussion

4.1. IR Research. Changes resulting in acylation reaction of potato starch by malic acid chloride are confirmed by a number of factors. Thus, in infrared spectrum of modified starch (Figure 1(b)), maximum at 1737.06 cm^{-1} has appeared, which is typical for $\text{C}=\text{O}$ in the ester group, which has appeared in modified starch as a result of acylation reaction.

The nature of the band of valence vibrations (ν_{ON}) in the IR spectra of potato starch (Figure 1(a)) and modified starch (Figure 1(b)) is a reliable confirmation of positive result of acylation reaction of starch by malic acid chloride. In the spectrum of native starch sample there is a sufficiently wide, intense band at 3389.35 cm^{-1} , and, in the spectrum of modified sample, the band is more intense and less broad and lies in the region of stronger vibrations at 3426.53 cm^{-1} . It is known [11] that the position and nature of ν_{ON} band depend on the degree of participation of hydroxyl group in hydrogen bonds. Hydrogen bonds reduce the frequency of oscillations. The hydroxyl group that participates in intermolecular hydrogen bonding is characterized by wide intensive absorption maximum of $3200\text{--}3600\text{ cm}^{-1}$.

Consequently, in IR spectrum of native starch, the band of valence vibrations ν_{ON} is wider and less intense than that of modified starch and lies at 3389.35 cm^{-1} , and, in modified starch spectrum, this band is narrower and more intense (see Figure 1) and lies at 3426.53 cm^{-1} . This confirms the fact that in modified starch there are fewer hydrogen bonds because less free hydroxyl groups are the part of

their esterification, which also has affected the nature and frequency of oscillations of ν_{ON} acetylated potato starch.

In addition, when comparing infrared spectra of native and modified starches (Figure 1), it has been found that spectra under investigation have different oscillations in a non-characteristic region. It is known [12] that numerous valent oscillations of the C-C , C-N , N-O and deformation oscillations are manifested in this area. This area of oscillation of a molecule carbon skeleton sharply reacts to minor changes in molecule structure.

Noncharacteristic oscillations form the main part of the spectrum and for each substance constitute their own unique set of bands [11, 13] and it is this factor that is used to determine identity of substances under study.

In IR spectrum of native starch (Figure 1(a)), there are a number of oscillations in noncharacteristic region, in particular 981.1 cm^{-1} , 923.07 cm^{-1} , 855.94 cm^{-1} , 763.63 cm^{-1} , 710.48 cm^{-1} , 609.79 cm^{-1} , 573.12 cm^{-1} , and 523.12 cm^{-1} , and in spectrum of modified starch (Figure 1(b)) – 1024.82 cm^{-1} , 866.66 cm^{-1} , 760.83 cm^{-1} , 707.69 cm^{-1} , 672.22 cm^{-1} , and 575.71 cm^{-1} .

When comparing these data, it is obvious that in spectrum of native starch oscillation frequency at 981.81 cm^{-1} has increased and in spectrum of modified starch it lies at 1024.82 cm^{-1} ; the band with oscillation frequency of 923.07 cm^{-1} has shifted to 866.66 cm^{-1} and the band with frequency of oscillations of 609.79 cm^{-1} has shifted to 672.22 cm^{-1} , indicating change in noncharacteristic region of native starch sample spectrum after acylation. In IR spectrum there are no signals of acylchloride group ($1785\text{--}1815\text{ cm}^{-1}$) and those of hydrolysis products of acetylmalic acid chloroanhydride, namely, oscillation band of carboxylic acid ($1750\text{--}1770\text{ cm}^{-1}$ and their salts 1640 cm^{-1}). This allows assuming that glucopyranose rings have been crosslinked due to reaction of both chloroanhydride groups.

Consequently, a sample of native and modified starches has a different chemical composition as a result of potato starch chemical modification by acetylmalic acid chloroanhydride.

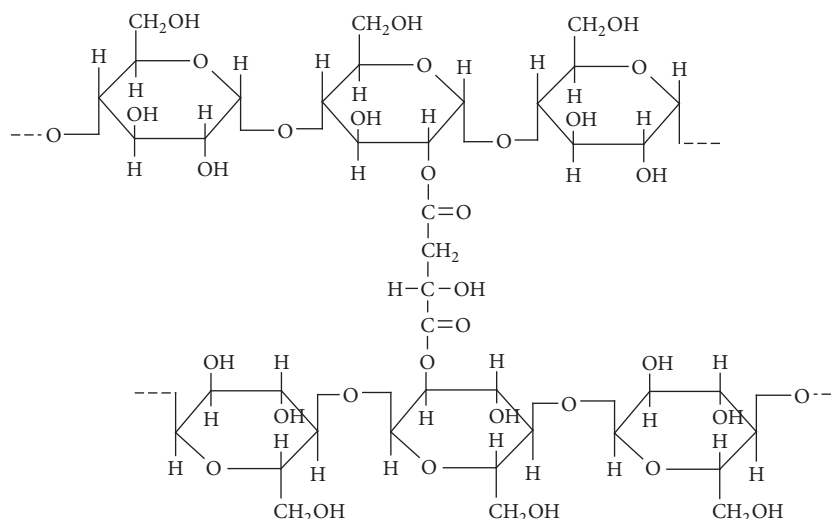


FIGURE 2: Structural formula of potato starch modification product.

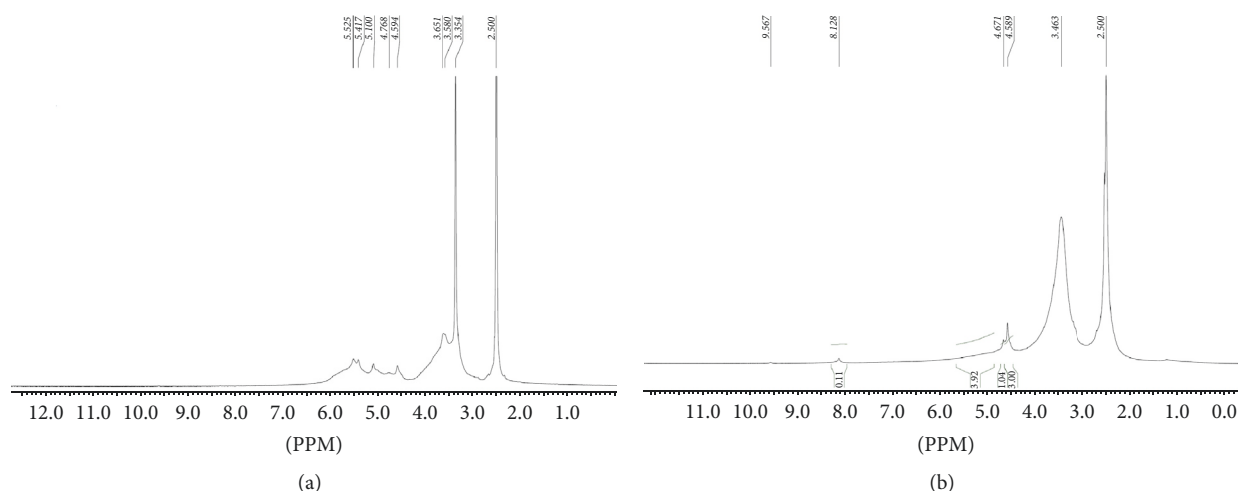


FIGURE 3: NMR spectra of native (a) and modified (b) potato starch.

4.2. Elemental Analysis. The obtained results of elemental analysis of acetylated potato starch by malic acid chloride are as follows: 44.47% of carbon has been found, 6.07% of hydrogen has been defined; 44.86% of carbon and 5.79% of hydrogen have been calculated. The results presented and infrared spectra (Figure 1) show that starch acylation by malic acid chloride was carried out by crosslinking of glucopyranose starch chains by malic acid chloride through the ratio of one molecule of malic acid chloride and six residues of glucopyranose rings (see Figure 2).

According to the previous paper [14], the most easily acetylated is a primary alcohol group and a hydroxyl alcohol group at C₂. The authors [5] prefer the hydroxyl group at C₂ to the former one.

4.3. NMR Research. On the basis of NMR spectrum of potato starch acylation product by malic acid chloride (Figure 3(b)) it is clear that there is no signal at 1 ppm which is characteristic for group -CH₃ within acetyl group.

Consequently, we can faithfully state that during acylation reaction of starch by acetylmalic acid chloroanhydride its deacetylation has occurred, which correlates perfectly with the data of elemental analysis. Determining the degree of crosslinking of glucopyranose starch chains and defining the position of the substituent on NMR spectrum have appeared to be impossible.

4.4. X-Ray Structural Study. In order to find out the influence of esterification process of malic acid chloroanhydride on potato starch structure crystallinity, X-ray diffraction analysis has been used [15]. The obtained diffractograms are shown in Figure 4.

X-ray of native starch (Figure 4) indicates its amorphous-crystalline structure with the degree of crystallinity of 12%. Modified starch has an amorphous structure with the degree of crystallinity only of 4%, which is quite logical, since the modification is carried out at the temperature (90°C) higher than that of gelatinization (59°C) of potato starch.

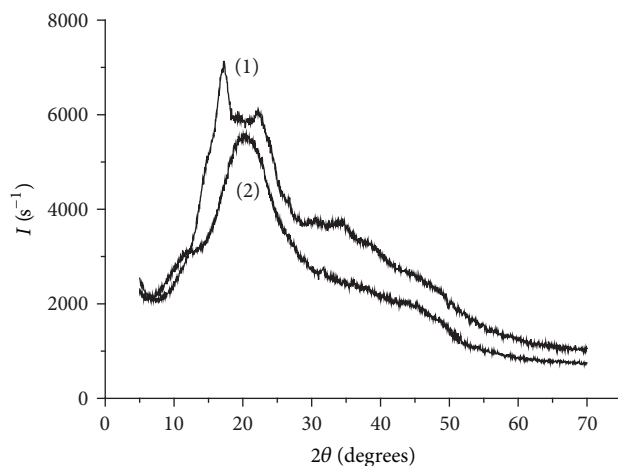


FIGURE 4: X-ray native (1) and modified (2) starches.

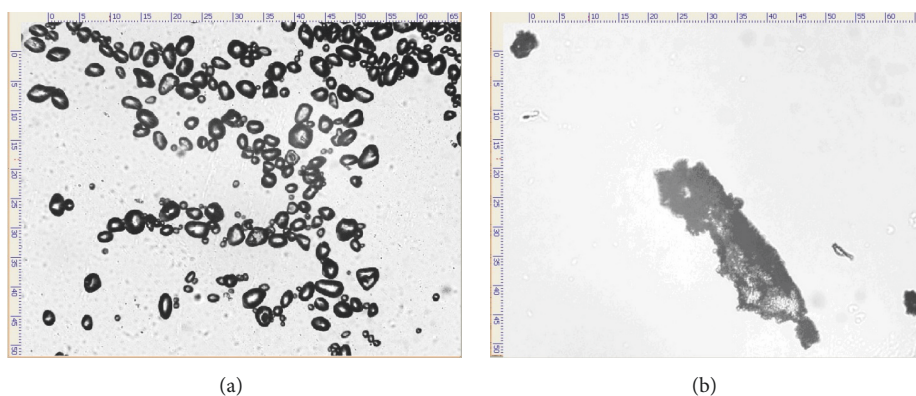


FIGURE 5: Appearance of grains of native (a) potato and modified (b) starches magnified $\times 400$.

In addition, the destruction of primary structure of starch grains is confirmed by studies using a microscope shown below. Consequently, chemical modification by acetylmalic acid results in reduction of starch crystalline structure.

4.5. Thermogravimetric Study. With the change of crystalline structure for amorphous one, we can expect a change in properties of substance to bind and retain water. Using thermal analysis some derivatograms have been obtained; the analysis of results is shown in Table 1.

According to results (Table 1), modified starch contains adsorbed water by 1.2% more due to modification in aqueous medium, and, due to this, the amount of crystallization water in modified starch is 9.7% higher. During modification, there is starch gelatinization, and when it is crosslinked, water is also retained. Due to the presence of water crystallization in modified starch, the amount of anhydrous products is lower and, as a result, in the third zone of thermolysis, the amount of anhydrous products is 11% less than that of native starch. In addition, thermolysis of anhydrous products begins at slightly lower temperature of 230°C , as compared with 300°C for native starch. Consequently, modification of potato starch by acetylmalic acid leads to the change in a shape and amount of potato starch water.

4.6. Research with a Microscope. Native starch is in the form of grains that can be seen under a microscope. For each species, depending on its origin, it has a different shape and size. As in the course of modification crosslinking of glucopyranose chains has occurred, so, one can also expect changes in the shape of grains. The results of the study are shown in Figure 5.

The appearance (Figure 5) shows that the carried out potato starch chemical modification by means of crosslinking causes destruction of initial form of grains, which is also confirmed by X-ray diffraction analysis. Consequently, change in the external shape of starch grains also confirms chemical modification by acetylmalic acid.

5. Conclusions

Modification of potato starch by acetylmalic acid chloride has been carried out and confirmed by elemental analysis. In infrared spectra, changes in native starch frequency oscillations in noncharacteristic region have occurred: frequency of oscillations at 981.81 cm^{-1} has increased and in spectrum of modified starch is at 1024.82 cm^{-1} ; the band with frequency of oscillations of 923.07 cm^{-1} has shifted to 866.66 cm^{-1} ; and

TABLE 1: Thermolysis zones of native and modified starches.

Kind of starch	Thermolysis zones			
	I	II	III	IV
	Adsorbed water	Crystallization water	Thermolysis of anhydrous products	Burning char
	Temperature range, °C	Temperature range, °C	Temperature range, °C	Temperature range, °C
	$\Delta m, \%$	$\Delta m, \%$	$\Delta m, \%$	$\Delta m, \%$
Native	65-100	100-140	300-380	500-600
Modified	60-100	100-230	230-370	500-670
			380-500	
			370-500	
			57.5	15.0
			46.5	13.8
				17.5
				21.5

the band with that of 609.79 cm^{-1} has shifted to 672.22 cm^{-1} , indicating the change in noncharacteristic region of native starch sample after acylation.

The properties of obtained modified product have been studied and it has been found that modification has changed the shape of moisture bonds with starch, the appearance of grains. The degree of crystallinity has decreased from 12 to 4%.

Conflicts of Interest

The authors, Oksana Shulga, Natalya Simurova, Sergii Shulga and Jelyzaveta Smirnova, declare that there are no conflicts of interest regarding the publication of this paper.

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