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STARCH MODIFICATION WITH ACETYLSALICYLIC ACID CHLOROHYDRIDE FOR THE FOOD AND PACKAGING INDUSTRY NEEDS

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ABSTRACT

The potato starch modification with acetylsalicylic acid chloride was carried out and was confirmed by elemental analysis, and the obtained product was investigated by physicochemical methods. There were changes in the vibration frequency bands of native starch in the uncharacteristic region in the IR spectra: the vibration frequency at 981.81 cm^{-1} increased and in the modified starch spectrum lied at 1022 cm^{-1}, and the band with the vibration frequency of 923 cm^{-1} shifted to 860 cm^{-1}, which indicated a change in the spectrum. A band at 1716 cm^{-1} was presented in the esterified starch spectrum, which was characteristic of C=O in the ester group.

X-ray phase analysis of native and modified starch showed that acylation led to a decrease in the crystalline phase from 12 to 3%.

There was occurred the deacylation of acetylsalicylic acid during the starch modification reaction since the the modified starch NMR spectrum lacks the methyl group signal, which was part of the acyl group, and a signal appeared at 9.6 ppm, which was characteristic of phenolic hydroxyl.

It was found that modified starch differs significantly from the native starch in terms of water retention and thermal stability according to the thermogravimetric research data.

The appearance of starches grains before and after acylation showed the potato chemical modification starch led to the destruction of the grains initial shape.

The thermogravimetric research showed that chemically modified starch with acetylsalicylic acid chloride differs in water retention characteristics from the original potato starch.

The obtained modification product can be used in various food industry branches, as well as for obtaining environmentally safe materials, in particular, biodegradable and/or edible films.

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МОДИФІКАЦІЯ КРОХМАЛЮ ХЛОРАНГІДРИДОМ АЦЕТИЛСАЛІЦИЛОВОЇ КИСЛОТИ ДЛЯ ПОТРЕБ ХАРЧОВОЇ ПРОМИСЛОВОСТІ ТА ПАКУВАЛЬНОЇ ІНДУСТРІЇ

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Проведена модифікація нативного картопляного крохмалю хлорангідридом ацетилсаліцилової кислоти, яка підтверджена елементним аналізом, ІЧ-спектроскопією, ЯМР аналізом, а також досліджено отриманий продукт фізико-хімічними методами. В ІЧ-спектрах відбулися зміни смуг частоти коливань нативного крохмалю в нехарактеристичній області: частота коливань при 981,81 см$^{-1}$ збільшилася і в спектрі модифікованого крохмалю лежить при 1022 см$^{-1}$, а смуга з частотою коливань 923 см$^{-1}$ змістилася до 860 см$^{-1}$, що вказує на зміну спектра. Після ацилування в спектрі етерифікованого крохмалю наявна смуга при 1716 см$^{-1}$, що характерно для С=О у складі естерної групи.

Рентгенофазовий аналіз нативного та модифікованого крохмалів показав, що ацилування призводить до зменшенням кристалічної фази з 12 до 3%. Під час проведення реакції модифікації крохмалю відбулося деацилування ацетилсаліцилової кислоти, оскільки в ЯМР спектрі модифікованого крохмалю відсутній сигнал метильної групи, що входить до складу ацилу і з'явився сигнал при 9,6 м.ч., що характерно для фенольного гідроксилу.

За даними термогравіметричних досліджень встановлено, що модифікований крохмаль за характеристиками водоутримання й термічної стабільності суттєво відрізняються від вихідного нативного крохмалю. Зовнішній вигляд крохмалів до і після ацилування показує, що проведена хімічна модифікація картопляного крохмалю призводить до руйнування початкової форми зерен.

Результати термогравіметричних досліджень показують, що хімічно модифікований крохмаль хлорангідридом ацетилсаліцилової кислоти за характеристиками водоутримання відрізняються від вихідного картопляного крохмалю. Отриманий продукт модифікації можливий до використання в різних галузях харчової промисловості, а також для отримання екологічно безпечних матеріалів, зокрема, плівки.

Ключові слова: *крохмаль, модифікація, саліцилова кислота, харчове пакування.*

Formulation of the problem. Starch is a reserve polysaccharide of plants which accumulates in seeds, potato tubers, roots, leaves, etc. Its composed of two polysaccharide components — amylose (20—30%) and amylopectin (70—80%). Starch is the main component of plant raw materials for the food production. Its various chemically modified derivatives offer a great scope of high technological value in both food and non-food industries. Modified starches are designed to overcome one or more of the shortcomings, such as loss of viscosity and thickening power upon cooking and storage, particularly at low pH, retrogradation characteristics, syneresis, etc., of native starches. Oxidation, esterification, hydroxyalkylation, dextrinization, and cross-linking are some

of the modifications commonly employed to prepare starch derivatives. In a way, starch modification provides desirable functional attributes as well as offering economic alternative to other hydrocolloid ingredients, such as gums and mucilages, which are unreliable in quality and availability (Tharanathan, 2005).

Native starch can be gelatinazed only under the condition of sufficient water and temperature, modified starches are pasteurized at room temperature, which makes it possible to use modified starches as thickeners and stabilizers (Hong, 2015; Rudrapatnam, 2005).

The authors (Shulga, Shulga, & Simurova, 2021; Шульга, 2019) were conducted by number of potato starch modifications, which made it possible to change the properties of the native starch for the needs of the packaging industry: biodegradable films for bakery and confectionery products. the modification of starch, because it provide the necessary properties of starch as a raw material for various industries.

Therefore, expanding the numerous of modified starches allows the needs the packaging, food or other industry.

The recent research analysis and publications. Starch-based materials are biodegradable, which makes it possible to use them as ecological packaging materials: for example, edible coatings based on chitosan, starch-salicylic acid and starch-cinnamaldehyde-thymol were applied to fresh cut-mango (Santacruz, 2021) or edible coatings was modified by adding salicylic acid or a cinnamaldehyde-thymol mixture to the cassava starch (Terán, 2022).

A series of modified starches were prepared by grafting acetylsalicylic acid (AsA) into starch by an esterification reaction then coated with polyvinylalcohol (Al-Adeemy, 2014).

Modification of starch by dicarboxylic acid anhydrides to starch esters, containing both hydrophilic and hydrophobic groups are known to improve its emulsification properties, and can also be used for encapsulation after hydrolysis (Bhosale, 2006).

The synthesis of long-chain fatty esters of corn starch (starch laurate and starch stearate) with a broad range in degree of substitution (DS=0.24—2.96) was described (Junistia et al., 2008). The fatty esters were prepared by reacting the starch with vinyl laurate or vinyl stearate in the presence of basic catalysts (Na_2HPO_4, K_2CO_3, and Na acetate) in DMSO at 110 °C.

An efficient method for synthesis of hydrophobically modified starch without using organic solvents was described. The esterification of starch was performed with long chain fatty acid chlorides (C8, C12, C16), at two stages. At the first stage, native starch was dispersed in an alkali reaction medium, and at the second stage, it was treated for esterification. Finally, hydrophobic starch esters were obtained with moderate degrees of substitution (DS-values<0.45). The reactivity of corn and potato starches under the same reaction conditions was also studied (Namazi et al. 2011).

Starch-based composite films incorporated with salicylic acid (SA) and waxy maize starch nanoparticles/κ-carrageenan (WMSNs/KC) were used to achieve antimicrobial activity and improve the mechanical properties. WMSNs were fabricated through enzymolysis and recrystallisation method, followed by individually adding KC to form WMSNs/KC by self-assembly, and used as a nanofiller and stabilizer to be incorporated into hydroxypropyl tapioca starch-based films at a concentration of 0—9% (Fang, 2020).

Filmogenic suspensions based on starch (S) and salicylic acid/starch (SA-S) were

prepared and used to produce casted films (TPS and SA-TPS). An extensive characterization was conducted on both suspensions and casted films to assess their properties. Results evidenced that after storage for 120 days at 4 °C and 25 °C, the mold and yeast counts were significantly lower in the SA-S than in the S suspensions (Díaz-Díaz, 2023).

A simple method of starch modification using dimethyl sulfoxide (DMSO) was proposed. The selected solvent was widely used in organic synthesis, as it is well soluble in water, which allows its residues to be completely removed after the reaction. Acetylsalicylic acid chloride was used as a modifier. It is used in analytical chemistry, medicine, aniline dyeing and food industry, for food preservation due to its antiseptic properties. Derivatives of salicylic acid (sodium salicylate, cetisalicylic acid, methyl and phenyl esters) are well-known medicinal products. In addition, salicylic acid affects the functional state of wheat sprouts (Дідик та ін., 2011), exhibits stress-protective and regulatory properties for plants (Kavulych, 2023), affects the rheological properties of starch (Nep, 2016).

The literary sources analysis shows the proposed polysaccharide modification schemes are multi-stage, complex, require expensive and toxic reagents, which is unacceptable for the food industry. All this complicates the new modified starch introduction derivatives into practice, but the starch modification potential is still not exhausted.

Thus, work in the starch modification field is relevant and useful, as the search for obtaining starch with the necessary technological properties continues.

The aim of the research was to carry out the modification of potato starch and investigate the physicochemical properties of the obtained product of starch modification with acetylsalicylic acid chloride.

Materials and methods. Potato starch, salicylic acid, thionyl chloride, acetic anhydride, solvents — dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol, ethanol were used in the research.

Preparation of starch for modification. 100 g of potato starch was placed in a 500 cm^3 flask, connected to a water jet pump and heated in a boiling water bath for 9 hours. At the end of heating, the flask is disconnected from the pump and the flask is quickly closed with a stopper with a calcium chloride tube. Allow to cool to room temperature. The dry starch is quickly weighed and placed in a glass with a well-polished stopper. The product output is 87.20 g (moisture loss due to drying — 12.8%).

Preparation of DMSO. 300 cm^3 of DMSO was poured into a flask with a well-polished stopper, 50 g of freshly roasted CaO at a temperature of 400 °C was added and kept for 2 days with periodic stirring. Next, DMSO was transferred to a 500 cm^3 flask and 30 cm^3 of dry benzene was added. Remaining water is distilled off under atmospheric pressure in the form of an azetrope with benzene, then DMSO is distilled in a vacuum using a water jet pump.

The acylation of salicylic acid scheme with acetic anhydride is shown in Figure 1.

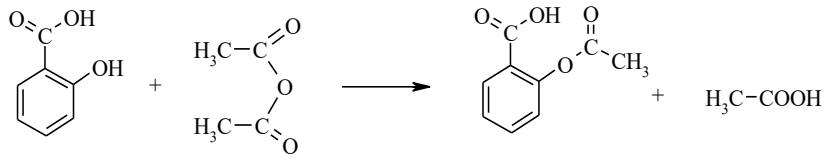


Figure 1. The scheme of salicylic acid acylation

In a 150 cm^3 reactor equipped with a heated magnetic stirrer 13.8 g (0.1 M) of salicylic acid are placed with a thermometer and a reflux condenser, 15.3 g (0.15 g M) of acetic anhydride and 1 drop of sulfuric acid are added. While stirring, the mixture is kept for 1.5 hours at a temperature of 50—60 °C. Then the temperature is raised to 90 °C and stirred for another 0.5 hours. The mixture is cooled and, with stirring, 25 cm^3 of cold water is added and the solid product is filtered, which is washed on the filter first with ice water and then with a small amount of toluene. The obtained product is dried in air. The product output is 15.1 g (90.1%). Acetylsalicylic acid is recrystallized from benzene or chloroform.

The synthesis scheme of acetylsalicylic acid chloride is shown in Figure 2.

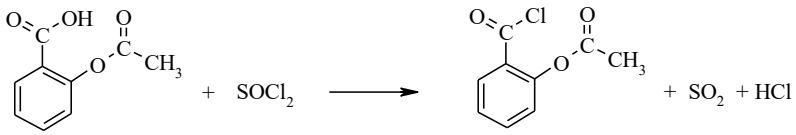


Figure 2. The scheme of acetylsalicylic acid chloride

16.8 g (0.1 M) of acetylsalicylic acid is placed in a 150 cm^3 reactor equipped with a heated magnetic stirrer, a dropper, a thermometer, and a reflux condenser. During stirring, 17.8 g (0.15 M) of thionyl chloride are added in small portions through a dropping funnel. Gas (SO_2) is released and the reaction mass is slightly heated. After 1 hour, three drops of DMF were added, the temperature was maintained at 50—60 °C for another 5 hours. The thionyl chloride excess is driven off in the water jet pump vacuum. 16.4 g (88.2%) of the product is obtained, which is used without additional purification.

The starch acetylsalicylic acid chloride esterification occurred according to the reaction shown in Figure 3.

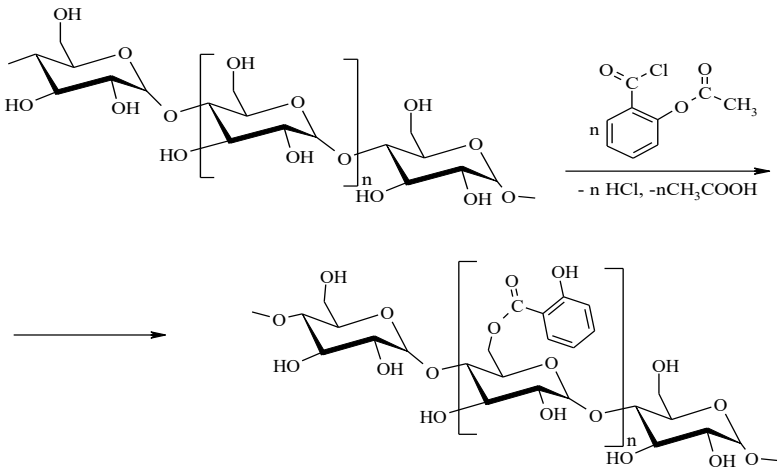


Figure 3. The reaction scheme of potato starch with acetylsalicylic acid chloride

1.8 g (0.01 M based on glucose) of dried starch and 200 cm^3 of anhydrous DMSO are placed in a 500 cm^3 three-necked reactor equipped with a heated magnetic stirrer, a

pouring funnel, a thermometer, and a reflux condenser. The contents of the flask are stirred for 3 hours at a temperature of 70 °C until a transparent, colorless jelly is formed. Next, stop heating the flask and add 0.12 g of K_2CO_3 (approximately 2% of the starch mass). During mixing, 2.8 g (0.15 M) of acetylsalicylic acid chloride is added in small portions through a funnel. The reaction mass thickened and the temperature rose to 75 °C. After 1 hour, the reaction mass turned into a thick, light-yellow pellet, the temperature decreased to room temperature. Then 150 cm^3 of methanol or ethanol was added and intensively stirred for 1 hour. The yellowish precipitate that has fallen out is filtered off under the water jet pump vacuum and washed with methanol or ethanol (3×20 cm^3). The product is air-dried at room temperature. The product output is 2.36 g (83.7%).

Research methods.

FT-IR. Infrared studies were conducted on the device Nexus — 475 firm Nicolet, KBr tablet (Chung et al., 2004).

X-ray. X-ray diffraction analysis was carried out by the DRON-3M device in CuKα emission with Ni filter; U=35 kV, I=20 mA; counterdisplacement angle Δ2Θ is 0,04 ; time of intensity reckoning is 3 s (Namazi et al., 2010).

TGA. TGA (Thermogravimetric Analysis) research was carried out by the Q-1500B device, at a heating rate of 20 °C/min (Prime et al., 2009).

NMR. NMR spectra were recorded by the Mercury NMR spectrometer, Varian, 400 MHz in DMSO-d6 (Namazi et al., 2010).

The main research results presentation.

Starch-salicylic acid (SA) inclusion complexes with different amounts of residual SA were obtained (Guo, 2023).

Authors of this research proposed an easy method of starch modification with acetylsalicylic acid chloride using dimethylsulfoxide (DMSO), which is well soluble in water, which allows to completely remove its residues after the reaction and minimize the danger of the final product.

IR spectrometric research.

The IR spectroscopy method was used to study the changes that occurred as a result of the starch acylation reaction.

The sample of the original native potato starch and the esterified derivative have a different spectrum from the analysis of their IR spectra uncharacteristic region (400—1000 cm^{-1}). As it is known (Thompson, 2018), numerical valence oscillations of C-C, C-N, N-O bonds and deformation oscillations are manifested in this region, which practically do not lend themselves to a certain attribution. This area of carbon skeleton vibration sensitively to minor changes in the structure of the molecule.

The changes took place as a result of the potato starch acylation reaction with acetylsalicylic acid chloride and they were confirmed by a number of factors, which are given below Thus, in the IR spectrum of the modified starch, a maximum appeared at 1716.82 cm^{-1}, which is characteristic of C=O in the composition of the ester group in the modified starch as a result of the acylation reaction.

The IR spectrum of the original native potato starch contains a number of fluctuations in the uncharacteristic region, in particular 982 cm^{-1}, 923 cm^{-1}, 856 cm^{-1}, 764 cm^{-1}, 710 cm^{-1} and in the spectrum of the etherified derivative sample — 1022 cm^{-1}, 858 cm^{-1}, 797 cm^{-1}, 759 cm^{-1}, 706 cm^{-1}.

In the uncharacteristic region spectrum of the original potato starch sample, the oscillations frequency at 982 cm^{-1} shifts to 1022 cm^{-1}, and the oscillations frequency at 923 cm^{-1} shifts to 858 cm^{-1}, which indicates a change in the native potato starch after acylation. Therefore, the original native potato starch sample and an esterified derivative have a different chemical composition due to the chemical modification of potato starch.

Confirmation of the potato starch acylation reaction was also a change in the nature of the valence vibrations νOH band. There was a sufficiently wide intense band located at 3389 cm^{-1} in the native potato starch spectrum and in the esterified derivative spectrum, this band is more intense and less wide and is located at 3409 cm^{-1}.

It is known (Suart, 2004) the position and character of the νOH band depend on the degree of hydroxyl group participation in hydrogen bonds. Hydrogen bonds change the force constant of the O-H bond, which reduces the oscillations frequency. The hydroxyl group, which participates in the intermolecular hydrogen bond, is characterized by a broad intense absorption maximum in the region of 3200—3600 cm^{-1}.

The νOH band of valence vibrations is narrower and more intense, lying at 3409 cm^{-1} in the spectrum of the modified starch sample, and, this band is wider and less intense, lying at 3389 cm^{-1} in the spectrum of native starch. This fact confirms that there are fewer hydrogen bonds in the modified starch, which is explained by the smaller number of free hydroxyl groups, which affected the nature and frequency of νOH oscillations of acylated potato starch.

Elemental analysis.

The elemental analysis obtained results of acylated potato starch with acetylsalicylic acid chloride are as follows: Carbon — 48.59%, Hydrogen — 5.80% were found. The calculated amount of Carbon is 48.48%, Hydrogen is 5.72%.

The IR spectra and elemental analysis results show acylation of starch occurred due to the addition of a salicylic acid residue to glucopyranose chains of starch in the ratio of acetylsalicylic acid chloride one molecule and three residues of glucopyranose rings. According to (Chi, 2008; Shulga, 2018), the primary alcohol and hydroxyl groups at C_2 are most easily acetylated. Taking into account the possible spatial hindrances in the second position, the authors preferred acylation of the primary alcohol group.

NMR research.

During the starch modification reaction with acetylsalicylic acid chloride, deacylation of acetylsalicylic acid occurred, since the NMR spectrum of the modified starch lacks the methyl group signal, which is part of the acyl group. In addition, a signal appeared in the spectrum at 9.6 ppm, which is characteristic of phenolic hydroxyl.

X-ray phase research.

To find out the degree of esterification process influence on the structure crystallinity of etherified potato starch, the X-ray phase analysis method was used. The diffractograms are shown in Figure 4.

According to the potato starch diffractogram (Figure 4), it was calculated the starch before esterification has an amorphous-crystalline structure with a crystallinity degree of 12%, while the modified potato starch has a crystallinity degree of 3%.

Therefore, the chemical modification of starch leads to the crystalline structure destruction, which was also observed by the authors (Nep, 2016) during the study of the rheological and structural properties of modified starches from young shoots of *Borassus aethiopium.*

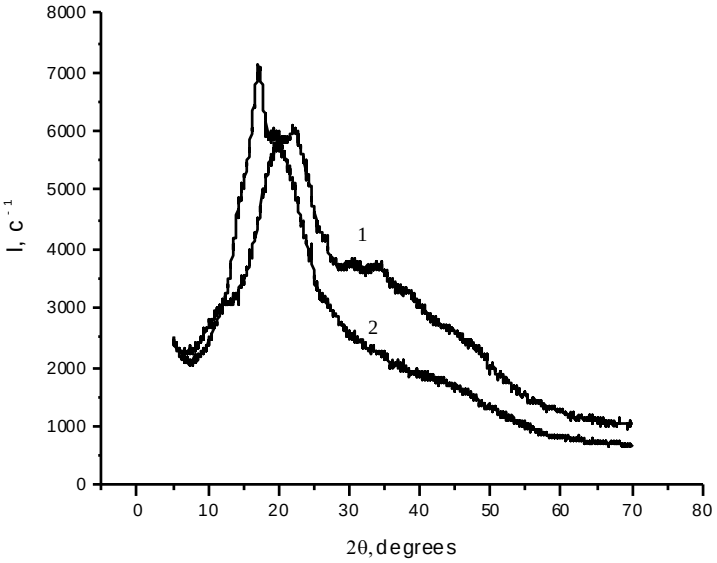
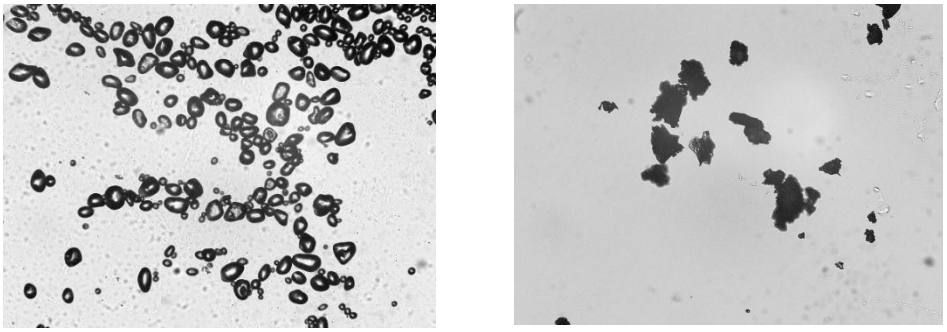


Figure 4. X-ray diffraction results of original native potato starch (1) and its esterified derivative (2) (*n*=3, *p*≤0,05)

Optical microscopy results.

Using the optical microscopy method, it was found that during the acylation of native potato starch with acetylsalicylic acid chloride, significant changes occurred in the appearance of native starch. The rounded native starch grains were destroyed during the modification, which is clearly visible in the comparative analysis of the microphotographs (Figure 5).



a b

Figure 5. Appearance of native potato (a) and esterified starches (b) under a microscope (×400) (n=3, p≤0,05))

Thermogravimetric research.

The results of thermogravimetric research show the chemically modified starch differs from the original native potato starch in its water retention characteristics.

There are four segments of mass loss: the 1st at temperatures of 63—140 °C is 3.7% on the TG curve of a native potato starch sample (Figure 6, a). The mass loss is caused by

the separation of adsorbed water (up to 100 °C) and crystallization water (100—135 °C). On the DTG curve of a sample of native potato starch (Figure 6, a), the given loss corresponds to a blurred effect of mass loss with a minimum at a temperature of 110 °C, which should be considered as an overlap of two separate effects associated with moisture removal. The second segment of mass loss corresponds to the temperature interval of 300—380 °C and is 57.3%. On the DTG curve, this process corresponds to a sharp and deep mass loss effect with a minimum at a temperature of 330 °C, which is caused by the thermal decomposition of polysaccharide.

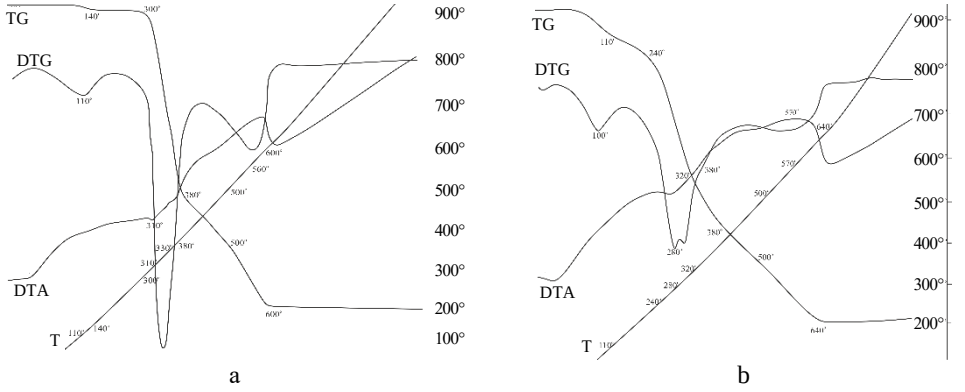


Figure 6. The derivatograms of native potato (a) and esterified starch (b) (n=3, p≤0,05)

In the third segment, mass loss occurs at a temperature of 380—500 °C and is 14.5% of the initial mass. In this temperature range, carbonization of previously formed intermediate products of thermolysis occurs up to 380 °C. On the fourth segment of the TG curve, the mass loss Δm_4=17.5%. This stage is caused by complete thermal decomposition and charring of starch at a temperature of 600 °C. The coke residue of this sample is 5.7% after heating to 950 °C.

Six segments can be distinguished on the TG curve of a esterified potato starch sample (Figure 6, b): 1st — 30—100 °C, associated with the release of adsorbed water Δm_1<7.5%. The mass loss at temperatures of 110—240 °C is a consequence of the separation of crystallization water, Δm_2=6.23%. In the third temperature interval of 240—280 °C and the fourth 280—320 °C Δm_3=36.20%, the process of anhydrous substance thermal decomposition the takes place, which depends on the chemical composition of the reaserch sample. The fifth temperature interval of 380—500 °C with Δm_5=13.75% is the charring result. The sixth temperature interval of 500—640 °C corresponds to the further decomposition of previously formed charred products., The mass of the modified starch sample does not change above 640 °C. The coke residue is 6.23% after heating to 900 °C.

Thus, the conducted thermogravimetric research confirm the difference in the chemical structure and properties of the original native starch and its esterified derivative. So, the modification has been successfully carried out. The established changes will also determine the starch gelatinization parameters and the water solubility of the modification starch.

Conclusions

The native potato starch modification with acetylsalicylic acid chloride was confirmed by elemental analysis, IR spectra, X-ray phase analysis, thermogravimetric and microscopic reaserches.

A band at 1716 cm^{-1} appeared in the spectrum of esterified starch after acylation, which is characteristic of C=O in the ester group composition.

The potato starch acylation leads to a decrease in the crystalline phase from 12 to 3%.

There is no signal of the methyl group, which is part of acyl in the NMR modified starch spectrum, and a signal appeared at 9.6 ppm, which is characteristic of phenolic hydroxyl.

The starch modification with acetylsalicylic acid changes the water retention and changes the appearance of the native starch.

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