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Modification of nanostarch by citric acid

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The negative impact of waste on the environment is growing with the declining oil reserves. Therefore, the attention to usage of green products and the green economy has grown worldwide. One manifestation of this is the growing demand for biomaterials. Starch is a biopolymer with large reserves of raw materials and chemical modification of its structure allows to obtain new materials. In this paper, we present the results of the experimental investigations on modifying of nanostarch with citric acid. Alcohol precipitation method was used for synthesis of nanostarch. The dispersion of the obtained nanostarch was studied by UV spectroscopy. The chemical structure of the modified nanostarch film was studied by FTIR spectroscopy. According to the results of FTIR, it was found that a new ester bonds are formed. Surface morphology was studied by scanning electron microscope and it was found that 0.1 g of film is completely soluble in water in 360 seconds according to the kinetics of water solubility.

Key words: nanostarch film, citric acid, FTIR, natural polymer.
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Introduction

Currently, there is a growing interest in the replacement of synthetic polymers with biologically based renewable, environmentally friendly natural polymers [1-2]. The main difference between natural polymers and synthetic polymers is biodegradation [3]. When the share of non-renewable oil reserves is spent on the production of chemical products, including the share of biodegradable polymeric materials, which in turn require complex and expensive disposal. Therefore, the study and development of biodegradable polymers, their introduction into everyday use is very important.

Starch is a low-cost natural polymer that is renewable and biodegradable. It is the second most common biomass material in nature. The main sources of starch worldwide are corn (82%), wheat (8%), potatoes (5%) and cashews (5%), including tapioca starch [4]. Currently, starch is widely used in the food industry [4], in the production of glue [5], in pharmaceuticals in the encapsulation of drugs [6], in the paper industry [7]. However, starch has disadvantages in terms of water resistance and mechanical strength [8]. To overcome these shortcomings, it is necessary to modify the starch [9, 10]. The physical properties of chemically modified starch increase and the field of application expands [11, 12]. Therefore, the modification of starch is relevant.

In this study, the possibility of modifying starch with citric acid was studied. Structural changes in starch were also studied by IR spectroscopy.

Materials and methods

Based on the methodology described in [13], nanostarch has been isolated from starch by precipitation with ethyl alcohol. The nanostarch suspension was obtained by centrifugation of the initial suspension (Figure 1). The optical absorption of the obtained nanostarch aqueous solution measured on spectrophotometer PE-5400UV with a scanning speed of 240 nm /min, in the wavelength range 190-1000 nm. Measurements were conducted using 10 mm thick quartz cuvette.

During the study, non-synthetic, organic plasticizer citric acid was obtained. To modify the starch with citric acid, a 3% nanostarch solution was prepared. Take 15 ml of nanostarch suspension and pour 97 ml of distilled water, the solution was stirred continuously by adding 3 g of citric acid, stirring at 90 ° C for 60 min. The resulting solution was dried at room temperature in a disc-shaped plastic container (Figure 2).

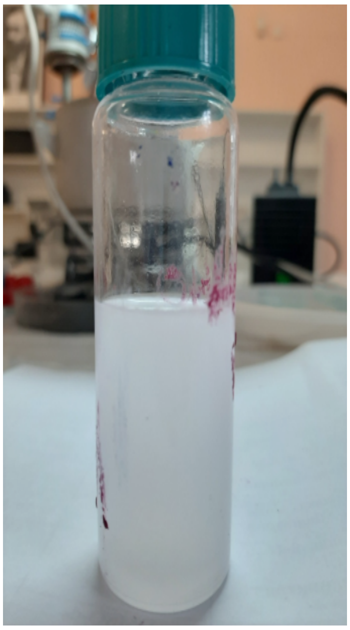

Figure 1 – The nanostarch suspension.

Figure 2 – Starch-based film modified with citric acid.

FTIR analysis of chemical structures of initial and modified nanostarch films was performed on a spectrometer FTIR FT-801 (Simex, Russia), which resolution was 1 cm^{-1}. Measurements were conducted in the region between 450–4700 cm^{-1} according to the standard method using a single-use universal full internal reflection and mirror-diffuse reflection with the upper position of the model, at a temperature of 25^{0}C.

The surface morphology of nanostarch films was studied by scanning electron microscope JSM-6390LV (Jeol Japan). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. The surface of the nanostarch film is coated with gold to improve the transfer of electrons. The specimens were mounted on aluminum pins with carbon tape.

In addition, we have carried out the investigations of the solubility of studied samples of nanostarch films. In order to do it 0.1 g of nanostarch film was placed in 20 ml of distilled water. From the initial 30 s, the mass change was measured on an analytical balance (SARTOGOSM LV 210-A Russia).

Results and discussion

Figure 3 illustrates an absorption spectra of nanostarch suspention in UV-Vis optical region. The absence of absorption peak in the spectrum means that starch particles in the solution have nanoscale sizes and their size distribution is homogeneous. It can be seen that the results of the study [14, 15] are well consistent with the research.

Figure 4 shows the FTIR spectra of starch, citric acid and nanostarch-based film. In the represented spectra region between 3500-3000 cm^{-1} indicates the presence of OH groups and signal on 1053 cm^{-1} is characterized by the absorption of the C-O bond. Corresponding absorption of all CH_2 groups was identified on 2868 cm^{-1}. Absorption at 1147 cm^{-1}, 1078 cm^{-1} and 990 cm^{-1}, respectively, reflects the valence oscillations of the C-O bond, C-O-H and C-O-C groups in the glucose ring. Absorption signals 855 cm^{-1}, 856 cm^{-1} and 867 cm^{-1} indicate a β-glycosidic bond. For starch-based film a new peak at 1738 cm^{-1} was characteristic of an ester group.

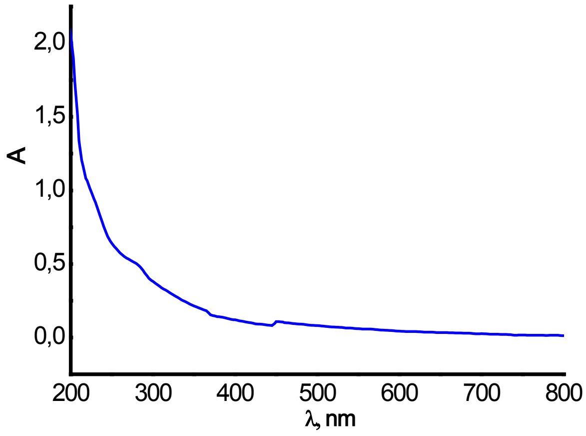

Figure 3 – Absorption spectra of nanostarch suspention in UV-Vis optical region

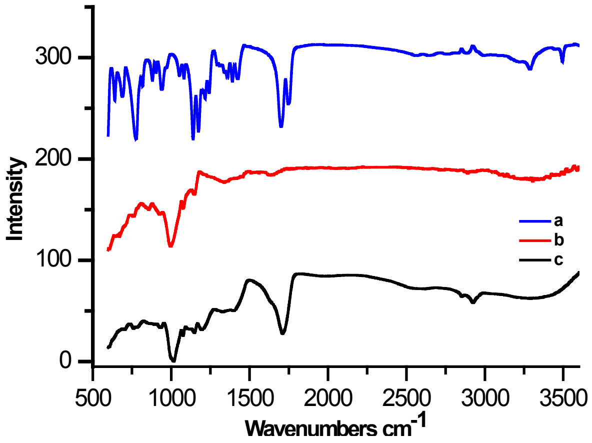

Figure 4 – IR spectrum of samples: nanostarch-based film; b- native starch; c-citric acid

The surface morphology of nanostarch film is shown in Figure 5. Depending on the surface morphology, the disrupt of intermolecular and intramolecular hydrogen bonds under the influence of citric acid increases the plasticity of nanocarches [16-18]. It also causes the aggregation of nanocarches.

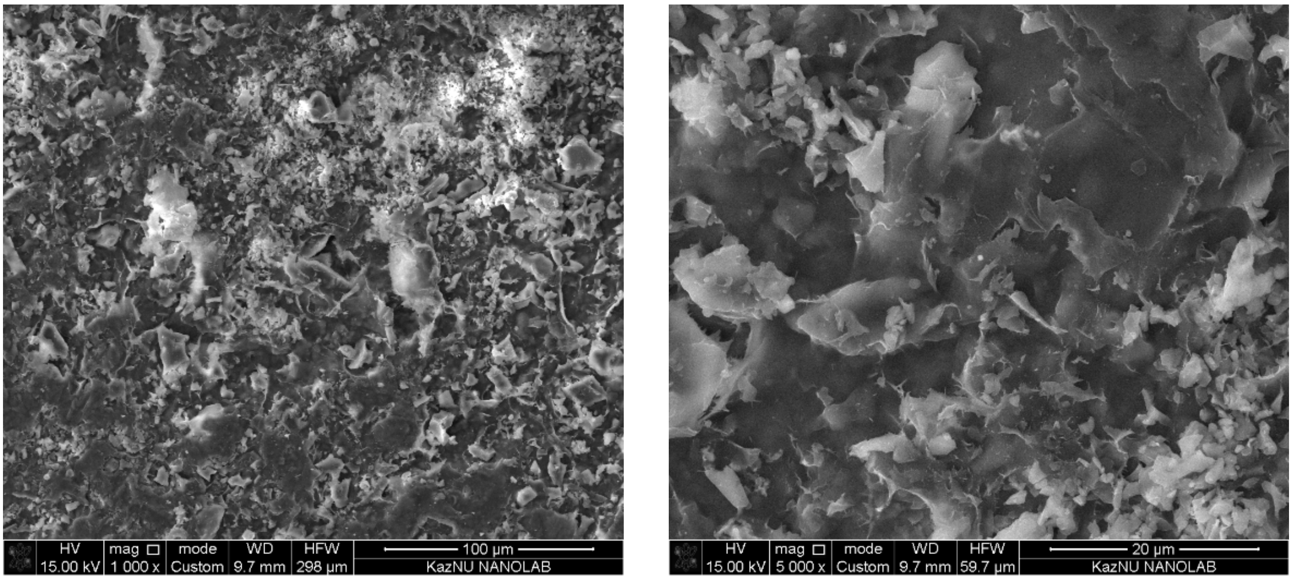

Figure 5 – SEM images of nanostarch film

The water solubility kinetics of the nanostarch film is shown in Figure 6. In the first 30 seconds we see that the process of dissolving in water is fast. Further, the kinetics of dissolution was relatively slow, and it was found that the film is completely soluble in water in 360 seconds.

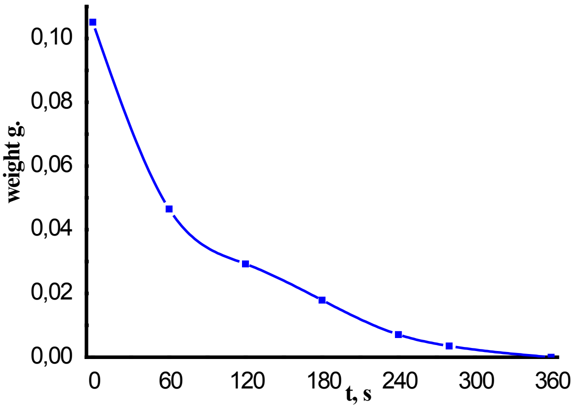

Figure 6 – Water solubility kinetics of nanostarch film

Conclusions

Nanostarch films were obtained by alcohol precipitation. In the next stage, a nanocomposite film was obtained by modifying the nanostarch with citric acid. The dispersion of the obtained nanostarch was studied by UV spectroscopy. The chemical structure of the modified nanostarch film was studied by FTIR spectroscopy. According to the results of IR, it was determined that a new ester bond will be formed. Surface morphology was studied by SEM and it was found that 0.1 g of film is completely soluble in water in 360 seconds according to the kinetics of water solubility.

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