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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

A Study of Physicochemical Properties of Extruded Starches of Varied Biological Origin

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Abstract—Morphological structure of native and extruded starches of varied biological origin was studied, their X-ray phase analysis was made, and their solubility in cold water was examined.

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Modified starch products are extensively used in food, pulp-and-paper, building, and other industries. Most widely occur starch products modified by various chemical and biochemical methods (esterification, oxidation, cross-linking, acid and enzymatic hydrolysis) [1–3].

At present, steadily increasing attention is being given to "healthy" feeding, with the result that a tendency is observed for chemically modified products to be gradually abandoned, which is due to difficulties in their purification to remove toxic low-molecular-weight chemical substances unreacted with a polysaccharide or formed in the course of its modification. In some cases, a thermomechanical modification of starch-containing products can serve as a good alternative to chemical modification. An extrusion treatment of starch in various modes can yield products with prescribed quality parameters, which can satisfy the demand of various food industries.

The key role in the formation of target properties of thermomechanically modified starch products is played by changes in their physicochemical properties in the course of an extrusion treatment. It is important to note that differences in morphology and physicochemical characteristics (moisture content, amount of amylose, etc.) between starches of varied origin affect the extent to which their structure and physicochemical properties change in the course of extrusion [3].

The aim of this study was to perform a morphological and X-ray diffraction analysis of potato, corn, and tapioca starch subjected to extrusion treatments under various conditions. In addition, the effect of extrusion on the moisture content and solubility in cold water of extruded starch products was analyzed.

EXPERIMENTAL

As objects of study served extra-quality potato starch [GOST (State Standard) 7699–78, Belarus), extra-quality corn starch (GOST 7697–82, Russia), and tapioca starch (Vietnam).

The extruded starches were obtained at Mashpishcheprod Open Joint-Stock Company (Mar'ina Gorka) on an RZ-KED-88 double-screw extrusion installation under the following conditions: temperature 140–170°C; rotation frequencies of the dosing screw, working screws, and cutting device, 90–92, 90–94, and 80–84 rpm, respectively; matrix (extrusion nozzle) diameter 4 mm; no preliminary moistening of the raw material.

The morphology of structural units constituting particles of native starches and extruded starch samples was studied with a LEO 1420 scanning electron microscope (Germany). When fabricating preparations, powdered starch samples were deposited onto a metallic substrate and fixed on its surface with an electrically conducting glue. Then a gold layer was deposited in an EMITECH K 550X vacuum installation (Germany).

Diffraction curves were recorded on an HZG-4A X-

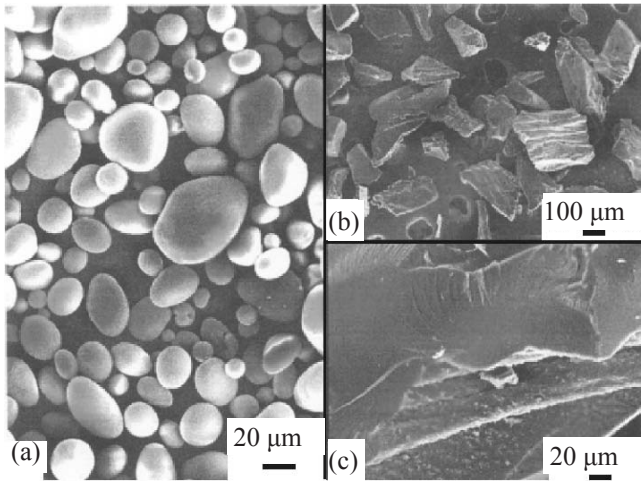

Fig. 1. Micrographs of potato starch. (a) Native starch, (b) particles of extruded starch, (c) surface of an extruded starch particle; the same for Figs. 2, 3.

ray diffractometer (Carl Zeiss, Jena) with $Cu_{K\alpha}$ radiation, Ni filter, and point-by-point recording. Samples were prepared by cold compaction into monolithic round pellets 2 mm thick and 18 mm in diameter. The relative degree of crystallinity was calculated from the intensity ratio I_c/I_t, where I_c is the intensity of X-ray diffraction on crystalline regions, and It is the total intensity of X-ray diffraction.

The solubility of starches in cold water was determined as follows. Approximately 20 g (weighed with an accuracy of 1 mg) of air-dry starch was suspended in a beaker in 200 ml of distilled water (in the case of extruded samples the weighed portion was reduced to 5 g) and the suspension was agitated for 30 min. The water was sucked-off on a filter, suction was switched off, starch was diluted with 100 ml of distilled water, suction was switched on, and next 100 ml of water was added. The procedure was repeated three times, with 100 ml of water expended per 20 g of starch in each stage. Then the filtrate was concentrated in a vacuum on a rotary evaporator to a volume of 80 ml, and the volume was brought to 100 ml with distilled water in a volumetric flask. To determine the content of components soluble in cold water, aliquot samples (20 ml) were taken with a pipette into preliminarily weighed and dried (at 150°C) beakers, and were evaporated at 105 ± 1°C to constant dry weight. The solubility S in cold water was calculated by the formula (in percent relative to dry mass):

$$S = \frac{(G_2 - G_1) \times 100 \times 100 \times 100}{m\,20(100 - \omega)},$$

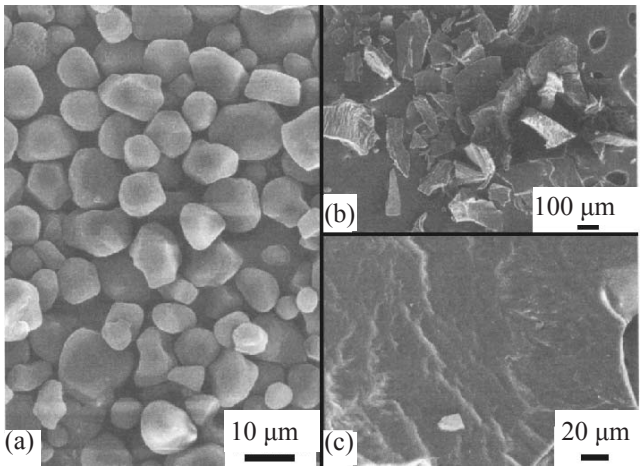

Fig. 2 Micrographs of corn starch.

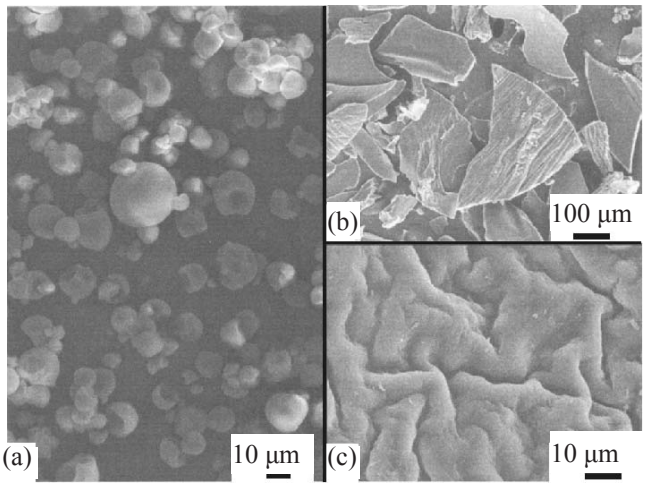

Fig. 3. Micrographs of tapioca starch.

where G_1 is the mass of an empty beaker (g); G_2, mass of a beaker with a dry residue (g); m, mass of the starting weighed portion of an air-dry sample (g); and ω, moisture content of an air-dry sample (%).

The moisture content of the samples was determined using the standard procedure (GOST 7698–93).

Results of a morphological analysis of starches of varied botanic origin before and after extrusion are shown in Figs. 1–3.

Plan-view imicrographs of native starches (Figs. 1a–3a) show that the samples under study have a typical morphology in the form of a set of grains with sizes dependent on the biological origin of starch [3, 4]. As can be seen in Fig. 1a, large grains of potato starch have an oval shape, whereas small grains are spherical. Grains of corn starch (Fig. 2a) are predominantly represented by small polyhedra, and grains of tapioca starch (Fig. 3a)

are mostly rounded, with numerous defects in the form of indentations. These results indicate that the outward appearance of starch grains can be used to rather precisely identify starch with some biological type.

Figure 4 shows differential size distributions of starch grains of varied origin. It can be seen that grains of corn and tapioca starch (unimodal distribution) are more uniform in size than potato starch grains (bimodal distribution).

A granulometric analysis of native starches demonstrated that the grain size of native potato starch varies from 8 to 60 μm, and that of corn and tapioca starches, from 4 to 19 and from 3 to 31 μm, respectively. Despite the considerable scatter of the size of starch grains, their average size is 21.7 ± 1.2 μm ($P < 0.05$), 9.7 ± 0.4 μm ($P < 0.05$), and 10.6 ± 0.5 μm ($P < 0.05$) for potato, corn, and tapioca starches, respectively. In addition, a statistically significant ($P < 0.05$) difference between the average sizes of starch grains of varied biological origin was revealed.

Extruded starch samples retain their powdered form (Figs. 1b–3b). As a result of the extrusion, the dispersity of the powders strongly decreases and the particle size substantially increases to several hundred micrometers. Comparison of the micrographs of native and extruded samples shows that native grains are completely disintegrated in starch extrusion, with large conglomerates formed, having various shapes and comparatively smooth and profileed surface.

It can be noted that extrusion dramatically changes the morphology of native starch. To study the morphological structure in more detail, electron micrographs of individual particles of modified starch were obtained. It can be seen in Fig. 2a that the surface of extruded corn starch is loose, and there are smooth fragments on the surface of particles of extruded potato starch (Fig. 1c). The surface of extruded tapioca starch is rather profiled and loose (Fig. 3c).

Thus, high-temperature extrusion of starches leads to a pronounced change in their initial morphological structure. In the course of extrusion, grains of native starch disintegrate to give tens of times larger particles with indeterminate morphology. Irrespective of the botanic origin of a starch, particles of extruded samples have close morphologies and the surface of their particles is strongly profiled.

It is also important to note that scanning electron microscopy can be used to analyze the extrusion (thermomechanical) modification of starch, because all samples of extruded starch products have about the same characteristic morphological structure.

The process of high-temperature starch extrusion changes not only the morphology of native grains, but also the supramolecular structure of starches, which is indicated by X-ray diffraction data.

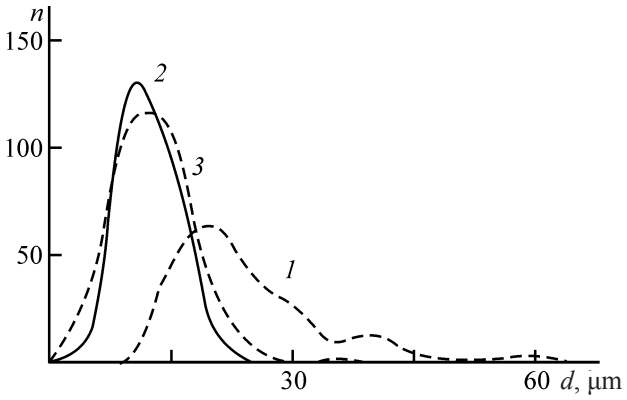

Fig. 4. Grain size distributions for starches of varied origin. (*n*) Differential distribution function and (*d*) grain size. Starch: (*1*) potato, (*2*) corn, and (*3*) tapioca.

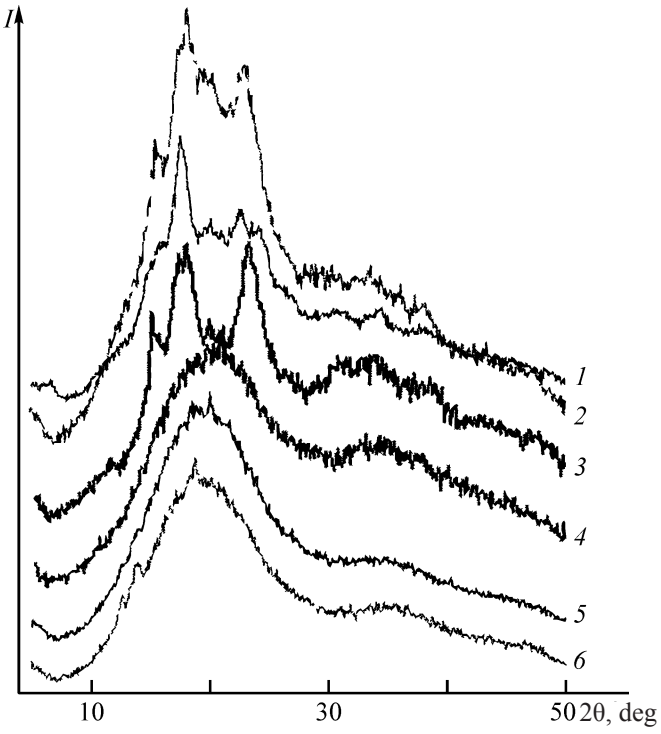

Fig. 5. X-ray diffraction patterns of native (*1*) potato, (*2*) corn, and (*3*) tapioca starches and of extruded (at 140°C) (*4*) tapioca, (*5*) potato, and (*6*) corn starches. (*I*) Relative intensity and (2θ) Bragg angle.

Solubility in cold water and moisture content of native and extruded starches of varied biological origin

Sample	Moisture content ω, %	Solubility *S*, %
Potato starch		
native	12.5	0.21
extruded		
140°C	7.9	95.1
150°C	7.9	98.9
170°C	13.8	99.9
Corn starch		
native	13.4	0.17
extruded		
140°C	9.4	90.3
150°C	8.7	92.3
170°C	7.7	93.3
Tapioca starch		
native	12.6	0.39
extruded (140°C)	8.8	99.9

Figure 5 shows X-ray diffraction patterns of native starches of varied origin and those extruded at 140°C. As follows from Fig. 5, the X-ray diffraction pattern of native potato starch contains distinct diffraction reflections at angles 2θ = 17.1 and 22.7°. Also, two shoulders at 2θ 15.5 and 24.3° were recorded. Potato starch belongs to a polymorphic modification of B-type, characteristic of tuberous starches. At the same time, the diffraction pattern contains a substantial fraction of an amorphous halo resulting from scattering from the disordered phase of starch. The fraction of the highly ordered fraction, i.e., crystallites of amylose and amylopectin, is about 35.0%.

The X-ray diffraction pattern of native corn starch contains three peaks at diffraction angles 2θ = 15.2, 18.0, and 23.0°. It should be noted that the intensity of the diffraction reflections is low and they are poorly resolved, which points to small size and defectiveness of corn starch crystallites. Together with discrete scattering from crystallites, the diffraction pattern shows a large fraction of diffuse scattering from the disordered phase of starch, a diffuse halo. The relative degree of crystallinity of native corn starch is approximately 20.5%.

The diffraction pattern of native tapioca starch contains highly distinct reflections at angles 2θ = 14.9, 17.2, 17.9, and 23.2°. These data suggest that, similarly to corn starch, tapioca starch belongs to a polymorphic modification of the A-type, which is the most characteristic of root and grain starches. The relative degree of crystallinity of tapioca starch is the highest among the polysaccharides studied (~39.4%).

It can also be seen in Fig. 5 that the diffraction patterns of potato, corn, and tapioca starch samples extruded at 140°C are diffuse. The discrete peaks typical of the diffraction patterns of native starches are not observed in the diffraction patterns of extruded starches, which points to complete disintegration of crystallites of the starting native starches in the course of extrusion. Indeed, only an amorphous halo resulting from diffuse scattering from the disordered phase of the polysaccharide is observed in the diffraction patterns of extruded samples. Thus, deep amorphization of the structure of native starches occurs upon extrusion at a temperature as low as 140°C.

A key target physicochemical property of extruded starch products is their solubility in water, which strongly increases upon an extrusion treatment [4, 5]. The results obtained in determining the moisture content of the samples under study and their solubility in cold water are listed in the table.

As can be seen in the table, native starches have the lowest, among all the samples, solubility in cold water, which may be due to presence of insignificant amounts of water-soluble mineral impurities, substances of protein nature, or oligosaccharides.

Extrusion of tapioca starch at 140°C yields a sample that is nearly completely soluble in cold water (99.9%). In addition, it should be noted that, among various kinds of extruded starches, the given sample is best soluble in cold water and yields the most transparent solutions. The only sample with a similar solubility is that of extruded potato starch; however, this sample was obtained under more severe conditions: the extrusion temperature was 170°C. A general pattern characteristic of starches of varied nature can be noted: as the extrusion temperature is raised (from 140 to 170°C), the solubility of modified starches steadily increases, even though reaches different values for different kinds of starch. As can be seen in the table, extrusion least affects the solubility when corn starch is used as the starting sample. As, for example, the extrusion temperature is raised from 140 to 170°C, the solubility increases from 90.3 to 93.3% and remains the lowest among all kinds of extruded starches, whereas elevating the extrusion temperature of potato starch from 140 to 170°C can raise its solubility in cold water from 95.1 to 99.9%.

CONCLUSIONS

(1) High-temperature extrusion of starches of varied biological origin leads to a substantial change of the initial morphological structure: grains of native starches are completely disintegrated to give particles that are tens of times larger and morphologically indeterminate.
(2) Irrespective of the biological origin of starch, particles of extruded samples have about the same morphology. Particles of extruded starches are distinguished by a pronounced surface profile.
(3) Thermomechanical treatment of starch samples of varied origin (potato, corn, and tapioca) in the course of extrusion leads to complete amorphization of native starches.
(4) The solubility of extruded starches in cold water grows by several orders of magnitude, compared with that of native starches and, as the extrusion temperature is raised, increases, all other conditions being the same, in the order: corn starch < potato starch < tapioca starch.

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