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X-ray Diffraction for Detecting Starch Adulteration and Measuring the Crystallinity Indices of the Polymorphic Modifications of Starch

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ABSTRACT

Introduction. Starch is widely used in the food industry and biotechnology, including for manufacturing food packaging materials. Native starches from various sources exist in the form of three polymorphic modifications (A-, B- and C-types) differing in their crystal structure, which has an indirect effect on their physicochemical and technological properties.

Purpose. To properly and efficiently use starch as a raw material for biotechnology, one needs to preliminarily identify its polymorphic modification and crystallinity, as well as detect and discard adulterants or substandard raw materials. X-ray diffraction is suggested to be a rapid and accurate method for solving the outlined problems.

Materials and Methods. In this study, properties of commercial starch from various plant sources (corn, rice, wheat, potatoes, peas, and tapioca) were analyzed by X-ray diffraction and scanning electron microscopy.

Results. Starch of some brands was shown to be adulterated: the more expensive potato starch was replaced with cheaper corn starch. The crystallinity indices were determined for all the selected samples; the crystal structure of corn starch was found to be most highly ordered. Contrariwise, the C-type pea starch was characterized by the lowest degree of crystal structure ordering. The findings obtained in this study show that it is necessary to preliminarily determine the source of starch in order to identify its polymorphic modification, as well as physical and chemical properties by X-ray diffraction.

Conclusions. This information will be demanded for developing the new types of functional foods and reproducing the currently used biotechnologies.

KEYWORDS
starch, crystal structure, polymorphic modifications, crystallinity index, X-ray diffraction, edible packaging, identification, adulterated food

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БИОТЕХНОЛОГИИ

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X-ray дифракция для выявления фальсификатов крахмала и определения степени кристалличности полиморфных модификаций

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АННОТАЦИЯ

Введение. Крахмал широко применяется в пищевой промышленности и биотехнологии, в том числе для изготовления упаковочных материалов для пищевых продуктов. Нативный крахмал из различных источников существует в виде трёх полиморфные модификаций (*A*-, *B*- и *C*-тип) с различной организацией кристаллической структуры, что непосредственно влияет на их физико-химические и технологические свойства.

Цель. Для корректного и эффективного использования крахмала как сырья для биотехнологии требуется предварительное определение полиморфной модификации и степени кристалличности, выявление и отбраковка фальсификатов или некондиционного сырья. Предполагается, что метод рентгеновской дифракции является экспрессным и точным для решения обозначенных задач.

Материалы и методы. В данной работе свойства коммерчески доступного крахмала из различных растительных источников (кукуруза, рис, пшеница, картофель, горох, тапиока) были исследованы с помощью X-ray дифракции и сканирующей электронной микроскопии.

Результаты. Показано, что некоторые торговые марки являются фальсификатом, подменяющим более дорогой картофельный крахмал дешевым кукурузным. Для всех отобранных образцов были определены степени кристалличности, наибольшей упорядоченностью кристаллической структуры обладает кукурузный крахмал. Напротив, наименьшей упорядоченностью кристаллической структуры обладает гороховый, относящиеся к *C*-типу. Результаты исследования указывают на необходимость проведения предварительной идентификации источника крахмала для установления полиморфной модификации и физико-химических свойств методом X-ray дифракции.

Выводы. Полученная информация будет необходима для разработки новых типов функциональных пищевых продуктов и воспроизводстве уже реализуемых биотехнологий.

КЛЮЧЕВЫЕ СЛОВА

крахмал, кристаллическая структура, полиморфные модификации, степень кристалличности, X-ray дифракция, съедобная упаковка, идентификация, фальсификат

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INTRODUCTION

There currently is an increasing interest in environmentally friendly materials for packaging, storage, and transportation of food products, which could potentially replace coatings and packaging produced using petroleum derivatives. The most promising trend is to manufacture edible films and coatings based on biopolymers fabricated using physicochemical methods, while harsh conditions, chemical and biological agents are used to a minimal extent (Li et al., 2020). However, nowadays it is rather challenging to produce biopolymer films complying with the modern requirements posed on the conventional packaging materials, since they are supposed to exhibit comparable performance characteristics (Pogorelov et al., 2019). The strand of research focusing on production of biodegradable starch-based films has been maximally developed (Agarwal et al., 2021; Ballesteros-Martinez et al., 2020).

Native starch granules are semi-crystalline aggregates of amylose and amylopectin consisting of ordered and non-ordered domains (Zhu et a., 2018). The double helix formed by amylopectin chains is connected to the crystalline domains arranged regularly with respect to each other (Vamadevan and Bertfort, 2020). The non-ordered amorphous domains are formed both by amylose chains and by non-ordered domains of branched amylopectin chains (Kim et al., 2020).

There are three main types of polymorphic modifications of native starch. Depending on structural organization of lamellae, starches are subdivided into the *A*-, *B*-, and *C*-types. The *A*- and *B*-types of amylopectin have identical conformation of the helix, while having different unit cells: the orthorhombic one for *A*-type amylopectin and hexagonal one for *B*-type amylopectin (Litvyak et al., 2019). Brief characteristics of the unit cells of starches are summarized in Table 1 (Sarko and Wu, 1978).

Starch and products of its modification are widely used in the food industry as components of preventive nutrition (Lemos et al., 2018; Firdaus et al., 2018; Chevigny et al., 2016; Ferreira et al., 2016). The applicability of starch for designing eco-friendly products can be attributed to its advantages such as renewability, biodegradability, versatility, affordability, and cost. The specific application of starch depends on its physicochemical properties such as the length of α-glucan chains, the degree of branching and crystallinity index, which are the parameters responsible for the granule size, shape, and structure (Lorente-Ayza et al., 2015). Potato starch was found to possess better film-forming properties than other sources of starch due to its greater solubility (Jiang et al., 2020). However, materials based on potato starch with high amylopectin content are extremely sensitive to moisture and mechanical impact (Żołek-Tryznowska and Holica, 2020). The chemical and structural modifications of starch-based nanocrystals have also been widely studied. Along with cellulose, chitin and chitosan nanocrystals, starch nanocrystals are used as polysaccharide fillers for reinforcing composites (e.g., polylactic acid-based nanocomposites) due to their high crystallinity (Jadhav et al., 2020). Starch nanoparticles can also be used as food supplements, drug vehicles, components of glues, plastics, and other biodegradable composites (Espino-Pérez et al., 2016; Garcia et al., 2009).

One of the relevant problems related to food biotechnology is designing special food products or their components that have tailored properties and improved bioavailability to compensate for deficiencies of essential nutrients (Rastogi and Bhatia, 2019).Controlled variation in crystallinity allows one to obtain a more reactive product possessing improved mechanical properties, since the crystallinity index of native starches depends on their source and varies broadly from 15% to 45% (Rodrigues et al., 2020; Litvyak et al., 2019; Pozo et al., 2018; Bajer et al., 2013). We have previously shown that the efficiency of native starch amorphization depends

Table 1
Brief characteristics of the polymorphic modifications of starch

Type	a, Å	b, Å	c, Å	α, °	β, °	γ, °	Source
A	11.90	17.70	10.52	90	90	90	Corn (Luchese et al., 2017), wheat (Alay and Meireles, 2015), rice (Nara et al., 1978)
B	18.50	18.50	10.40	90	90	120	Potato (Singh et al., 2006), banana (Chavez-Salazar et al., 2017), sago (Katsumi et al., 2015)
C	18.50	18.50	10.47	90	90	120	Soybean (Purohit et al., 2019), tapioca (Singh et al., 2006), chickpea (Ghosal and Kaushal, 2019)

Note. a, b, and c are the unit cell parameters; α, β, γ are the angles formed between the edges of a unit cell.

on the type of the crystalline structure of starch (Author et al., 2020). Findings on the efficiency of mechanical activation of starch-containing raw materials have also been obtained (Author et al., 2022).

The initial step to identify the range of applicability of starch should involve confirming the type of polymorphic modifications of starch from various plant sources (corn, rice, wheat, potatoes, peas, and tapioca), measuring the crystallinity index, as well as potentially identifying and discarding adulterants and substandard raw materials.

MATERIALS AND METHODS

Thirty samples of commercially available starches (see Table 2) derived from various plant sources (corn, rice, wheat, potato, peas, and tapioca) were used as study objects.

The morphology of the selected starch samples was characterized by scanning electron microscopy (SEM) on a TM-1000 microscope (Hitachi, Japan) at a voltage of 15 kV; gold was pre-deposited onto the surface of the material on a JFC-1600 magnetron sputtering machine (Jeol, Japan). The sputtering time was 30 s; ion current was 30 mA.

The structural properties of starches were characterized by X-ray diffraction on a D8 Advance powder diffractometer (Bruker, Germany) with monochromatic CuKα radiation in the Bragg–Brentano reflection geometry. The step size was 0.0195°. The analysis was performed within a wide range of 2θ angles (3÷70°) at a voltage of 40 kV and current of 40 mA. X-ray wavelength was 1.5406 Å.

Amorphous standards were obtained for each sample by prolonged mechanical activation of native samples in an AGO-2 planetary ball mill (20 *g*) identically to the procedure described in ref. (Author et al., 2020). The activation time was 10 min.

The crystallinity indices of starches under study were calculated using the procedure proposed by Nara and Komiya (Frost, 2009; Nara et al., 1978). A fit curve connecting the base lines of the peaks was plotted on the recorded XRD pattern (see Figure 1). The area above the fit curve corresponded to the crystalline portion of starch, and the area below the curve corresponded to its amorphous portion.

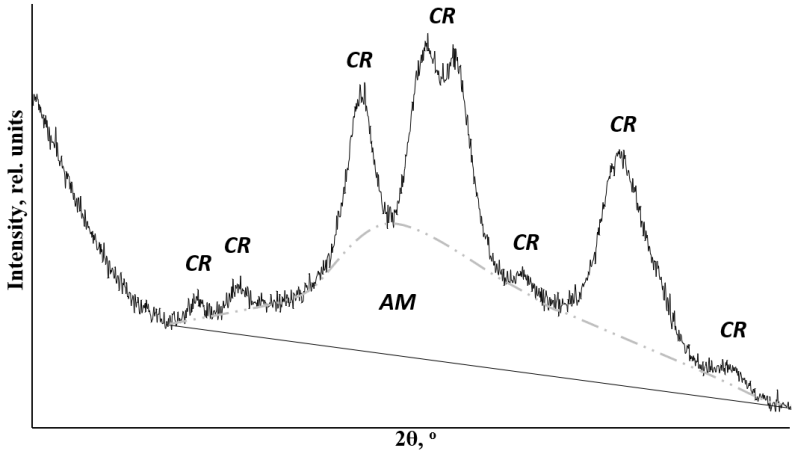
The crystallinity index (*CI*) was calculated as the ratio between the area of the crystalline phase and the total area under the XRD curve using the formula:

$$CI = \frac{S_{cr.phase}}{S_{total}} \cdot 100\ \%, \quad (1)$$

where $S_{cr.phase}$ is the area of crystalline phase and S_{total} is the total area below the XRD pattern curve.

Figure 1

Graphic illustration of the method used to calculate the crystallinity index of starch



Note. ***CR*** – the crystalline phase; ***AM*** – the amorphous phase.

RESULTS

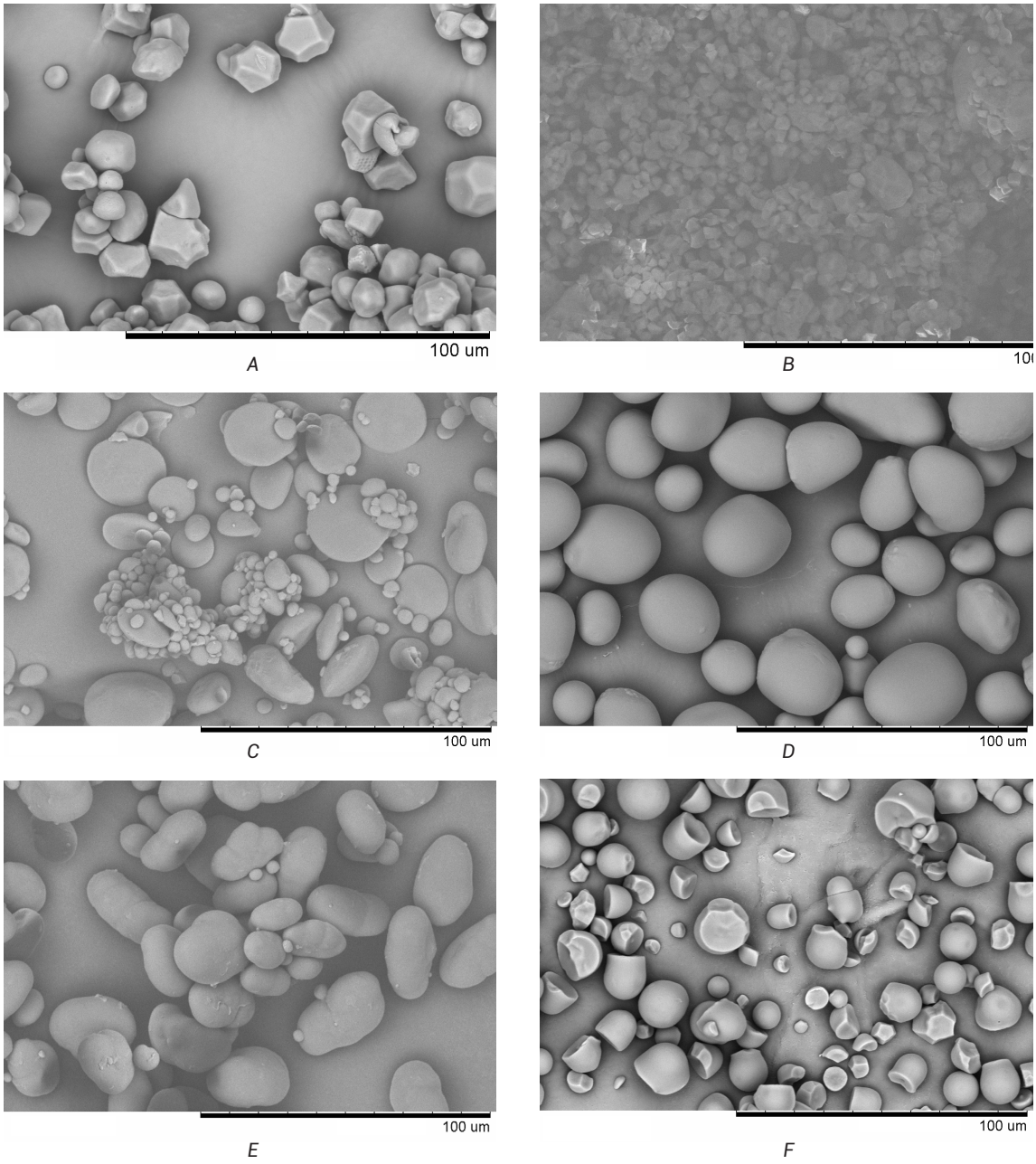
The microimages of the analyzed starches having different crystal structures were recorded by electron microscopy (Figure 2).

Figures 3A-C show the X-ray diffraction patterns recorded for the analyzed starches depending on the type of crystal structure.

Table 2 lists the crystallinity indices for the 30 analyzed starch samples.

Figure 2

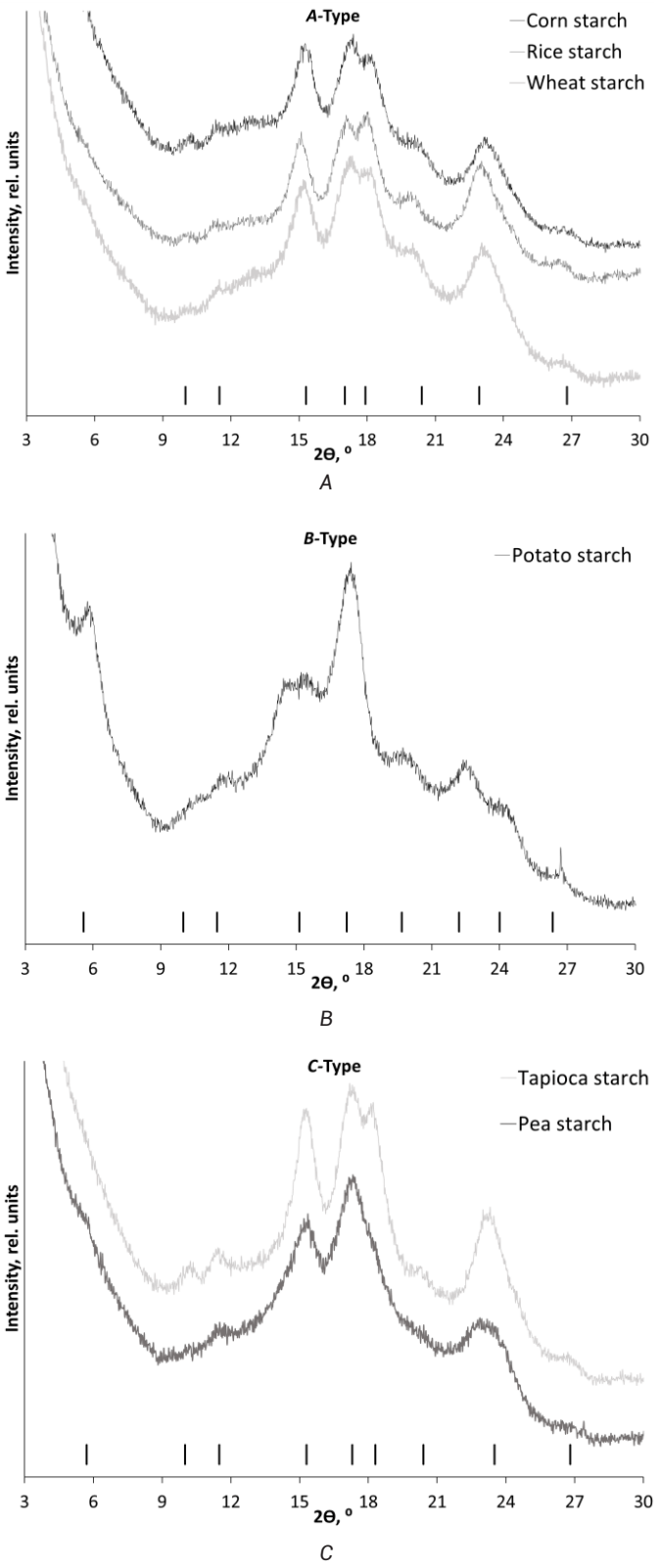
SEM images of *A*-, *B*-, and *C*-type starches obtained from different sources



Note. A-type starches: A – corn starch, B – rice starch, and C – wheat starch; B-type starch: D – potato starch; C-type starches: E – pea starch and F – tapioca starch.

Figure 3

Examples of X-ray diffraction patterns typical of *A*-, *B*-, and *C*-type starches



Note. *A*: X-ray diffraction patterns of corn, rice, and wheat starches; *B*: X-ray diffraction pattern of potato starch; *C*: X-ray diffraction patterns of tapioca and pea starches.

Table 2

Crystallinity indices of starches depending on their source and type of crystal structure

No.	Polymorphic type	Source	Country of manufacture	CI, %
1	A	Corn	France	45 ± 1
2			France	42 ± 3
3			Russia	43 ± 3
4			Russia	42 ± 2
5			Russia	42 ± 3
6			Russia	40 ± 2
7			Russia	37 ± 2
8			Russia	39 ± 2
9			Russia	41 ± 3
10			Russia	41 ± 2
11		Rice	Vietnam	39 ± 2
12		Wheat	China	35 ± 2
13	B	Potato	Finland	40 ± 3
14			Russia	40 ± 3
15			Russia	36 ± 2
16			Russia	40 ± 4
17			Russia	37 ± 2
18			Russia	38 ± 4
19			Russia	38 ± 3
20			Russia	41 ± 2
21			Russia	36 ± 3
22			Russia	40 ± 2
23			Russia	37 ± 1
24			Russia	42* ± 3
25			Russia	42* ± 3
26			Russia	38* ± 2
27			Russia	40* ± 2
28	C	Tapioca	Russia	41 ± 2
29		Peas	Russia	26 ± 3
30			China	29 ± 2

Note. CI – crystallinity index. * – Starch mismatches the declared type of polymorphic modification.

DISCUSSION

The polymorphic modifications of starch have different crystal structures and different crystallinity indices (the ratio between the number of crystalline and amorphous regions) in particular. Starch that was already amorphized is often used in food industry as a thickener, a stabilizer, a gelling agent, a food filler, or a water retention agent. The amorphized starch can also be used for manufacturing biodegradable films to store the finished product. As shown earlier (Author et al., 2020), mechanical pretreatment of potato (*B*-type) starch requires less energy than pretreatment of corn (*A*-type) or tapioca (*C*-type) starch does. In order to enhance the efficiency of starch application in the food industry, one needs to acquire information about the polymorphic modification and crystallinity index of starch being used.

Granules of the *A*-type corn and rice starches have an irregular polyhedral shape (see Figure 2A-B). Granules of wheat starch (see Figure 2C) are different: they have a flattened round shape and can form aggregates under normal storage conditions. Granules of *B*-type potato starch are preferentially shaped as spheres or ellipsoids and have a smooth surface characterized by slight roughness (see Figure 2D). Granules of *C*-type starches have different structures depending on their source. Thus, granules of pea starch are likely to have an elliptical shape (see Figure 2E), while granules of tapioca starch (see Fig. 2F) are irregularly shaped.

The XRD patterns of corn, rice, and wheat starches contain diffraction peaks characteristic of *A*-type starch at (*2θ*): 15.00°, 17.02°, 17.92°, and 22.93° (Munoz, 2015; Singh et al., 2006). The XRD pattern of potato starch contains diffraction peaks characteristic of *B*-type starch at (*2θ*): 5.58°, 15.13°, 17.23°, 19.67°, 22.20°, 24.00°, and 26.35° (Munoz, 2015; Singh et al., 2006). The polymorphic modification of *C*-type starch is a mixed crystal structure: a starch granule has a hilum with a *B*-type structure surrounded with *A*-type crystallites (Zobel, 1988). Therefore, crystallites having different structures coexist. The XRD patterns of pea and tapioca starches recorded in the Bregg–Brentano geometry contain the following characteristic diffraction peaks at (*2θ*): 5.58°, 15.15°, 17.12°, 18.19°, and 22.78° (Munoz, 2015; Singh et al., 2006).

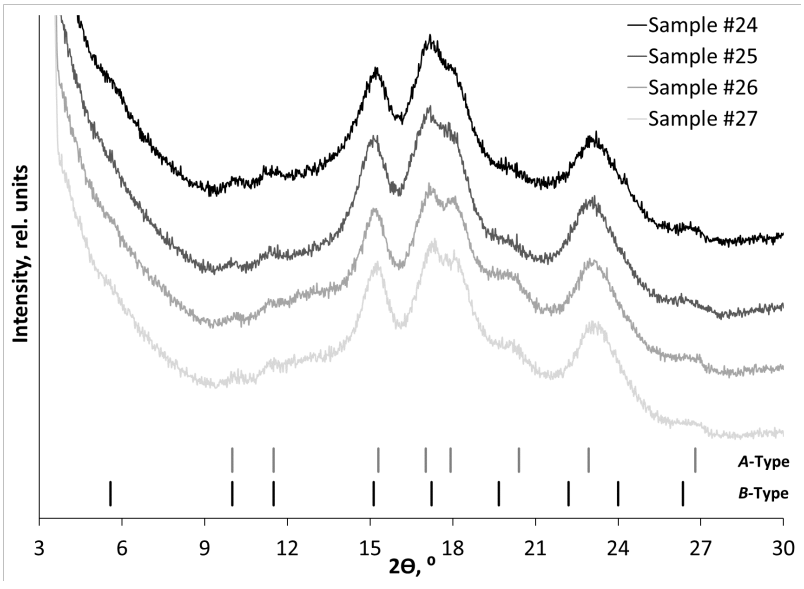
X-ray diffraction analysis revealed a mismatch of the crystal structures of declared potato starch for a number of brands (see samples Nos. 24–27 in Table 2). Figure 4 shows the XRD patterns of isolated samples compared to the theoretical profiles of the *A*- and *B*-type polymorphic modifications. The XRD patterns recorded for these potato starch samples were shown to contain diffraction peaks typical of *A*-type starch. The difference in costs of potato and corn starches (the average cost of potato starch is 1.1–1.2-fold higher than that of corn starch) gives grounds to assume that the analyzed packages contained corn starch.

CONCLUSIONS

The findings obtained in this study prove that X-ray diffraction can be used not only to routinely determine the crystallinity index of starch but also to identify its crystal structure,

Figure 4

X-ray diffraction patterns of samples Nos. 24-27 and the diffraction peak profiles typical of *A*- and *B*-type starch



thus affecting the choice which source of starch to use (e.g., corn, rice, wheat, potatoes, peas, tapioca, etc.).

Identifying the samples of commercial starch of different brands has revealed a number of mismatches: the starch declared to be potato starch by the manufacturer was actually corn starch. The crystallinity indices were determined. The *A*-type corn starch was found to have the most highly ordered crystal structure. Contrariwise, the lowest ordering of crystal structure was revealed for the *C*-type pea starch.

This information can be used when developing the novel types of safe functional foods characterized by better nutrient bioavailability.

AUTHOR CONTRIBUTIONS

E. M. Podgorbunskikh: conceived and designed the analysis, designed the method and its analysis, contributed data or analysis tools, performed the analysis, wrote the paper

K. V. Dome: conceived and designed the analysis, designed the method and its analysis, contributed data or analysis tools, performed the analysis, wrote the paper

V. A. Buchtoyarov: conceived and designed the analysis, contributed data or analysis tools, performed the analysis, wrote the paper

A. L. Bychkov: conceived and designed the analysis, designed the method and its analysis, contributed data or analysis tools, wrote the paper

REFERENCES

Agarwal, S., Singhal, S., Godiya, C. B., Kumar, S. (2021). Prospects and applications of starch based biopolymers *International. Journal of Environmental Analytical Chemistry,* 1963717. https://doi.org/10.1080/03067319.2021.1963717

Alay, S. C. A., & Meireles, M. A. A. (2015). Physicochemical properties, modifications and applications of starches from different botanical sources. *Food Science and Technology (Campinas), 35*, 215–236. https://doi.org/10.1590/1678-457X.6749

Bajer, D., Kaczmarek, H., & Bajer, K. (2013). The structure and properties of different types of starch exposed to UV radiation: A comparative study. *Carbohydrate Polymers, 98*, 477–482. https://doi.org/10.1016/j.carbpol.2013.05.090

Ballesteros-Martinez, L., Perez-Cervera, C., & Andrade-Pizzaro, R. (2020). Effect of glycerol and sorbitol concentrations on mechanical, optical, and barrier properties of sweet potato starch film. *NFS Journal, 20*, 1–9. https://doi.org/10.1016/j.nfs.2020.06.002

Chavez-Salazar, A., Bello-Perez, L. A., Agama, E., Castellanos-Galeano, F. J., & Alvarez-Barreto, C. I. (2017). Isolation and partial characterization of starch from banana cultivars grown in Colombia. *International Journal of Biological Macromolecules, 98*, 240–246. https://doi.org/10.1016/j.ijbiomac.2017.01.024

Chevigny, C., Foucat, L., Rolland-Sabate, A., Buleon, A., & Lourdin D. (2016). Shape-memory effect in amorphous potato starch: The influence of local orders and paracrystallinity. *Carbohydrate Polymers, 146*, 411–419. https://doi.org/10.1016/j.carbpol.2016.03.065

Dome, K., Podgorbunskikh, E., Bychkov, A., & Lomovsky, O. (2020). Changes in the crystallinity degree of starch having different types of crystal structure after mechanical pretreatment. *Polymers, 12*, 641. https://doi.org/10.3390/polym12030641

Dome, K., Podgorbunskikh, E., Bychkov, A., & Lomovsky, O. (2022). Influence of mechanical treatment on the crystalline structure of pea starch. *AIP Conference Proceedings*, *2390*(1), # 030013. https://doi.org/10.1063/5.0069197

Espino-Pérez, E., Gilbert, R.G., Domenek, S., Brochier-Salon, M.C., Belgacem, M.N., & Bras, J. (2016). Nanocomposites with functionalised polysaccharide nanocrystals through aqueous free radical polymerisation promoted by ozonolysis. *Carbohydrate Polymers, 135*, 256–266. https://doi.org/10.1016/j.carbpol.2015.09.005

Ferreira, A. R. V., Alves, V. D., & Colehoso, I. M. (2016). Polysaccharide-based membranes in food packaging applications. *Membranes, 6*, 1–17. https://doi.org/10.3390/membranes6020022

Firdaus, J., Sulistyani, E., & Subagio, A. (2018). Resistant starch modified cassava flour (MOCAF) improves insulin resistance. *Asian Journal of Clinical Nutrition, 10*, 32–36. https://doi.org/10.3923/ajcn.2018.32.36

Frost, K., Kaminski, D., Kirwan, G., Lascaris, E., & Shanks, R. (2009). Crystallinity and structure of starch using wide angle X-ray scattering. *Carbohydrate Polymers, 78*, 543–548. https://doi.org/10.1016/j.carbpol.2009.05.018

Garcia, N. L., Ribba, L., Dufresne, A., Aranguren, M. I., & Goyanes, S. (2009). Physico-mechanical properties of biodegradable starch nanocomposites. *Macromolecular Materials and Engineering, 294*, 169–177. https://doi.org/10.1002/mame.200800271

Ghosal, G., & Kaushal, K. (2019). Extraction, characterization, physicochemical and rheological properties of two different varieties of chickpea starch. *Legume Science, 2*, 17. https://doi.org/10.1002/leg3.17

Jadhav, H., Jadhav, A., Takkalkar, P., Hossain, N., Nizammudin, S., Zahoor, M., Jamal, M., Mubarak, N. M., Griffin, G., & Kao, N. (2020). Potential of polylactide based nanocompos-

ites-nanopolysaccharide filler for reinforcement purpose: a comprehensive review. *Journal of Polymer Research, 27*, 330. https://doi.org/10.1007/s10965-020-02287-y

Jiang, F., Du, C., Jiang, W., Wang, L., & Du, S. (2020). The preparation, formation, fermentability, and applications of resistant starch. *International Journal of Biological Macromolecules, 150*, 1155–1161. https://doi.org/10.1016/j.ijbiomac.2019.10.124

Katsumi, N., Okazaki, M., Yonebayashi, K., Kawashima, F., Nishiyama, S., & Nishi, T. (2015). Chemical and physical characterizations of cooked rice using different cooking methods. *Sago Palm, 22*, 25–30. https://doi.org/10.12691/jfnr-8-11-4

Kim, H. R., Choi, S. J., Choi, H., Park, C., & Moon, T. W. (2020). Amylosucrase-modified waxy potato starches recrystallized with amylose: The role of amylopectin chain length in formation of low-digestible fractions. *Food chemistry, 318*, 126490. https://doi.org/10.1016/j.foodchem.2020.126490

Lemos, P. V. F., Barbosa, L. S., Ramos, I. G., Coelho, R. E., & Druzian J. I. (2018). The important role of crystallinity and amylose ratio in thermal stability of starches. *Journal of Thermal Analysis and Calorimetry, 131*, 2555–2567. https://doi.org/10.1007/s10973-017-6834-y

Li, C., Sheng, L., Sun, G., & Wang, L. (2020). The application of ultraviolet-induced photo-crosslinking in edible film preparation and its implication in food safety. *Lwt — Food Science and Technology, 131*, 109791. https://doi.org/10.1016/j.lwt.2020.109791

Litvyak, V., Sysa, A., Batyan, A., & Kravchenko, V. (2019). Features of the formation of taste sensations. *Ukrainian Food Journal, 8*, 597–619. https://doi.org/10.24263/2304-974X-2019-8-3-15

Lorente-Ayza, S. M. M. M., Orts, M. J., & Pérez-Herranz, V. (2015). Role of starch characteristics in the properties of low-cost ceramic membranes. *Journal of the European Ceramic Society, 35*, 2333–2341. https://doi.org/10.1016/j.jeurceramsoc.2015.02.026

Luchese, C. I., Spada, J. C., & Tessaro, I. C. (2017). Starch content affects physicochemical properties of corn and cassava starch-based films. *Industrial Crops and Products, 109*, 619–626. https://doi.org/10.1016/j.indcrop.2017.09.020

Munoz, L. A., Pedreschi, F., Leiva, A., & Aguilera, J. M. (2015). Loss of birefringence and swelling behavior in native starch granules: Microstructural and thermal properties. *Journal of Food Engineering, 152*, 65–71. https://doi.org/10.1016/j.jfoodeng.2014.11.017

Nara, S., Mori, A., & Komiya, T. (1978). *Study on relative crystallinity of moist potato starch. Starch, 4*, 111–114. https://doi.org/10.1002/star.19780300403

Pogorelov, A. G., Kuznetsov, A. L., Pogorelova, V. N., Suvorov, O. A., Panait, A. I., & Pogorelova M. A. (2019). Destruction of a bacterial biofilm with an electrochemically activated solution. *Biophysics, 64*, 583–587. https://doi.org/10.1134/S000635091904016X

Pozo, C., Rodriguez-Llamazares, S., Bouza, R., Barral, L., Castano, J., Muller, N., & Restrepo, I. (2018). Study of the structural order of native starch granules using combined FTIR and XRD analysis. *Journal of Polymer Research, 25*, 266. https://doi.org/10.1007/s10965-018-1651-y

Purohit, S., Jayachandran, L. E., Raj, A. S., Nayak, D., & Rao, P. S. (2019). X-ray-diffraction for food quality evaluation, In J. Zhong, X. Wang (Eds.), *Evaluation Technologies for Food Quality, 1st ed.* (914 p.). Woodhead Publishing.

Sarko, A., & Wu, C. H. (1978). The crystal structures of A-, B- and C-polymorphs of amylose and starch. *Starch, 30*, 73–78. https://doi.org/10.1002/star.19780300302

Rastogi, H., & Bhatia, S. (2019). Future prospectives for enzyme technologies in the food industry. In M. Kuddus (Ed.), *Enzymes in food biotechnology*. Academic Press.

Rodrigues, S. C. S., da Silva, A. S., de Carvalho, L. H., Alves, T. S., & Barbosa, R. (2020). Morphological, structural, thermal properties of a native starch obtained from babassu mesocarp for food packaging application. *Journal of Materials Research and Technology, 9*, 15670–15678. https://doi.org/10.1016/j.jmrt.2020.11.030

Shi, M., Jing, Y., Yang, L., Huang, X., Wang, H., Yan, Y., & Liu, Y. (2019). Structure and physicochemical properties of malate starches from corn, potato, and wrinkled pea starches. *Polymers, 11*, 1523. https://doi.org/10.3390/polym11091523

Shusaku, N., Horiuchi, S., Ikehata, A., & Ogawa, Y. (2021). Determination of starch crystallinity with the Fourier-transform terahertz spectrometer. *Carbohydrate Polymers, 262*, 117928. https://doi.org/10.1016/j.carbpol.2021.117928

Singh, V., Ali, S. Z., Somashekar, R. & Mukherjee, P. S. (2006). Nature of crystallinity in native and acid modified starches *International Journal of Food Properties, 9*, 845–854. https://doi.org/10.1080/10942910600698922

Thakur, R., Pristijono, P., Scarlett, C. J., Bowyer, M., Singh, S. P., & Vuong, Q. V. (2019). Starch-based films: Major factors affecting their properties. *International Journal of Biological Macromolecules, 132*, 1079–1089. https://doi.org/10.1016/j.ijbiomac.2019.03.190

Vamadevan, V., & Bertfort, E. (2020). Observations on the impact of amylopectin and amylose structure on the swelling of starch granules. *Food Hydrocolloids, 103*, 105663. https://doi.org/10.1016/j.foodhyd.2020.105663

Zhang, D., Chen, L., Dong, Q., Din, Z., Hu, Z., Wang, G., Ding, W., He, J., & Cheng, S. (2021). Starch/tea polyphenols nanofibrous films for food packaging application: From facile construction to enhance mechanical, antioxidant and hydrophobic properties. *Food Chemistry, 360*, 129922. https://doi.org/10.1016/j.foodchem.2021.129922

Zhu, X., He, Q., Hu, Y., Huang, R., Shao, N., & Gao, Y. (2018). A comparative study of structure, thermal degradation, and combustion behavior of starch from different plant sources. *Journal of Thermal Analysis and Calorimetry, 132*, 927–935. https://doi.org/10.1007/s10973-018-7030-4

Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch, 40*. 1–7. https://doi.org/10.1002/star.19880400102

Żołek-Tryznowska, Z., & Holica, J. (2020). Starch films as an environmentally friendly packaging material: Printing performance. *Journal of Cleaner Production, 276*, 124265. https://doi.org/10.1016/j.jclepro.2020.12426