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Technological Properties of Tritordeum Starch

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Abstract: Tritordeum is a new promising cereal derived from wild barley and cultivated durum wheat; such a combination allowed for the transfer of some useful barley traits to the resulting hybrid. In the future, the importance of this cereal can increase, becoming a raw material for the production of various products, including starch. So far, tritordeum starch has attracted little interest from researchers, and therefore, an attempt was undertaken to investigate its properties. Its morphological features, chemical composition, thermal and pasting properties, particle size, and retrogradation kinetics were investigated. These properties were compared to other cereal starches. Tritordeum starch granules resembled wheat starch in shape, and they were characterized by a relatively small size and the highest lipid and non-starch material content among the investigated starches. Tritordeum starch's pasting profile showed a unique character, resulting in high pasting temperature and low, but stable, hot paste viscosity. Also, its rate of retrogradation was the lowest, probably due to the high lipid content, and the retrogradation extent was restricted.

Keywords: tritordeum starch; chemical composition; particle size; thermal properties; pasting properties; retrogradation

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1. Introduction

Drought is an important abiotic stress influencing crop production, including cereals, and it is anticipated to increase with ongoing climate change. Recently, cereal breeders focused their efforts on the creation of interspecific hybrids to obtain new cereals with improved phytochemical contents and agronomic performances. Tritordeum is the cereal derived from the cross between a South American wild barley (*Hordeum chilense Roem. et Schultz.*) and a cultivated durum wheat (*Triticum turgidum ssp. durum Desf.*). It allowed for transferring useful barley traits to wheat, and a new cereal crop was developed [1,2]. Tests conducted in Central European climatic conditions proved that winter tritordeum is more suitable for cultivation due to a higher yield. Although the protein content in tritordeum was higher than in wheat, due to its poor baking properties, the obtained breads were characterized by a lower loaf volume compared to wheat. This could suggest that this crop would be more suitable for feeding purposes [3].

The main component of cereal kernels is starch, which is a storage carbohydrate, and it constitutes more than half of their dry mass, which makes them a perfect raw material for industrial starch separation. Starch can be obtained during the industrial separation of other valuable components like gluten or β-glucans [4,5]. Tritordeum contains higher amounts of protein and gluten than its wheat progenitor and could become a raw material suitable for gluten separation; therefore, starch can be obtained as a by-product of such an operation.

Native starch occurs in the form of semi-crystalline granules with very distinctive shape and dimensions depending on their botanical origin. Its functional properties are strongly influenced by its botanical origin and result from its characteristics like granule size, chemical composition, and internal structure. The presence of lipids has an especially great impact on starch properties such as water binding capacity, pasting phenomena, or retrogradation [4,6–8]. Starch in most applications is used as a water-governing agent and is responsible for creating texture. A small presence (0.4%) of minerals (calcium, magnesium, phosphorus, potassium, and sodium) can be observed in starches, and except for phosphorus, they have almost no functional significance.

Starch finds really broad applications in different branches of industry. Starches are applied in food formulations due to their impact on viscosity, paste and gel formation, texture creation, the binding of water, moisture retention, or film formation. Therefore, starches are broadly used in formulations of soups, sauces and gravies, bakery products (starch is the main component of flours), dairy confectionery, snacks, batter and coatings, and meat products [9,10].

The increasing industrial demand for starches suited for specific applications results in the search for new sources. So far, tritordeum starch has not attracted much interest from researchers. However the introduction of this cereal into broader cultivation, due to its specific features, could lead to a situation in the future in which tritordeum will become the raw material for gluten separation. Then, large amounts of starch will also be produced. Therefore, an attempt was undertaken to investigate some basic properties of starch isolated from tritordeum and compare them to other cereal starches.

2. Materials and Methods

2.1. Materials

Tritordeum kernels of the Bulel variety (formerly breeding line HT1608) were supplied by Agrasys SL (Barcelona, Spain); durum wheat (Pentadur variety) was grown in an experimental station (Prusy, Poland); common wheat of the Artist variety was bought from a local supplier. Also, commercial flours, wheat, barley, and, buckwheat (PZZ, Kraków, Poland), were used.

2.2. Methods

2.2.1. Isolation of Starches

Tritordeum and wheat kernels were tempered to 14% moisture, and they were milled in a Brabender Quadrumat mill (Duisburg, Germany).

Tritordeum and wheat starches were isolated according to the modified Czuchajowska and Pomeranz method using a 1% NaCl solution. The modification included a hand-washing procedure, to avoid starch granule damage, except for high-speed blending. For barley starch, the Paton method was applied [4]. Buckwheat starch was separated as described by Liu et al. [11].

Isolated starches were denoted as BaS (barley), BuS (buckwheat), and TrS (tritordeum), and for wheat starches, WaS (isolated from regular Artist variety), WdS (isolated from durum Pentadur variety), and WhS (wheat isolated from commercial wheat flour).

2.2.2. Analytical Determinations

Chemical Composition of Starches

Ash was determined according to procedure 930.22. The amount of protein was calculated by multiplying % N × 5.7 (950.36); the lipid content (930.05) was analyzed according to the AOAC procedure, whereas the apparent amylose content was measured according to Morrison and Laignelet [4]. The phosphorus content was evaluated according to the ISO 3946:2000 standard [12].

Color Measurement

The color parameters were measured by an instrumental method in the CIE L*a*b* system using a spectrophotometer Konica Minolta CM5 [10]. In this scale, L* describes lightness, and the value ranges from 0 (black) to 100 (white). Factor a* describes the red–green axis, with negative values representing green and positive values representing red, and b* describes the blue–yellow axis, with negative values representing blue and positive values representing yellow. The values of a* and b* range from −128 to +128.

Data on the whiteness index (WI) were obtained as follows:

$$WI = \sqrt{(100 - L^{*2}) + a^{*2} + b^{*2}} \quad (1)$$

and the color difference ΔE* was calculated:

$$\Delta E^{*} = \sqrt{\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}} \quad (2)$$

Granule Morphology

The morphology of native starches was studied by scanning electron microscopy. The starch samples were applied to a graphite sticker, placed on an aluminum table, sputtered with gold (90 s), and observed using a scanning electron microscope (Hitachi VP-SEM S-3400 N, Tokyo, Japan, accelerating voltage 25 kV).

Particle Size Distribution

The particle size distribution (PSD) of starches was measured using video-enhanced microscopy (VEM) as previously described [10]. The starch samples were stained with iodine solution on glass microscopic plates and were analyzed using a Nikon Eclipse E200 microscope (Nikon Instruments Inc., Tokyo, Japan) coupled with a digital camera (GKB high-resolution ccd camera, CC-8706S, Taichung, Taiwan). At least 200 micrographs were recorded. The obtained micrographs were subjected to image analysis using the open-source software ImageJ (v. 3.17). PSD was calculated on an equivalent diameter basis.

Thermal Properties

The thermal properties of the investigated starches were studied by employing a Shimadzu DSC-60 differential scanning calorimeter (DSC). Starch was mixed with distilled water at a ratio of 1:3 and allowed to equilibrate overnight. The heating procedure was performed within the 20–100 °C range, and the temperature increase was set at 10 °C/min. An empty pan was applied as a reference [10].

Pasting Properties

Starch pasting properties were studied on 5% (*w*/*w*) starch suspensions using a Micro Visco Amylo-Graph (Brabender, Duisburg, Germany) [10]. Starch dispersions were pasted using the following temperature profile: initial temperature of 45 °C, heating to 95 °C, holding for 10 min, cooling to 50 °C, and holding for another 10 min. The heating and cooling rate was 4.5 °C /min, and the measuring cylinder rotated at 150 rpm. The obtained data were analyzed using the instrument's software Data Correlator. The following points of the pasting curve were analyzed: PT—pasting temperature (temperature at which an initial increase in viscosity was observed); PV—peak viscosity (maximum viscosity observed during the initial phase of the measurement); tPV—time to peak viscosity; TPV—temperature at PV; MV—minimum viscosity observed at the end of the high-temperature holding period; TV—trough viscosity (viscosity observed at the beginning of the second hold period, when the final temperature was reached (50 °C)); FV—final viscosity observed at the end of measurement; BD—breakdown (a decrease in viscosity during the first holding period (BD = PV − MV)); SB—setback (an increase in viscosity during the cooling period (SB = TV − MV)); BD% = (PV − MV)/PV; SB% = (TV − MV)/TV; and HPSI—hot paste stability index (HPSI = Ac/Ap), where Ac is an area under a pasting curve

measured between PV and the end of the holding period, and Ap is the area of a hypothetical rectangle, with the height of PV, and the other side is the distance between the peak viscosity and the end of holding period (the same value as for Ac).

To evaluate and describe the initial stage of the pasting phenomenon, a logistic model was applied [9]:

$$V = \frac{V_{peak} \cdot t^s}{R^s + t^s} \quad (3)$$

where
V—viscosity during processing;
V_{peak}—peak viscosity;
T—processing time parameter;
R—the time that gives rise to 50% of peak viscosity;
s—starch coefficient.

Retrogradation

Retrogradation was measured as turbidance changes of 2% starch pastes. To study retrogradation kinetics, the Avrami equation was applied [13]. To enable the direct comparison among all investigated starches, the equation exponent n was set as 1, and the final form of the equation was

$$\Delta A_t = \Delta A_\infty - (\Delta A_\infty - \Delta A_0) \cdot e^{-kt^n} \quad (4)$$

where
t—time;
ΔA_0—turbidance at zero time;
ΔA_∞—turbidance at ∞ time;
K—rate constant;
n—equation exponent (n =1).

2.2.3. Statistical Evaluation of Results

To determine statistically significant differences among the means, we performed an analysis of variance (ANOVA), and the least significant difference (LSD) at the significance level of 0.05 was calculated using the Tukey test. Calculations were performed using Statistica 12.0 (StatSoft Inc., Tulsa, OK, USA). All analyses were performed in duplicate.

3. Results and Discussion

3.1. Chemical Composition

Data related to the chemical composition of the investigated cereal starches are presented in Table 1.

Except for carbohydrate material, cereal starch granules contain small amounts of other components, like proteins, lipids, pentosans, and minerals. Among them, proteins and lipids are present in larger quantities and have an influence on starch properties. Their content depends on both the botanical origin of the starch and its degree of purification during extraction. Although these constituents are deemed minor, their presence significantly affects both the properties of the starch and the properties of starch-derived products. Their presence results in delayed and restricted granular swelling, leading to the creation of less viscous pastes. Also, it manifests as a lower transparency of the resulting pastes and gels, which can be considered as a drawback in some applications. On the other hand, they play a crucial role in retarding starch retrogradation [6–8,14].

Table 1. Chemical composition of investigated starches.

Sample	Chemical Composition [%]				
	Protein	Lipid	AAM	Ash	P
BaS	1.01 ± 0.01 ^{d}	0.74 ± 0.01 ^{d}	19.2 ± 0.03 ^{b}	0.10 ± 0.00 ^{a}	0.025 ± 0.001 ^{a}
BuS	1.30 ± 0.01 ^{e}	0.62 ± 0.04 ^{c}	22.4 ± 0.01 ^{e}	0.41 ± 0.00 ^{e}	0.066 ± 0.001 ^{d}
TrS	1.55 ± 0.01 ^{f}	0.91 ± 0.03 ^{e}	18.7 ± 0.02 ^{a}	0.35 ± 0.00 ^{d}	0.063 ± 0.001 ^{d}
WaS	0.68 ± 0.02 ^{c}	0.36 ± 0.03 ^{b}	20.5 ± 0.1 ^{c}	0.26 ± 0.01 ^{c}	0.047 ± 0.001 ^{b}
WdS	0.51 ± 0.03 ^{b}	0.41 ± 0.03 ^{b}	27.3 ± 0.12 ^{f}	0.29 ± 0.01 ^{c}	0.054 ± 0.001 ^{c}
WhS	0.25 ± 0.01 ^{a}	0.21 ± 0.03 ^{a}	20.9 ± 0.08 ^{d}	0.22 ± 0.01 ^{b}	0.046 ± 0.000 ^{b}

Values with similar superscripts in the column do not differ significantly ($p < 0.05$). P—phosphorus; AAM—apparent amylose; Ash—mineral compounds.

The protein content in investigated starches was in a broad range (Table 1), reaching the highest amount (1.55%) for tritordeum starch (TrS). Except for TrS, protein content over 1% was also observed for buckwheat and barley starches, whereas in wheat starches, it was much lower, below 1%. According to data from the literature, the protein content in barley starch is usually within the 0.14–1.26% range [15–18], whereas for buckwheat starch, it is 0.16–1.35% [19–21]. For wheat starch, the protein content was observed to be within the 0.16–0.86% range [6,20,22]. High protein content could be linked both to the purification procedure and starch granule bounded protein, like remnants of starch synthesizing enzymes [6–8,14]. In this aspect, tritordeum starch is much more similar to barley starch than wheat ones.

The lipid content in all investigated samples was below 1% (Table 1), and it is essentially consistent with data from the literature for barley (0.10–1.2%) [15–18], wheat (0.25–0.80%) [6,22], and buckwheat (0.1–1.30) [20,21] starches. Tritordeum starch was noted to have the highest lipid content among the investigated starches, and it was far more similar in this aspect to BaS than to wheat starches, with a lipid content over two times lower.

Starch granules are mostly composed of two types of alpha-glucan, amylose (AM) and amylopectin (AP), which represent approximately 98–99% of their dry weight. The ratio of these two polysaccharides varies according to the botanical origin of the starch, and it influences starch properties. The AM/AP ratio influences crystallinity, swelling, gelatinization temperature, and the pasting/gelling behavior of starches. Basically, AM as an essentially linear polymer with a lower molecular mass is leached out of swelling starch granules when heated in water, and is responsible for gelling properties and short-term retrogradation. On the other hand, AP is a highly branched polymer responsible for water binding, the creation of starch paste, and long-term retrogradation [6–8,14].

The apparent amylose (AAM) content in the investigated material was within the broad range, with the lowest value of 18.72% observed for TrS. The other starch with the closest AAM content was BaS (Table 1), slightly over 1% more. For the remaining investigated starches, this value was over 20%. Data from the literature related to amylose content are given in a broad range—17.6–31.00% for barley, 18.2–34.7% for wheat [6,17–19,22], and 3.8–46.6% for buckwheat [19,21]—but usually, values of about 20% are observed.

The mineral compound (ash) content in the investigated cereal starches was within a relatively narrow range (Table 1). The observed values are within the range of data for barley (0.09–0.40%) [16,21], wheat (0.13%) [20], and buckwheat (0.1–1.47%) [20,21] starches. For tritordeum starch, the mineral compound content was higher than for wheat starches, but slightly lower than for barley starches.

Phosphorus is a compound occurring at very low concentrations, but it plays an important role in starch functional properties. Phosphorus in starch can be found as inorganic phosphate, phosphate monoester, and phospholipids. When present in the form of phosphate monoester, it increases paste clarity and viscosity, for example, in potato starch, whereas phospholipids have the opposite effect on starch, making starch paste

opaque and decreasing its viscosity. In cereal starches, it is mainly present in the form of phospholipids [7,23].

Its content was within the range of 0.025% (barley) to 0.66% (buckwheat) in starch (Table 1), and it was positively correlated with ash content ($p > 0.001$). Data from the literature related to phosphorus content in barley gave a rather broad range from 0.004 to 0.075% [17,18]; for wheat starch, it was from 0.040 to 0.053% [24,25], whereas for buckwheat starch, this amount is rather negligible at 0–95 ppm (0.0095%) [21]. As observed, the phosphorus content analyzed in this research was consistent with the data in the literature, and its level in tritordeum starch was essentially the same as in buckwheat starch, whereas barley starch was characterized by the lowest amount of this compound.

Among the investigated starches, tritordeum was characterized by the highest share of minor non-carbohydrate material (protein, lipids, phosphorus, and mineral compounds). Such non-starch material can create problems in starch processing; for example, during glucose syrup production, more extensive purification will be required.

3.2. Color of Starches

The color of starch, to some extent, can be treated as an indicator of the purification process. Also, in some specific applications, like the production of cosmetics or as a filling material, it can be important. Data related to the color of the investigated starches are summarized in Table 2. The darkest among them was buckwheat starch (lowest L* value), which can be related to the high content of non-starch material (lipid and ash content). On the other hand, the lightest was starch separated from commercial wheat flour (WhS) with the lowest content of non-starch material. A negative correlation was observed between L* value and lipid content ($p = 0.007$). The observed L* values [19] for buckwheat starch were within the 67.66–72.23 range, and were 74.40 for wheat starch, so the starches analyzed in this research were lighter in color, which could be influenced by both the nature of the starch and the separation method.

Table 2. Color parameters of investigated starches.

Sample	Color Parameters [-]			
	L*	a*	b*	WI
BaS	83.81 ± 0.17 ^{a}	0.59 ± 0.02 ^{d}	5.79 ± 0.08 ^{e}	82.80 ± 0.19 ^{a}
BuS	86.17 ± 0.03 ^{c}	0.45 ± 0.01 ^{c}	5.30 ± 0.04 ^{d}	85.18 ± 0.04 ^{b}
TrS	84.21 ± 0.05 ^{b}	0.43 ± 0.01 ^{c}	6.51 ± 0.03 ^{f}	82.91 ± 0.06 ^{a}
WaS	87.37 ± 0.00 ^{d}	0.56 ± 0.01 ^{d}	1.94 ± 0.02 ^{b}	87.21 ± 0.01 ^{c}
WdS	88.09 ± 0.95 ^{e}	0.15 ± 0.13 ^{b}	0.96 ± 0.58 ^{a}	88.05 ± 0.86 ^{d}
WhS	90.00 ± 0.02 ^{f}	-0.11 ± 0.01 ^{a}	2.13 ± 0.01 ^{c}	89.77 ± 0.02 ^{e}

Values with similar superscripts in the column do not differ significantly ($p < 0.05$). L*—lightness; a*—color parameter ranging from green to red; b*—color parameter ranging from blue to yellow; WI—whiteness index.

All samples except WhS were characterized by a relatively low share of red color (a* value). For WhS, this value was negative, indicating a small shift toward green color. The b* values for all samples were positive and close to zero, indicating a small share of yellow color, and a positive correlation was observed between the b* value and lipid content ($p = 0.014$).

The whiteness index (WI, Equation (1)) indicates the degree of departure of an object's color from that of a model white (WI = 100). Taking it into account, it could be observed that both barley and tritordeum starch colors departed the most from the model white, whereas that of wheat starches departed the least.

The calculated ΔE (Equation (2)) values were the highest for WhS vs. other starches, indicating an easily discernible difference in color. On the other hand, the color difference

between barley and tritordeum starch was very low, so it was not possible to spot the existing difference because, usually, a ΔE value of 2.3 corresponds to a just-noticeable difference [10].

The general appearance of tritordeum starch allows it to be easily distinguished from other investigated starches. Also, relatively low L* and WI values do not allow for application where brightness and lightness are desired, like, for example, cosmetics.

3.3. Morphology of Starch Granules

Microscopic observations of starch grains allow, to some extent, the determination of the botanical origin of starch, but also enable measurement of their size and shape [10]. In addition, they make it possible to determine the presence of any damage that the granules may have suffered. Micrographs of tritordeum starch (TrS) are shown in Figure 1, whereas barley (BaS) and wheat starch (WhS) are in Figure 2. In the case of the TrS granule population, both large and small granule fractions can be observed, but the presence of small granules in TrS is much more noticeable than in the case of WhS. TrS granules have a slightly flattened spherical shape, but grains with a more elongated shape, as well as clearly flattened or lenticular shapes, can also be observed. The surface of the granules appears to be smooth, without any visible cracks, gaps, or depressions. The shape of TrS granules resembles wheat starch granules more than barley starch ones (Figures 1 and 2).

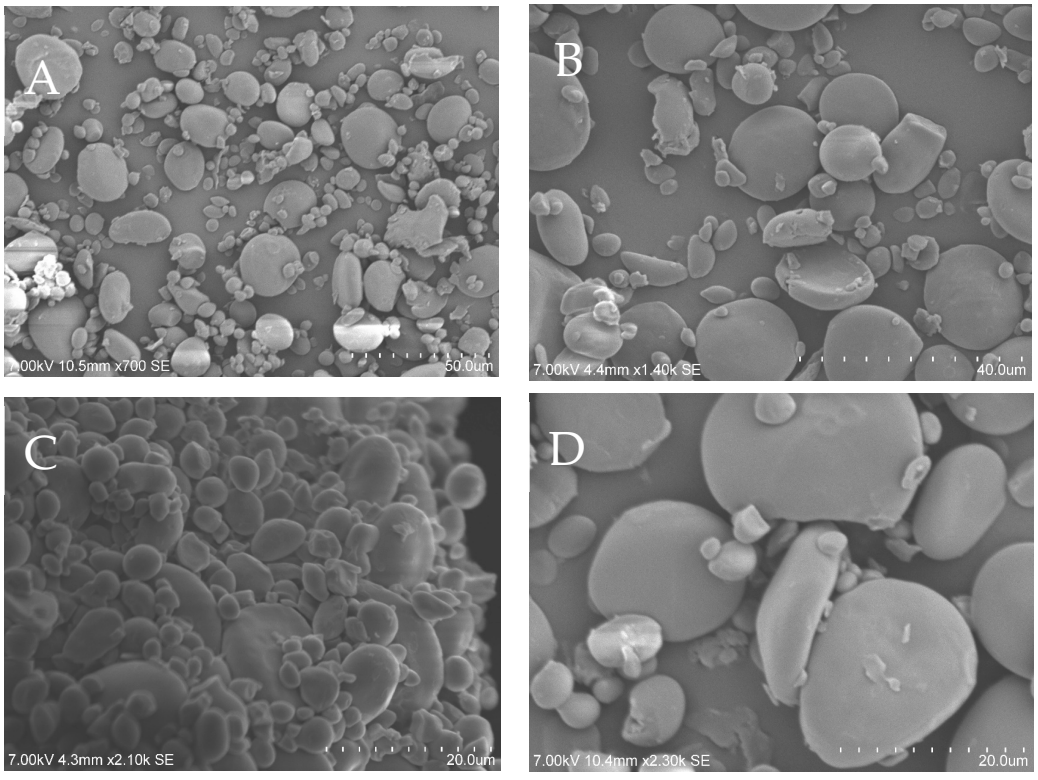

Figure 1. Scanning electron micrographs of tritordeum starch observed at different magnifications (**A**—700×; **B**—1400×; **C**—2100×; **D**—2300×).

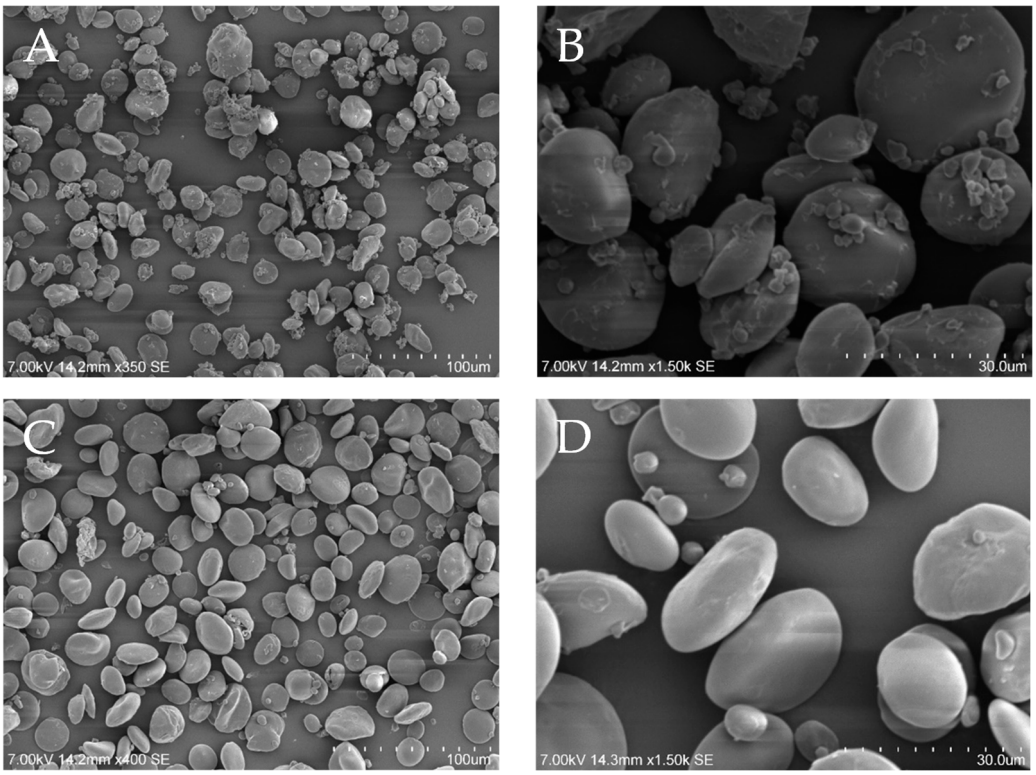

Figure 2. Scanning electron micrographs of barley (**A**—350× and **B**—1500×) and wheat (**C**—400× and **D**—1500×) starches observed at different magnifications.

3.4. Particle Size Distribution of Starches

The morphological features of starch granules, like their physical dimension, can decide some of their properties and, as a consequence, their possible application. For example, face powder formulations should be characterized by a relatively small size of granules, like oat starch. Also, smaller starch granules are more resistant to swelling [7,10].

Among the investigated samples (Table 3), the lowest average granule diameter was observed for BuS (6.8 μm), whereas the highest was for wheat starch (Whs) (15.0 μm), and the average diameter for tritordeum starch (7.1 μm) was close to buckwheat as well as to barley starch. The diameter d_{90} proved that buckwheat starch granules (9.8 μm) were the finest among all samples of starch granules, whereas the biggest were for Whs (28.3 μm). The observed diameters were consistent with data in the literature for wheat and barley starches [16,18,20,24] and buckwheat [5,20,26,27].

Table 3. Granularity of investigated starches.

Sample	Granularity [μm]			
	$d_{(10)}$	$d_{(50)}$	$d_{(90)}$	Avd
BaS	0.6	8.3	21.5	8.3
BuS	2.8	7.0	9.8	6.8
TrS	1.4	5.6	14.1	7.1
WaS	2.6	12.9	26.1	14.8
WdS	2.3	14.3	25.4	14.6
WhS	2.4	14.5	28.3	15.0

$d_{(10)}$, $d_{(50)}$, and $d_{(90)}$ are the equivalent diameters at 10%, 50%, and 90% of cumulative distribution, respectively.

The granularity of tritordeum starch was between small granules of cereal starches like buckwheat or oat [4] and bigger ones like wheat, barley, or even potato starches [10].

3.5. Thermal Properties of Starches

Differential scanning calorimetry (DSC) is a powerful tool in understanding important structural characteristics of starch, as well as the transitions it undergoes during heating. Moreover, in many applications, the initial step of starch processing is heating it up in the presence of water, like, for example, wort preparation in the brewing industry; sometimes, the amount of water is limited, like during bread baking.

Heating starch in the presence of water leads to the destruction of its crystalline structure. Such a process is called gelatinization, and DSC is used to study it. Gelatinization begins in amorphous regions, where hydrogen bonds are weaker. Observed differences in the transition temperatures between different starches depend on the degree of their crystallinity. The endothermic peak reflects the energy required to disrupt the double helical order of the starch, and the lower gelatinization enthalpy (ΔH_{gel}) value suggests a lower level of ordering, or a lower stability of the starch crystals, whereas higher enthalpy and peak temperature will indicate a greater amount of crystalline material. The gelatinization transition temperatures (T_o—onset, T_p—peak, T_c—peak) and ΔH_{gel} are determined by the molecular architecture of the crystalline region, as well as by measurement conditions. More perfect crystals possess only a negligible amount of intermediate-order material at the crystalline–amorphous transition region, resulting in a sharp melting point (lower ΔT values) [7,16,21,28].

Data related to the gelatinization phenomenon of investigated starches are summarized in Table 4.

Tritordeum starch was characterized by the lowest transition temperatures (T_o, T_p, T_c) within the analyzed starches, as well as by the lowest gelatinization enthalpy, which can suggest a lower crystalline arrangement of this starch as compared to other starches. The transition temperatures were the same magnitude as for starch from durum wheat (WdS), whereas ΔH_{gel} was similar in value to barley starch. The highest ΔH_{gel} values were observed for BuS and WdS. Moreover, BuS was characterized by the highest transition temperature, and also by the broadest difference between onset and conclusion temperature (ΔT) suggesting an increased proportion of intermediate material [7,16,21,28]. Also, some explanation can be related to granule size, since small starch granules are characterized by a higher gelatinization temperature [29]. The results of thermal analysis obtained for BaS, BuS, and WdS are consistent with the data in the literature [6,16,18,21].

Table 4. Thermal properties of investigated starches.

	T_o [°C]	T_p [°C]	T_c [°C]	ΔT [°C]	ΔH_{gel} [J/g]
BaS	58.26 ± 0.07 ^{b}	63.13 ± 0.14 ^{b}	69.51 ± 0.04 ^{a}	11.25 ± 0.11 ^{a}	7.25 ^{a} ± 0.04 ^{a}
BuS	60.85 ± 0.24 ^{c}	67.78 ± 0.00 ^{c}	76.18 ± 0.3 ^{b}	15.33 ± 0.06 ^{b}	9.21 ^{b} ± 0.25 ^{b}
TrS	55.33 ± 0.04 ^{a}	60.75 ± 0.27 ^{a}	67.65 ± 0.17 ^{a}	12.33 ± 0.13 ^{a}	7.18 ^{a} ± 0.01 ^{a}
WdS	56.13 ± 0.68 ^{a}	61.58 ± 0.30 ^{a}	67.72 ± 0.43 ^{a}	11.59 ± 0.25 ^{a}	8.71 ^{b} ± 0.09 ^{b}

Values with similar superscripts in the column do not differ significantly ($p < 0.05$). T_o—onset temperature; T_p—peak temperature; T_c—conclusion temperature; $\Delta T = T_c - T_o$; ΔH_{gel}—enthalpy of gelatinization.

3.6. Pasting of Starches

Starch pasting is a phenomenon in which starch granules are heated in the presence of water. They absorb and bind water, which results in granular swelling. As a consequence, the amount of available water is reduced and physical interactions among granules occur. These interactions result in a sudden increase in the viscosity of starch in water suspension. The combined action of shear forces and temperature leads to a disruption of

granules, which releases starch molecules in the solution, where they interact. The maximum viscosity, or peak viscosity (PV), is attained when the rate of granule swelling is equal to their disruption caused by shear forces and temperature [9,10]. This phenomenon is usually monitored by means of a rapid visco analyzer (RVA) or Brabender apparatus. The obtained results will depend on many parameters like the applied starch suspension concentration, equipment used, and measuring protocol [30]. The analysis of the pasting profile provides valuable information about the real performance of starch during heating in the presence of water. Data related to the pasting properties of the investigated starches are summarized in Tables 5 and 6 and are also presented in Figure 3.

Analyzing the course of the pasting curves (Figure 3), a distinct viscosity peak (PV) was observed only in the case of buckwheat (BuS), regular wheat (WaS), and durum wheat (WdS) starches. For the remaining samples, a relatively slow viscosity development was observed.

Pasting temperature (PT) provides information on the minimum temperature required for gelatinization to occur, and except for WdS, it was close to 80 °C, ranging from 65.9 °C (WdS) to 84.2 °C (TrS) (Table 5). Data from the literature related to these parameters are in a broad range: 86.5–90.9 °C for barley [16], 75–84 °C for buckwheat starch, and 61.0 °C to 87.1 °C for wheat starches [4,30,31].

Table 5. Pasting parameters of investigated starches.

Sample	PT [°C]	tPV [sec.]	PV [BU]	PVT [°C]	MV [BU]	TV [BU]	FV [BU]	BD [BU]	SB [BU]	BD% [%]	SB% [%]	HPSI [%]
BaS	82.1 ± 1.4 ^{bc}	820.0 ± 7.1 ^{d}	61.0 ± 0 ^{c}	92.9 ± 0.8 ^{bc}	44.5 ± 0.7 ^{b}	101.0 ± 2.1 ^{c}	82.0 ± 1.4 ^{b}	16.5 ± 0.7 ^{b}	57.0 ± 1.4 ^{d}	27.0 ± 1.2 ^{bc}	56.2 ± 0.2 ^{c}	95.6 ± 1.6 ^{c}
BuS	79.0 ± 0.1 ^{b}	677.5 ± 10.6 ^{b}	146. ± 2.1 ^{d}	90.2 ± 2.3 ^{b}	126. ± 1.4 ^{c}	218.0 ± 1.4 ^{d}	216.0 ± 4.2 ^{c}	20.5 ± 0.7 ^{b}	92.0 ± 0 ^{e}	14.0 ± 0.3 ^{ab}	42.2 ± 0.3 ^{a}	91.5 ± 0.1 ^{bc}
TrS	84.2 ± 1.1 ^{cd}	1147.5 ± 24.7 ^{cd}	31.5 ± 1.4 ^{a}	95.0 ± 0.1 ^{c}	32.0 ± 1.4 ^{a}	71.0 ± 1.4 ^{ab}	56.0 ± 1.4 ^{a}	0.0 ± 0.0 ^{a}	39.0 ± 0.0 ^{c}	0.0 ± 0 ^{a}	54.9 ± 1.1 ^{c}	96.3 ± 4.7 ^{c}
WaS	87.5 ± 0.6 ^{d}	717.5 ± 3.5 ^{bc}	63.0 ± 2.8 ^{c}	95.0 ± 0.6 ^{c}	49.0 ± 1.4 ^{b}	105.0 ± 1.4 ^{c}	87.0 ± 2.8 ^{b}	13.5 ± 4.9 ^{b}	54.5 ± 0.7 ^{d}	21.3 ± 6.9 ^{bc}	51.9 ± 1.4 ^{bc}	80.0 ± 5.9 ^{ab}
WdS	65.9 ± 0.8 ^{a}	520.0 ± 7.1 ^{a}	50.0 ± 0 ^{b}	83.5 ± 0.5 ^{a}	36.0 ± 2.8 ^{a}	64.5 ± 3.5 ^{a}	65.0 ± 2.8 ^{a}	14.0 ± 2.8 ^{b}	28.0 ± 0 ^{a}	28.0 ± 5.7 ^{bc}	43.5 ± 2.4 ^{a}	68.6 ± 4.7 ^{a}
WhS	82.7 ± 0.6 ^{a}	825.0 ± 21.2 ^{d}	53.0 ± 0 ^{b}	93.7 ± 0.8 ^{bc}	36.5 ± 0.7 ^{a}	72.5 ± 0.7 ^{b}	60.5 ± 0.7 ^{a}	16.5 ± 0.7 ^{b}	36.0 ± 0 ^{c}	31.1 ± 1.3 ^{a}	49.7 ± 0.5 ^{b}	95.6 ± 1.3 ^{c}

Values with similar superscripts in the column do not differ significantly ($p < 0.05$). PT—pasting temperature; PV—peak viscosity; tPV—time at which PV was attained; PVT—temperature at PV; MV—minimum viscosity; TV—trough viscosity; FV—final viscosity; BD—breakdown, BD = PV − MV; SB—setback, SB = TV − MV; BD% = (PV − MV)/PV; SB% = (TV − MV)/TV; HPSI—hot paste stability index.

Table 6. Parameters of equations describing the initial phase of pasting profile (up to peak viscosity) and retrogradation kinetics of investigated starches.

Sample	The Initial Phase of Pasting				Avrami Equation Parameters				
	V_{peak} [BU]	R [sec.]	s [-]	R^2 [-]	k [1/h]	ΔA_∞ [-]	ΔA_0 [-]	Rn [-]	R^2
BaS	60.573	646.078	15.521	0.999	0.0030	2.0967	1.8582	0.2385	0.9994
BuS	159.699	601.013	19.977	0.996	0.0171	2.2395	2.0864	0.1531	0.9986
TrS	29.189	606.907	16.836	0.998	0.0022	2.1278	1.9927	0.1351	0.9984
WaS	62.471	617.609	23.739	0.999	0.0548	2.2205	2.6696	0.0804	0.9917
WdS	86.457	496.846	3.607	0.984	0.0084	2.4667	1.9686	0.9981	0.9979
WhS	53.556	608.117	10.463	0.997	0.0075	1.9919	1.9078	0.0841	0.9833

V_{peak}—calculated peak viscosity; R—time that gives rise to 50% of V_{peak} value; S—starch coefficient; k—a constant rate of retrogradation process; ΔA_0—turbidity at zero time; ΔA_∞—turbidity at ∞ time; Rn—the extent of retrogradation ($\Delta A_\infty - \Delta A_0$).

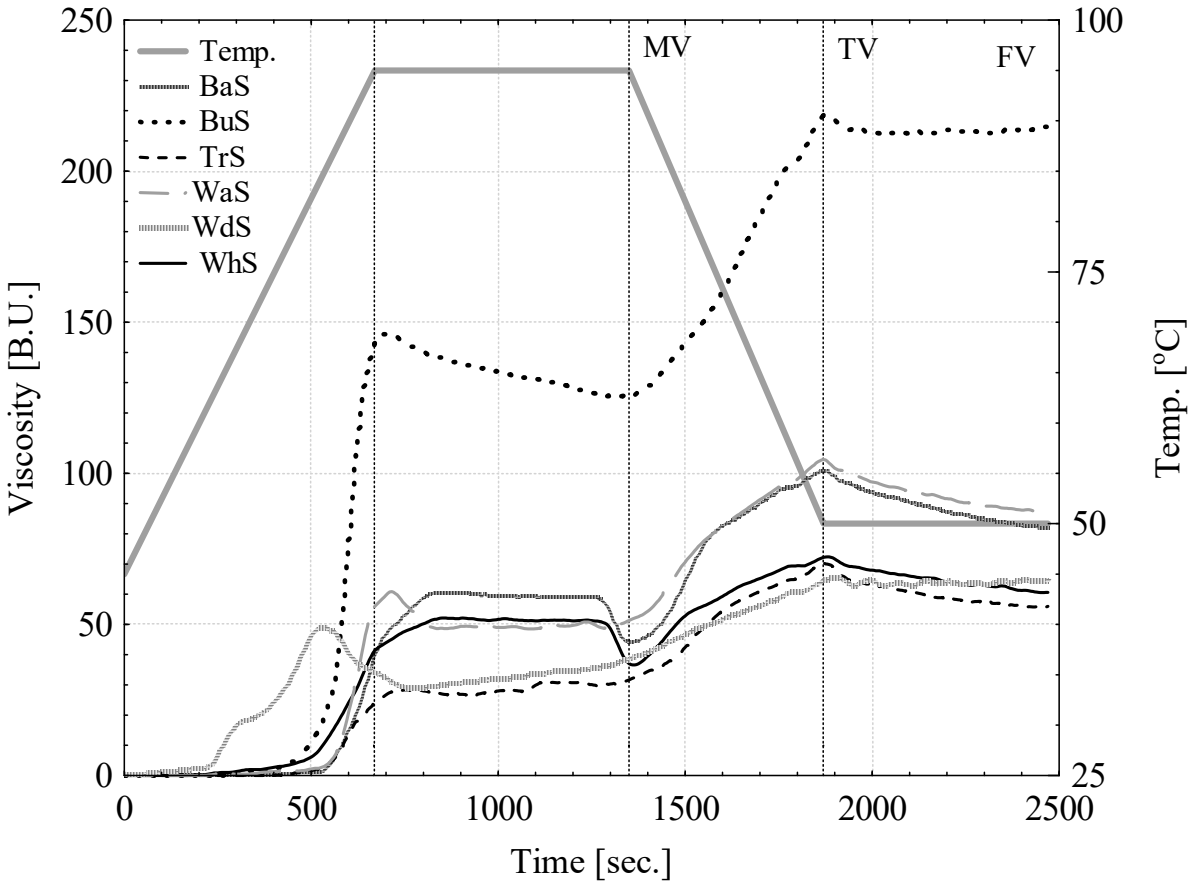

Figure 3. Pasting profiles of investigated starches (vertical lines mark the beginning of the temperature change).

The maximum viscosity for all starches was reached (tPV) within the holding period at elevated temperature (95 °C), except for durum wheat starch (WdS). It took place between 520 (WdS) and 1148 s (TrS) (Table 5). Such behavior is typical for cereal starches due to the presence of lipid complexes that retard granular swelling [4,18,30,31], resulting in higher pasting temperature and lower viscosity, but also in greater hot paste stability.

The observed PV values for durum wheat (WdS) and commercial wheat flour (WhS) starches were close to those previously reported [4,30], whereas for barley and regular wheat starches, these values were slightly higher. The highest PV value was observed for buckwheat (146.5 BU). Among the investigated starches, tritordeum starch was characterized by a slightly different pasting profile (Figure 3). Its PT was the highest among all samples (Table 5), and the PV for this starch was reached almost at the end of the holding period and was the lowest among all analyzed samples. This indicates high resistance to swelling of tritordeum starch granules, due to slow water diffusion into them, probably due to their high lipid content.

Palabiyik et al. [9,32] proposed a numerical approach to the interpretation of the pasting phenomenon. For the initial pasting stage (up to reaching PV), a logistic-type model (Equation (3)) was proposed, and data calculated using it were collected and are shown in Table 6. Relatively high values of R^2 indicated that this model describes this part of the pasting curve fairly well, except for WdS. In this instance, the course of the pasting curve was untypical because an inflection point was observed at about 310 sec (Figure 3). Therefore, the proposed model did not fit that well into the experimental data.

The calculated V_{peak} value (Table 6) corresponds with the PV value (Table 5), and calculated values are consistent with PV values, and observed discrepancies were bigger only for durum wheat (WdS) and buckwheat (BuS) starches. Another parameter, namely R (the

time that gives rise to $V_{peak}/2$), could determine the resistivity of starch granules against the combined action of temperature and shearing force. The R values for all analyzed starches were within the 496.8–646.1 s range, with the highest value noted for barley starch, indicating the highest resistivity of this starch towards granular swelling. On the other hand, for durum wheat starch (WdS), the observed value was less than 500 s, which was about 100 s less than the remaining starches. For tritordeum starch, this parameter was very similar to the value calculated for starch isolated from wheat flour (WhS).

The starch coefficient (s, Table 6) indicates the swelling rate of the starch granules. This parameter is responsible for the slope of the pasting curve (the higher the s value, the greater the slope of the curve), i.e., faster granular swelling. The highest s value was observed for regular wheat (WaS) and buckwheat (BuS) starches, 23.7 and 20.0, respectively, whereas the lowest was noted for durum wheat starch (WdS)—about 3.6. The values calculated for barley (15.5) and tritordeum (16.8) were similar to each other.

The results of the pasting analysis are strongly dependent on various factors (equipment used, starch slurry concentration, and measurement protocol) [30], so it is very hard to perform a direct comparison of the obtained data. There are available data related to the mathematical modeling of the pasting curve course, but these data were based on RVA measurements, and a different starch suspension concentration was applied (14% instead of 5%) [9,32], or exactly the same regime was performed but for potato starches [10].

The V_{peak} values calculated for potato starches were much higher (596.0–1249.7), which could be ascribed to their nature (higher viscosities of such pastes are due to the presence of covalently bonded phosphate moiety). On the other hand, the R values for potato starches were lower than for cereal starches and in a broad range from 364.0 to 550.0, indicating fast granular swelling not restricted by lipids. Also, the s values calculated for potato starches were widely distributed from 5.6 to 15.9, with the lowest value observed for soil-cultivated potatoes. The average s value for all potato starches was 10.6 [10], so it was close to the s value calculated for wheat starch isolated from commercial flour (WhS) (Table 6).

During the holding period, a drop in viscosity, so-called breakdown (BD), is usually observed. It is a result of a rupture of swollen starch granules, caused by the combined action of shear forces and temperature. It was clearly visible for buckwheat (BuS) and regular wheat (WaS) starches, whereas for durum wheat starch (WdS), the viscosity drop started before the holding period (Figure 3). In the case of barley (BaS) and wheat starch separated from flour (WhS), such a viscosity drop was observed only in the final moments of the holding period. On the contrary, for tritordeum starch, slow viscosity development was observed, so no BD was observed. Such behavior could be a consequence of the highest lipid content among all investigated starches (Table 1) resulting in delayed starch granule swelling, which manifested as the highest tPV value (Table 5). All samples were characterized by good hot paste stability, which manifested as high values of HPSI and low BD values (Table 5), and starch from durum wheat (WdS) was the least stable among the investigated samples.

After holding a starch paste (at elevated temperature), a viscosity development (from MV to TV) upon cooling was observed due to the aggregation of the amylose molecules. This increase is described as a setback (SB) and could be interpreted as starch susceptibility to retrogradation [4,14,31]. The highest SB value was observed for buckwheat starch (BuS)—92 BU—and the lowest for durum wheat starch (WdS). But when the SB% was taken into consideration, for BuS (and also for WdS), this increase was the lowest, and the highest values were observed for regular wheat (WaS) and tritordeum (TrS) starches (Table 5). In this research, no correlation was found between SB (or SB%) and retrogradation parameters (Tables 5 and 6).

After reaching a final temperature (50 °C), samples were kept for another 10 min and a slight decrease in viscosity (from TV to FV) was observed as a consequence of shear force action. This cold paste stability was the highest for buckwheat (BuS) and durum wheat

(WdS) starches (almost no viscosity drop), whereas tritordeum (TrS) and barley (BaS) starches were characterized by the lowest ones.

In summary, tritordeum starch was characterized by a relatively high pasting temperature (PT) compared to the other investigated starches. Moreover, it created the paste with the lowest viscosity (PV), caused by restricted granular swelling, probably due to the high lipid content. But on the other hand, the resulting paste was stable at elevated temperature (Table 5). So, this starch will not find application in situations where high viscosity is required, but its high stability at elevated temperature (high HPSI and low BD values) could be an advantage.

3.7. Starch Retrogradation

Starch retrogradation is a process in which disaggregated amylose and amylopectin chains in a gelatinized starch paste reassociate to form more ordered structures, leading to the creation of crystallites. It is accompanied by a gradual increase in rigidity and phase separation between polymers and leads to syneresis. Retrogradation is influenced by many factors, like the botanical origin of starch as well as its concentration and temperature and the presence of additional substances present in food, like, for example, salts, carbohydrates, etc. This process has a negative effect on the sensory and storage features of many starchy foods, like, for example, bread staling. But, on the other hand, this process is desirable for some starchy food products in terms of texture development and nutritional benefits, since retrograded starch is not digested by enzymes. The recrystallization kinetics of aging gelatinized starch can be described by the Avrami equation (Equation (4)). In general, changes occurring during retrogradation can be described by the extent of this process ($\Delta A\infty - \Delta A_0$ in the Avrami formula), and also by its rate (rate constant k). The higher the value of the constant rate k, the faster the process occurs in the initial period (the course of the curve is sharper) [13,14].

Data related to the starch retrogradation phenomenon are shown in Figure 4, and calculated the Avrami equation parameters are collected in Table 6.

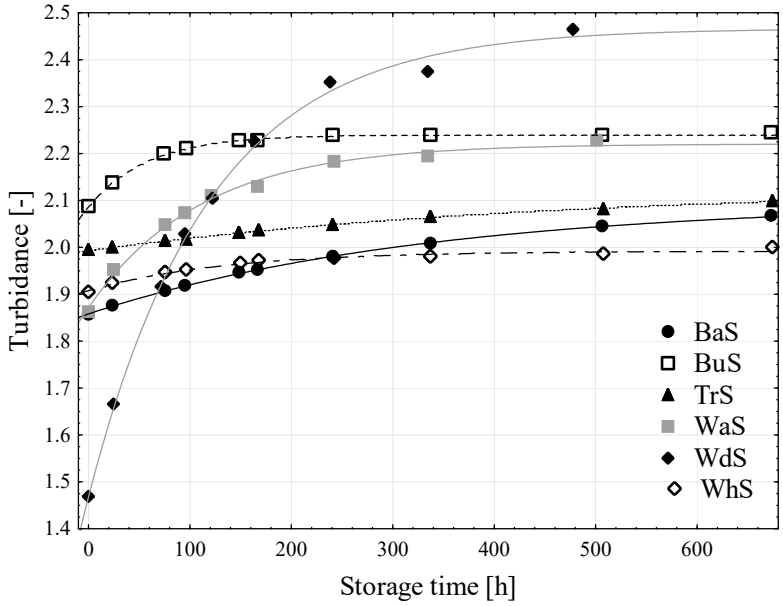

Figure 4. The course of retrogradation of the investigated starches.

The rate constants (k values) decreased in the following order: WaS > BuS > WdS > WhS > BaS > TrS. As can be observed, WaS was characterized by a distinctively different course of retrogradation process, compared to the other analyzed samples, that

manifested as a much higher value of the k constant (0.0548), resulting in a faster course of retrogradation at the beginning of this process.

The calculated k values for tritordeum (0.0022) and barley (0.0030) starches were rather similar, whereas for wheat starches (WhS and WdS), these values were 3–4 times higher, reaching 0.075 and 0.0084, respectively (Table 6). Data in the literature [13] related to k based on a turbidimetric method for cereal starches were in a rather broad range (0.0007–0.0787). For oat starch, the reported k value (0.0018) was close to those calculated for tritordeum and barley starches. On the other hand, the highest value (0.0787) was recorded for wheat starch [13], and it was the same magnitude as that for regular wheat starch (WaS).

But at the same time, it was an order of magnitude larger than the k values calculated in this research for WdS and WhS. The starch retrogradation process is disturbed by the presence of lipids [13], and the lowest k value was calculated for TrS, which was also characterized by the highest lipid content (Table 1).

The extent of the retrogradation process ($\Delta A_\infty - \Delta A_0$) decreased in the following order: WdS > BaS > BuS > TrS > WhS. For the final value (ΔA_∞), this order was different: BuS > TrS > BaS > WhS > WaS (Table 6). Reported data [31] for the extent of retrogradation were similar or higher (0.8244–1.2444), and the lowest value was observed for wheat starch, and also, this starch was characterized by the lowest final value (2.1442), which was close to the value observed for WdS in this research.

Taking into consideration the above-mentioned data, it could be concluded that tritordeum starch would be rather stable during prolonged storage due to the low k value, and also the relatively low extent of this process. This can be an indicator that TrS could become a good additive for commercial food products when changes related to the retrogradation process could worsen the quality of the product.

4. Conclusions

Tritordeum starch revealed its own distinctive character. Its granules had a slightly flattened spherical shape, and the presence of smaller and larger granule fractions was observed. Its shape resembled wheat starch granules more than barley ones. But, on the other hand, tritordeum starch granules were smaller than wheat starch granules. Tritordeum starch granules were rather fine, with an average diameter similar to buckwheat starch, but the majority of starch granules (d_{90}) placed it between buckwheat and wheat/barley starches. Among the investigated starches, it was characterized by the lowest apparent amylose content. Moreover, it was also characterized by the highest lipid content and a relatively high phosphorus and mineral compound content. Taking into consideration all non-carbohydrate material (protein, lipids, and mineral compounds), tritordeum had the greatest share of them among other starches. Its color was the most similar to barley starch, and partially to buckwheat starch. Its whiteness index was essentially the lowest, which could restrict its potential use when a general appearance is essential. Tritordeum starch was also characterized by the lowest transition temperatures and gelatinization enthalpy among the examined samples, suggesting relatively low crystallinity. Moreover, its paste was the least viscous among the studied cereal starches, especially when compared to buckwheat starch paste. Also, it reached a maximum viscosity at an elevated (maximum) temperature, and no breakdown was recorded, which makes it stable at high temperatures. Also, its pasting temperature was the highest among the investigated samples. Additionally, it was characterized by the slowest course of retrogradation and the relatively small extent of this process occurring during prolonged storage. A possible application of tritordeum starch could be in the production of thermally preserved (appertized) products, due to its stable viscosity at high temperatures and slow retrogradation rate and the low extent of this process.

So far, tritordeum is cultivated on a relatively low scale, but this situation is changing. Cultivation trials have started to spread to other countries. Therefore, further studies on tritordeum and its starch should be conducted.

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Abbreviations

BaS	barley starch
BuS	buckwheat starch
TrS	tritordeum starch
WaS	wheat starch isolated from regular Artist variety
WdS	wheat starch isolated from durum Pentadur variety
WhS	wheat isolated from commercial wheat flour
WI	whiteness index
ΔE	difference between two colors
PSD	particle size distribution
DSC	differential scanning calorimeter
PT	pasting temperature; temperature at which an initial increase in viscosity was observed
PV	peak viscosity, maximum viscosity observed during the initial phase of the measurement
tPV	time to peak viscosity
TPV	temperature at PV
MV	minimum viscosity observed at the end of the high-temperature holding period
TV	trough viscosity; viscosity observed at the beginning of the second hold period, when the final temperature was reached
FV	final viscosity observed at the end of measurement
BD	breakdown, a decrease in viscosity during the first holding period (BD = PV − MV); BD% = (PV − MV)/PV
SB	setback, an increase in viscosity during cooling period (SB = TV − MV); SB% = (TV − MV)/TV
HPSI	hot paste stability index
V	viscosity during processing
Vpeak	peak viscosity
T	processing time parameter
R	the time that gives rise to 50% of peak viscosity
s	starch coefficient
t	time
ΔA_0	turbidance at zero time
ΔA_∞	turbidance at ∞ time
K	rate constant

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