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PROPERTIES OF CORN AND WHEAT STARCH PHOSPHATES OBTAINED FROM GRANULES SEGREGATED ACCORDING TO THEIR SIZE

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ABSTRACT

Corn and wheat starches were segregated into big and small granules. Unsegregated starches and their fractions were phosphorylated with sodium trimetaphosphate. Due to applied modification method, the highest amount of phosphorus was incorporated to small granule fraction of corn starch. The least of the phosphorus was bound by small granule fraction of wheat starch. It was also shown that obtained preparations were characterised by different physico-chemical properties.

Key words: starch, phosphorylation, starch phosphates

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INTRODUCTION

Starch is one of the most widespread thickening agents used in food industry. However, the use of native starch, causes several problems related to syneresis, retrogradation, little stability and low resistance of pastes to pH and temperature changes [17]. This is why starches are modified by physical, chemical and enzymatic methods or their combinations. Among chemically modified starches, starch phosphates are of special interest. They are acquired by estrification of starch with phosphoric(V) acid or phosphate salts [2, 7, 8]. Depending on the method, starch phosphates with various substitution level are produced, that exhibit different physico-chemical properties [4, 7, 8, 12]. Basing on the way of phosphoric acid(V) incorporation, mono- and di-starch phosphates can be distinguished. The first are obtained by heating starch with sodium or potassium phosphate(V) [8], the latter, which are a type of network starch, are synthesised by using phosphorus oxychloride or sodium trimetaphosphate [7, 9]. In case of di-starch phosphates, phosphoric groups make crosslinks between neighbouring glucose chains, thus stabilising and strengthening the structure. Phosphorylation is mainly controlled by: the modifying agent, reaction conditions and botanical origin of starch [1, 2, 4, 7, 12]. Trials were made to obtain starch phosphates in a microwave field [10].

Starch phosphates are used as additives in manufacturing of desserts, sweet creams, cakes, sauces, mayonnaise, canned vegetables, yoghurts [17] as well as in non-food industry.

Research made on starch phosphorylation are restricted to modification of starch of uniform origin and properties of obtained phosphates are compared to native starches and not to so called blank samples, which would eliminate the influence of modification conditions on the acquired product. It's also believed that small granules of starch are more resistant to modifying agents.

The following study attempts to evaluate how the granule size influences corn and wheat starch phosphorylation. To this end, native corn and wheat starch were fractionated to large and small granules, then modified by using sodium trimetaphosphate and the properties of acquired products were studied in comparison to respective blank samples.

MATERIALS AND METHODS

The following commercial starches were used:

- corn starch (Netherlands),
- wheat starch (Germany).

Separation of native starch to two fractions with different granule size was done by using the sedimentation method [14]. Large granule fraction was obtained after 25 minutes of sedimentation and small granule fraction after 90 min.

Phosphorylation was conducted according to Lim and Seib [12] in aqueous alkaline suspension (pH=9.0). Trimetaphosphate was used as a modifying agent. For native starches and their fractions, blank samples were prepared in identical way, but with no addition of modifying agent.

In the obtained preparations the following measurements were done:

- granularity by means of 'Analysette 22' (Fritsch) granule size laser analyser,
- total phosphorus content by Marsch method [13]. Absorbance measurements were done at 310 nm using VSU 2-P spectrophotometer,

- amylose content - spectrophotometrically at 635 nm by the Morrison and Laignelet [16] iodine-staining method using a Specord M-42 spectrophotometer,
- pasting characteristics of aqueous starch dispersions were done in Rheotest 2 rotating viscometer with pins as a measuring element [5] at concentration 8.5 g/100g. Samples were heated at constant mixing with 27 rpm, from 50 to 96°C, then held at this temperature for 20 min and cooled back to 50°C and allowed to stand at this temperature for the next 10 min. Rates of temperature increase and decrease were 1.5°C/min. Viscosity values and temperatures were collected for the following points of pasting characteristics: pasting temperature (t_k), [°C], maximum viscosity (eta_{max}) [a.u.-arbitrary units], temperature at maximum viscosity (t_{max}) [°C], viscosity at 96°C (eta_{96}) [a.u.], viscosity after 20 min of heating at 96°C ($eta_{96/20}$) [a.u.], viscosity after cooling to 50°C (eta_{50}) [a.u.], viscosity after holding for 10 min at 50°C ($eta_{50/10}$) [a.u.],
- flow curves of starch phosphate pastes and blanks were measured in Rheotest 2 rotating viscometer at 50°C, using coaxial cylinders as the measuring element, in the range of shear rate from 0.5-437.4 s^{-1}. The initial starch concentration was 8.5 g/100 g. The obtained experimental data were described using Ostwald de Waele rheological model.

RESULTS AND DISCUSSION

Figure 1 presents percentage of granules with diameter less then 10 micrometers in wheat and corn starch before separation and their large and small granule fractions. The results show that large granule fractions contained low number of granules with diameter lower than 10 micrometers (corn starch 11.6%, wheat starch 3.5%), while small granule fraction 49.3% and 59.9%, respectively. Because the obtained starch fractions were significantly different according to granule size, they were used to produce starch phosphates and respective blanks.

Figure 1. Content of starch granules with diameter below 10 micrometers

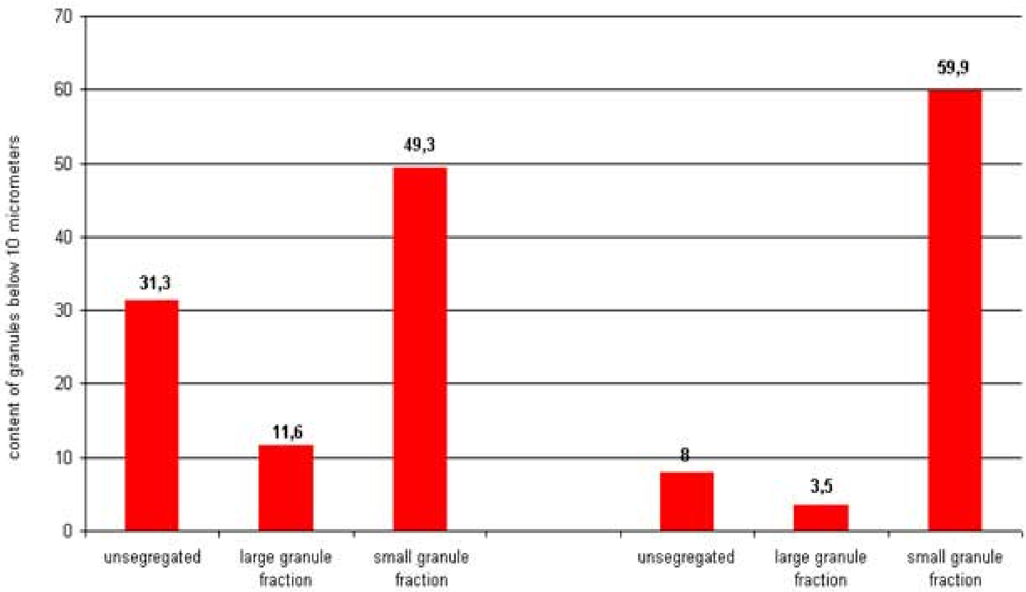

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Table 1 contains data about phosphorus and amylose content as well as calculated incorporated phosphorus. Phosphorus content in all phosphates was higher than in blank samples which proves that its incorporation to starch was due to the applied phosphorylation.

Table 1. Total phosphorus and amylose content of blanks and starch phosphates

Kind of preparation		Total phosphorus content [mg/100 g d.m.]	Amount of incorporated phosphorus [mg/100 g d.m.]	Amylose content [g/100 g d.m.]
Unsegregated Corn starch	blank	19	-	18.2
	starch phosphate	127	108	15.0
Corn starch Large granule fraction	blank	20	-	18.0
	starch phosphate	112	92	16.3
Corn starch Small granule fraction	blank	24	-	16.0
	starch phosphate	139	115	13.8
Unsegregated Wheat starch	blank	56	-	19.6
	starch phosphate	162	106	19.2
Wheat starch Large granule fraction	blank	50	-	20.6
	starch phosphate	158	108	19.3
Wheat starch Small granule fraction	blank	64	-	16.3
	starch phosphate	161	97	15.9

The results confirmed the relations observed by others, that with lowering starch granule size, phosphorus content increases [6, 14, 15]. Earlier research proved that blank samples have less phosphorus than native starches [4] which suggests a release of this component under phosphorylation conditions.

During phosphorylation the largest amount of phosphorus was incorporated to small granules of corn starch, and the smallest to large granule fraction. In case of wheat starch, amount of phosphorus incorporated to unsegregated starch and its large granule fraction was on the same level. The least of the phosphorus was bound by small granule fraction of wheat starch which could be due to its highest level in this fraction before phosphorylation.

The results from Table 1 concerning amylose content in starch phosphates showed some variation. In all cases starch phosphates had lower amount of amylose than respective blank samples. For corn starch and its fractions this difference reaches about 2-3%. In case of wheat starch and its fractions it is, however, insignificant.

Such relations show the influence of modification conditions, alkaline environment and temperature on the amount of found amylose [4, 12]. Moreover it supports previous reports [6, 14] about lower content of amylose in small granule fraction.

Pasting curves of starch phosphates obtained from unsegregated starch and its fractions are presented on Figures 2 and 3. Basic pasting characteristics parameters are collected in Table 2. In case of corn, unsegregated starch phosphate had a little lower viscosity values than phosphates obtained of large and small granule fractions. The highest viscosity was obtained for large granule fraction of this starch.

Figure 2. Pasting curves of corn starch phosphates: unsegregated (US), large granule fraction (LF), small granule fraction (SF)

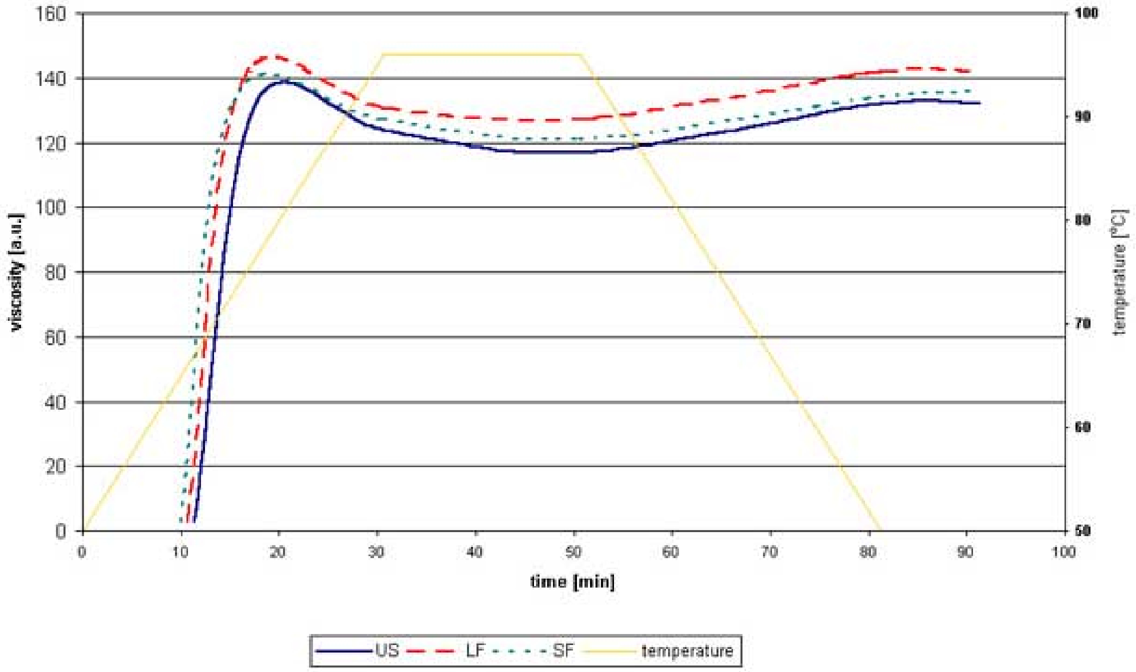

Figure 3. Pasting curves of wheat starch phosphates: unsegregated (US), large granule fraction (LF), small granule fraction (SF)

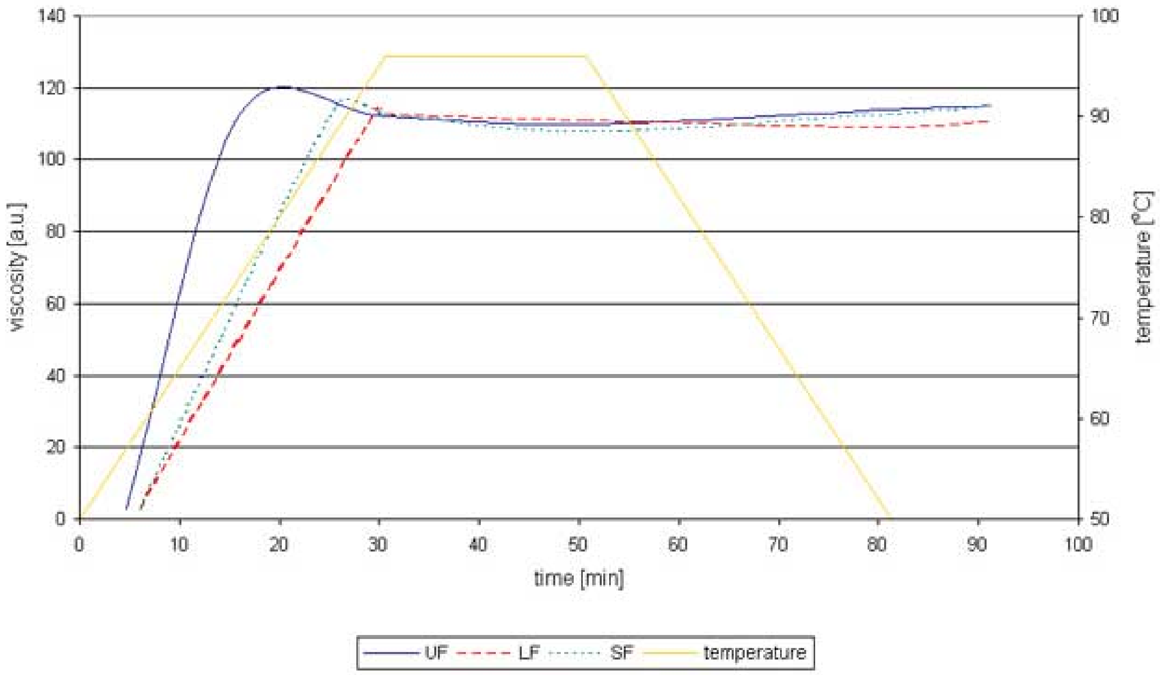

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Table 2. Pasting characteristics of blanks and starch phosphates

Kind of preparation		t_k [°C]	eta_{max} [a.u.]	t_{max} [°C]	eta_{96} [a.u.]	$eta_{96/20}$ [a.u.]	eta_{50} [a.u.]	$eta_{50/10}$ [a.u.]
Unsegregated Corn starch	blank	71	114	76	114	109	117	117
	starch phosphate	67	132	76.5	124	117	132	132
Corn starch Large granule fraction	blank	70	115	90	115	111	117	118
	starch phosphate	66	139	74.5	131	127	142	142
Corn starch Small granule fraction	blank	71	118	90.5	117	109	118	117
	starch phosphate	65	133	73	127	121	134	136
Unsegregated Wheat starch	blank	67	129	97	123	125	139	142
	starch phosphate	57	113	74	112	110	114	115
Wheat starch Large granule fraction	blank	71	131	96	129	122	139	143
	starch phosphate	59	114	94.5	113	111	109	111
Wheat starch Small granule fraction	blank	69	40	96	40	28	53	58
	starch phosphate	59	115	88.5	113	108	113	115

Unsegregated wheat starch phosphate displayed higher viscosity values in temperature range between 50 and 96°C and sooner reached maximum viscosity than phosphates obtained from the fractions. During holding at 96°C and cooling, both unsegregated and fractionated wheat starch phosphates showed similar viscosity value.

The data in Table 2 indicates that all starch phosphates displayed lower pasting temperature than respective blanks. For corn starch, this difference was about 4-6°C and for wheat starch 10-12°C. The same relation for starch phosphates obtained from unsegregated starch of different botanical origin was previously reported [4, 12].

Starch phosphates obtained from corn starch and its fractions showed higher values of viscosity in all pasting characteristics points than respective blanks.

Unsegregated corn starch phosphate reached maximum viscosity in the same temperature as the respective blank sample. Phosphates obtained from the fractions of corn starch revealed much lower temperature at maximum viscosity than the respective blanks.

In wheat starch, phosphates of unsegregated starch and large granule fraction showed lower viscosity values in all pasting characteristics points than blanks. Phosphorylated small granule fraction, however, was much more viscous than the blank sample, which was similar to native starch in its pasting curve and small viscosity values [4, 6]. The reason of such behaviour of wheat starch could be the different resistance of fractions to modification conditions. In unsegregated wheat starch and its large granule fraction reaction conditions (temperature, pH,

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aqueous environment) could cause swelling and loosing granule structure, which in effect influenced the obtained results of blank samples pasting characteristics. In case of small granule fraction, the same conditions did not change the granule structure that much, so their pasting curves and low viscosity values were close to the values obtained for native starches [2, 4, 6]. Gambuś et al. [6] report that small granule fraction has lower water binding capacity, solubility and lower pasting temperature in comparison to unsegregated starch and large granule fraction. It is in accordance with the well-known thesis that small granules are more resistant to environmental factors [1, 10]. Lim and Seib [12] reported that starch phosphates reveal lower pasting temperatures and higher viscosity values than unmodified starch and these values depend on pH at which phophorylation is conducted.

Figures 4 and 5 present flow curves of starch phosphate pastes, prepared from unsegregated starch and its fractions. Table 3 contains consistency coefficients 'K' and flow indices 'n' of Ostwald de Waele model for the phosphates and blanks. All studied pastes revealed non-newtonian flow type, characteristic for shear thinning fluids. In case of pastes made of corn starch and its fractions, it was observed that the highest shear stress in the studied range of shear rate was characteristic for large granule fraction starch phosphate. The sample obtained from small granule fraction gave a little higher stress values than unsegregated starch phosphate under the shear rate 100 s^{-1}. Over this value the behaviour changed.

Corn starch phosphate pastes obtained from large and small granule fractions had about 2-times higher values of consistency coefficient than blanks or unsegregated corn starch phosphate paste. So significant rising of consistency coefficient obtained from the fractions indicates their higher viscosity. Flow indices of phosphate pastes obtained from corn starch and its large granule fraction were similar as of the respective blanks. Only small granule fraction starch phosphate paste revealed much lower flow index than the respective blank sample, which indicates its more pronounced deviation from Newtonian flow type.

Figure 4. Flow curves of corn starch phosphate pastes: unsegregated (US), large granule fraction (LF), small granule fraction (SF)

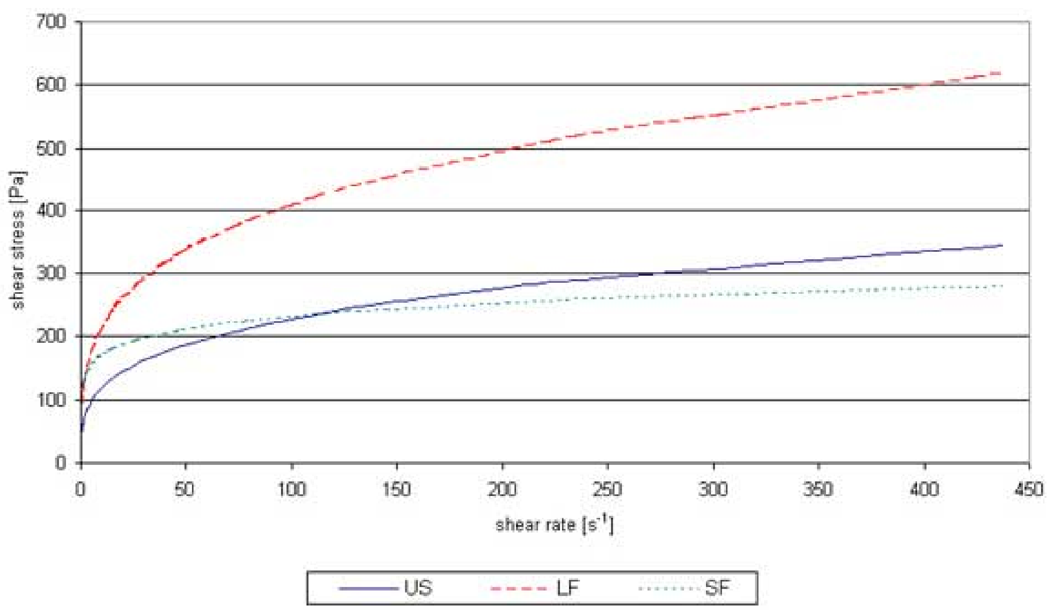

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Figure 5. Flow curves of corn starch phosphate pastes: unsegregated (US), large granule fraction (LF), small granule fraction (SF)

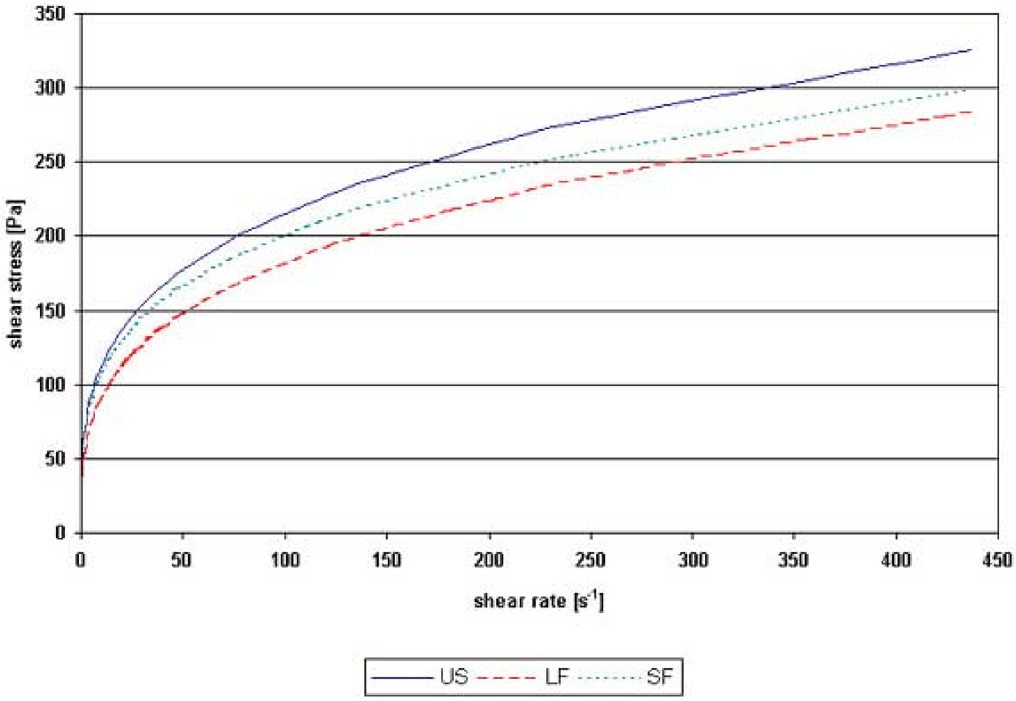

Table 3. Rheological values of Ostwalda de Waele model for blanks and starch phosphate pastes

Kind of preparation		Consistency coefficient "K" [Pa s^n]	Flow index "n"
Unsegregated Corn starch	blank	75.659	0.27
	starch phosphate	62.790	0.28
Corn starch Large granule fraction	blank	69.144	0.27
	starch phosphate	112.977	0.28
Corn starch Small granule fraction	blank	54.903	0.28
	starch phosphate	127.451	0.13
Unsegregated Wheat starch	blank	8.132	0.43
	starch phosphate	59.375	0.28
Wheat starch Large granule fraction	blank	7.757	0.46
	starch phosphate	45.872	0.30
Wheat starch Small granule fraction	blank	36.899	0.26
	starch phosphate	57.961	0.27

Flow curves of phosphate pastes obtained from wheat starch (Fig. 5) show, that the highest shear stress values in the whole shear rate range were characteristic for paste of unsegregated starch phosphate. All starch phosphate pastes had significantly larger consistency coefficients than the respective blanks. Similar relation for unsegregated wheat starch and its phosphate was observed by Fortuna and Juszczak [4]. Flow index was lower for phosphates than blanks in case of unsegregated starch and large granule fraction. Small granule fraction starch phosphate and the respective blank sample were characterised by similar values.

SUMMARY

The samples obtained by phosphorylation of corn and wheat starch and their large and small granule fractions were characterised by different physico-chemical properties. Due to the applied modification method, the highest amount of phosphorus was incorporated to small granule fraction of corn starch. In case of wheat starch, amount of phosphorus incorporated to unsegregated starch and its large granule fraction was on the same level. The least of the phosphorus was bound by small granule fraction of wheat starch which could be due to its highest level in this fraction before phosphorylation.

A small decrease of amylose was noticed after phosphorylation. Differences in pasting characteristics and flow curves related to starch origin were observed. Corn starch phosphate was characterised by a little lower pasting temperature and smaller viscosity values than phosphates made of its fractions. In case of wheat starch all phosphates revealed similar values. All studied starch phosphate pastes were non-newtonian fluids and had higher consistency coefficients (with the exception of unsegregated corn starch phosphate) than the respective blanks. It was also stated, that consistency coefficients of starch phosphate pastes obtained from corn starch are much higher than in case of wheat starch.

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