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Mixed pastes of starches with guar gum

Summary — Gelation characteristics (Brabender viscograph) and flow curves (Haake rheometer) were taken for corn, oat, potato and tapioca starch — guar gum 3 wt. % aqueous, binary blends at following ratios: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10. It was concluded, that increasing amount of guar gum added to the starches increased the Brabender viscosity of the composites, and this phenomenon was more pronounced in tuber starches. An addition of guar gum also increased the set back viscosity, hysteresis loop areas and shear thinning (pseudoplasticity) of the composites. Blends of both tuber and cereal starches with guar gum provided negative synergistic effects at elevated temperatures, whereas the cooling of cereal starches — guar gum systems led to weak but noticeable positive synergistic effects. The water deficiency in the starch granule environment caused by guar gum perturbed the course of gelation. Thermodynamic incompatibility of guar gum and starches in blends complicated the pattern of the gelation characteristics.

Key words: rheology, corn starch, oat starch, potato starch, tapioca starch.

MIESZANE KLEIKI SKROBIOWE Z GUMĄ GUAROWĄ

Streszczenie — Wyznaczono charakterystyki kleikowania (za pomocą wiskografu Brabendera) oraz krzywe płynięcia (reometrem Haakego) 3-proc. mas. wodnych kleików ze skrobi roślin bulwiastych lub zbożowych: kukurydzianej (CS), owsianej (OS), tapiokowej (TS) lub ziemniaczanej (PS) z gumą guarową (GG), zmieszanych w stosunku skrobia:guma guarowa 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 i 0:10 (tabela 1, 2, rys. 1, 2). Stwierdzono, że wraz ze zwiększającym się udziałem gumy guarowej w kleiku rosła ich lepkość a obserwowany efekt był wyraźniejszy w przypadku mieszanin ze skrobiami bulwiastymi (PS i TS). Dodatek gumy guarowej zwiększał lepkość skrobi również po oziębieniu do 25 °C, obszar pętli histerezy a także efekt rozrzedzania ścinaniem (pseudoplastyczność) mieszanych kleików. Mieszaniny wszystkich rodzajów skrobi z gumą guarową, w podwyższonej temperaturze wykazywały ujemne efekty synergistyczne, podczas gdy ochłodzone układy skrobi zbożowych zGG charakteryzowała słaby, lecz znamienny dodatni efekt synergistyczny (tabela 3). Obecność gumy guarowej powodowała niedobór wody wokół ziaren skrobiowych, co zaburzało przebieg kleikowania. Przebieg brabenderowskiej charakterystyki kleikowania zaburzał brak termodynamicznej kompatybilności skrobi i GG w badanych kleikach.

Słowa kluczowe: reologia, skrobia kukurydziana, skrobia owsiana, skrobia tapiokowa, skrobia ziemniaczana.

Starch — non-starchy hydrocolloid blends might offer unique texture of foodstuffs, enhance their overall quality and/or stability, and improve economy of food production [1—7]. Some factors influencing the pasting of starches in aqueous solutions of plant gums and the properties of resulting gels have already been discussed in our former papers [6, 7]. In this paper, the validity of some rules governing rheology of the gels are tested for blends obtained from corn (CS), oat (OS), potato (PS) and tapioca (TS) starches with guar gum (GG), with particular attention to the effect of the starch/GG ratio. The interest generating research in the problem can be rationalized in terms of the opinions about the character of amylose interactions with amylopectin. These two polysaccharides have been considered thermodynamically incompatible [8]. Lii *et al*. [9] observed however, some symptoms of compatibility in blends of both these polysaccharides provided their ratio is about 9:1 and 1:9.

The mer of GG is composed of four 1 → 4 linked β-D-mannopyranose units. Approximately every second mannopyranose unit carries one 6 → 1 bound α-D-galactopyranose unit making it a non-ionic gum.

GG has formed several applications in food technology for improving functional properties of bakery, dairy

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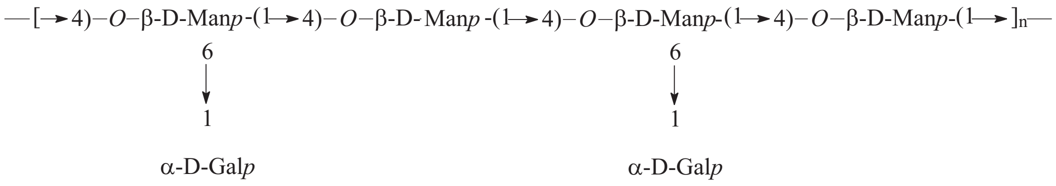

$$-[\rightarrow 4)-O-\underset{\substack{6\\ \downarrow\\ 1\\ \alpha\text{-D-Gal}p}}{\beta\text{-D-Man}p}\text{-}(1\rightarrow 4)-O-\beta\text{-D-Man}p\text{-}(1\rightarrow 4)-O-\underset{\substack{6\\ \downarrow\\ 1\\ \alpha\text{-D-Gal}p}}{\beta\text{-D-Man}p}\text{-}(1\rightarrow 4)-O-\beta\text{-D-Man}p\text{-}(1\rightarrow]_n-$$

(I)

and meat products, and also in dressings and sauces. Food technology accounts for the main demand for GG in the market. It is used as a water soluble fiber controlling constipation and peristaltics of bowels and intestine. It also sorbs toxins and prevents diarrhea. GG in the diet reduces the level of cholesterol [10—13]. Textile, paper, explosives, pharmaceutical, cosmetics and toiletries industries, oil and gas drilling as well as mining also consume considerable amounts of GG. The broad field of application requires more detailed studies on its concentration — rheology dependencies in blends with various starches. In this paper, the preparation and rheological properties of starch — GG blends of the total concentration of 3 wt. %, at 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10 ration are described. Two tuber starches — potato and tapioca, and two cereal starches — isolated from corn and oat were blended with GG then pasted in a Brabender viscograph. The resulting pastes were rheologically examined.

EXPERIMENTAL

Materials

— PS "Superior" was isolated from Glada variety, provided by Experimental Station of Potato Variety Evaluation in Wegrzce at Cracow, Poland. Its average molecular number (M_n), average molecular weight (M_w) and polydispersity (Pd) were $1.18 \cdot 10^7$, $5.65 \cdot 10^5$ and 21.5, respectively.

— CS ($M_n = 1.20 \cdot 10^7$, $M_w = 1.63 \cdot 10^5$, $Pd = 75.00$) [7] was purchased from Dia-Cel, Łódź, Poland.

— OS ($M_n = 1.10 \cdot 10^7$, $M_w = 1.95 \cdot 10^5$, $Pd = 57.89$) [7] was isolated from oat grains, according to Paton [14].

— TS ($M_n = 1.25 \cdot 10^7$, $M_w = 4.86 \cdot 10^5$, $Pd = 24.49$) [7] was purchased from National Starch and Chemicals.

— The amylose content in PS, TS, CS and OS were 24.0, 21.4, 20.7 and 11.9 %, respectively [7].

— GG, catalogue nr G 4129 ($M_n = 0.42 \cdot 10^7$, $M_w = 4.52 \cdot 10^5$, $Pd = 9.78$] [7] was purchased from Sigma Co., St. Louis, MO., USA.

Sample preparation

Starch-GG systems of following ratios: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10 were prepared in aqueous solutions. The total concentration of polysaccharides was 3 wt. %. The blends were prepared in cups covered with an aluminum foil at 95 °C on 20 min intensive stirring.

Methods of testing

Pasting characteristics

The pasting characteristics of starch or starch — GG systems of the following ratios: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, and 0:10 were determined with Brabender amylograph (Brabender GmbH, Duisburg, Germany). The starch — GG systems of other ratios, *e.g.*: 4:6, 3:7, 2:8, 1:9 were too thick for measurement of pasting characteristics. The measurements were carried out in duplicates.

Rheological measurements — flow curves determination

The measurements were performed with a RheoStress RS 1 (Gebrueder Haake GmbH, Karlsruhe, Germany) rheometer at 50 °C, in the CR mode with Z-34 measuring system. The shear rate increased within 10 min, from 1 to 300 s^{-1}, followed by constant 1 min shear rate of 300 s^{-1}, and subsequent 10 min decrease in shear rate from 300 to 1 s^{-1}. Ostwald de Waele rheological model was fitted to the resulting flow curves [15]. Additionally, the areas of thixotropy hysteresis loops and apparent viscosities of all samples at shear rate of 100 s^{-1} were calculated.

Statistical analysis

The experimental data were subjected to variance analysis (Duncan test), at the confidence level of $p < 0.05$ using the Statistica version 7.0 software (Statsoft, Inc., Tulsa, OK., USA).

A two-way analysis of variance was applied for comparison of the parameters collected for both gelation characteristics and rheological study. The Fischer test from the two-way analysis model of variance was used [16].

Mutual correlations and regression between both gelation characteristics and rheological parameters of the blends were calculated.

RESULTS AND DISCUSSION

The most viscous paste among the examined starches was obtained with 3 % sol of PS (Table 1).

Full sol gelatinization characteristics of the same concentration could be taken also for another tuber starch — TS whereas pastes of both cereal starches developed measurable Brabender viscograph viscosity just at 96 °C. After cooling to 25 °C, viscosity of PS paste decreased insignificantly, whereas the pastes of other starches,

T a b l e 1. Parameters of pasting characteristics of starch blends with guar gum

Starch:gum ratio*)	η_0**), B.u.	T_0, °C	η_{max}, B.u.	T at η_{max} °C	η at 96 °C B.u.	η after 20 min at 96 °C, B.u.	η_{min}, B.u.	T at η_{min} °C	η after cooling to 25 °C, B.u.
10:0 PS	17^{a}	57^{ab}	802^{a}	78^{b}	667^{b}	422^{b}	377^{b}	82^{b}	622^{b}
TS	40^{a}	70^{c}	160^{a}	85^{c}	157^{a}	137^{a}	130^{a}	88^{c}	337^{a}
CS	5^{a}	91^{e}	—	—	30^{a}	40^{a}	—	—	100^{a}
OS	15^{a}	91^{b}	—	—	76^{a}	74^{a}	—	—	427^{a}
9:1 PS	62^{a}	64^{c}	1142^{b}	91^{d}	1107^{c}	775^{c}	750^{c}	90^{a}	1175^{c}
TS	45^{a}	64^{a}	465^{b}	84^{bc}	405^{b}	280^{a}	277^{b}	91^{ac}	600^{b}
CS	42^{a}	68^{ab}	—	—	185^{b}	219^{b}	—	—	510^{b}
OS	57^{a}	92^{b}	—	—	140^{a}	252^{b}	—	—	720^{b}
8:2 PS	205^{b}	64^{bc}	1795^{c}	85^{c}	1632^{a}	1190^{a}	1160^{a}	91^{a}	1610^{a}
TS	296^{ab}	63^{a}	865^{c}	75^{a}	630^{c}	452^{b}	447^{c}	94^{b}	935^{c}
CS	160^{b}	70^{bc}	—	—	537^{c}	579^{c}	—	—	1232^{c}
OS	217^{a}	84^{a}	—	—	597^{b}	607^{c}	—	—	1352^{c}
7:3 PS	375^{c}	61^{abc}	2165^{d}	81^{a}	1887^{a}	1400^{a}	1370^{a}	91^{a}	1820^{a}
TS	486^{b}	63^{a}	1445^{d}	75^{a}	970^{d}	742^{c}	730^{d}	92^{ab}	1400^{d}
CS	547^{c}	74^{c}	—	—	1132^{d}	1105^{d}	—	—	2210^{d}
OS	590^{b}	84^{a}	1230^{a}	96^{a}	1215^{c}	1142^{d}	1127^{a}	91^{a}	2225^{d}
6:4 PS	755^{e}	56^{a}	2905^{e}	81^{a}	2485^{d}	1835^{d}	1815^{d}	91^{a}	2365^{d}
TS	975^{c}	61^{a}	2365^{e}	74^{a}	1650^{e}	1280^{d}	1275^{e}	93^{ab}	2290^{e}
CS	925^{d}	68^{ab}	—	—	1767^{e}	1660^{e}	1647^{a}	91^{a}	2870^{e}
OS	1280^{c}	82^{c}	1937^{b}	96^{a}	1890^{d}	1715^{e}	1695^{b}	91^{a}	2947^{e}
5:5 PS	670^{d}	58^{abc}	3720^{f}	77^{b}	2900^{e}	2275^{e}	2250^{e}	91^{a}	3025^{e}
TS	1990^{d}	62^{a}	3255^{f}	73^{a}	2165^{f}	1970^{e}	1927^{f}	93^{ab}	3150^{f}
CS	1897^{e}	64^{a}	2840^{a}	90^{a}	2705^{f}	2475^{f}	2455^{b}	90^{a}	3815^{f}
OS	2475^{d}	80^{d}	2880^{c}	92^{c}	2825^{e}	2555^{f}	2490^{c}	90^{a}	3725^{f}
0:10***)	5955^{f}	49^{d}	6375^{g}	81^{a}	6135^{f}	5890^{f}	—	—	5790^{f}

*) PS — potato starch, TS — tapioca starch, CS — corn starch, OS — oat starch.

**) Parameters in columns denoted with the same letter (*e.g.*: a, b, c) do not differ statistically significant at the level of confidence $p < 0.05$. Parameters should be compared within data for the same starch variety.

***) Data for the pure guar gum solution.

particularly those of OS this parameter increased remarkably. As compared to starch pastes, Brabender characteristic parameters for the GG 3 % solution were approximately one order higher. Its initial maximum viscosity only slightly decreased on heating to 96 °C that storing at that temperature.

Generally, the replacement of starch in content of 10 to 50 wt. % in the blends with GG resulted in an increase in the viscosity at every measurement temperature. However, the replacement of OS with just 30 % content with GG produced a paste of measurable gelatinization characteristics, and for CS-GG blends characteristics of gelatinization could be taken when the blend contained 50 % GG. Regardless of the starch origin, Brabender viscosity could not be measured for mixed gels in which the starch: gum proportion was below 1.

An increase in the viscosity could be interpreted as a synergism in blend component interaction. The Ikeda [17] definition of synergism is presented in Eq. (1)

$$\eta_{blend} = \eta_s \cdot \alpha_s + \eta_{gg} \cdot \alpha_{gg} \qquad (1)$$

where: η_s, η_{gg}, η_{blend} — *viscosities for particular starches, GG and their blends, respectively*, α_s, α_{gg} — *the deals of starches and GG in blends, respectively*.

Taking this into consideration, synergism could be recognized when experimental viscosities differed from calculated values based on the additivity of viscosity of both partners. Fig. 1 shows the domination of a negative synergism at 25 °C in the blends of GG with PS and a weak positive synergism could be observed in the pastes with the lowest GG content. In the TS — GG blends a negative synergism was observed almost in the whole investigated range. In CS and OS a week positive synergism was more common, particularly in the pastes with higher GG content.

Under experimental conditions, the response of particular starches to GG was diverse. It is commonly known (Muzimbaranda and Tomasik [18]) that PS develops pastes

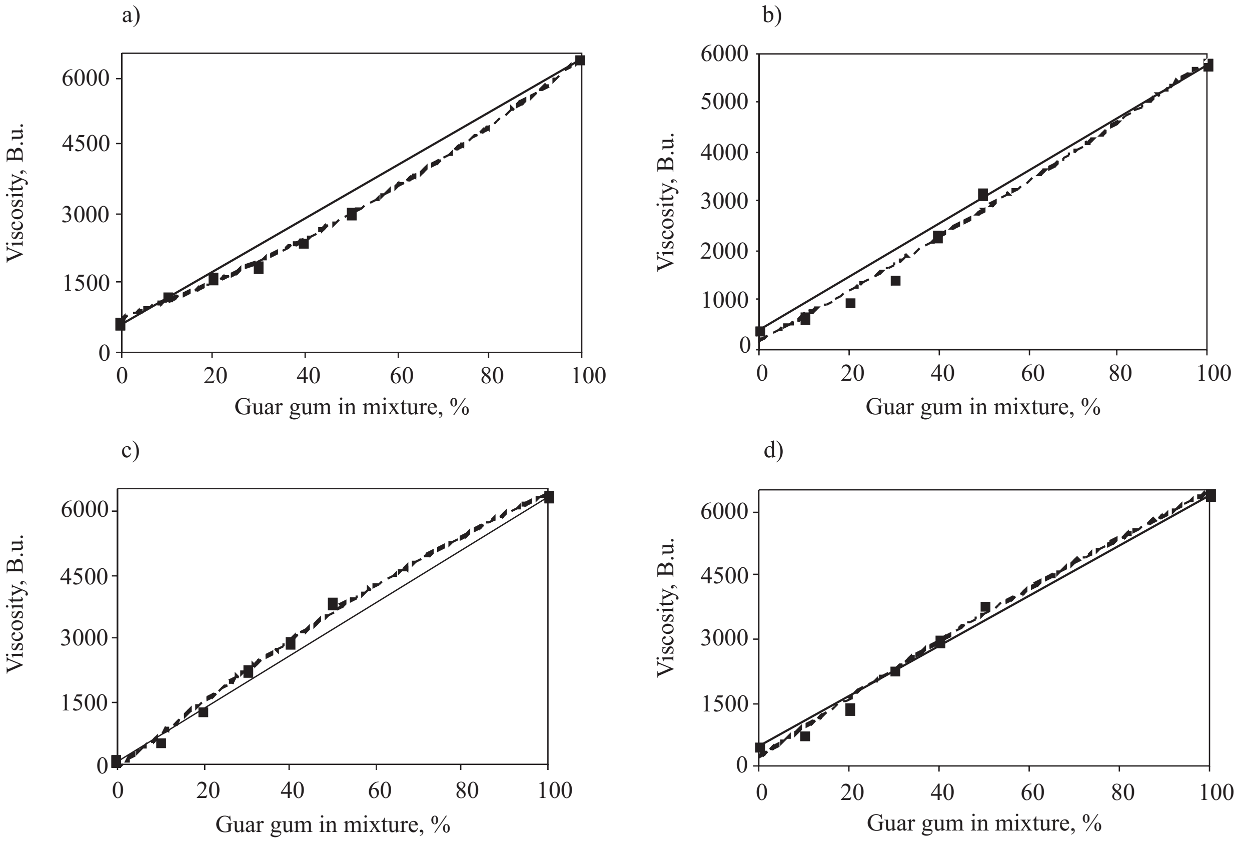

Fig. 1. Brabender viscosity after cooling to 25 °C for a) potato, b) tapioca, c) corn and d) oat starches — guar gum blends at different ratio; solid line — calculated data, dotted line — experimental data (3 % total concentration)

of the highest viscosity. This is because of its exclusive anionic character [19]. The four starches studied can be arranged in the following order of decreasing viscosity (η at 96 °C): PS >> TS > OS > CS. GG admixing perturbed this order, particularly when viscosity at 96 °C and above was considered. The perturbation rose significantly with an increase in GG concentration in the blends. In blends cooled to 25 °C, beginning from the blend with 30 % GG, the viscosity order reversed into OS ≈ CS > PS > TS (Table 1).

Every admixture of GG to the plain starch pastes resulted in an increase in viscosities although lower doses of GG to pastes of CS and OS did not evoke any measurable viscosity before cooling to 25 °C.

The properties of starch — hydrocolloid blends depend on several potential factors [20]. Observed phenomena could result from the association of polysaccharide chains [21]. Chain — chain interactions compete with chain — water interactions so a decrease in water activity might contribute to an increase in interchain binding. A reduction of interchain repulsions should therefore facilitate association. However, Alloncle *et al.* [22] suggested that an increase in the viscosity of starch was caused by a polymer phase separation, rather than intermolecular associations. Interchain associations can take place with similar or different polysaccharides hence, conditions of thermodynamic compatibility or incompatibility have to be considered [23—26]. The exclusion effect of swollen granules also has to be taken into account [25, 27]. Moreover, the interference of a non-gelling polysaccharide coexisting with a gelling polysaccharide can also be a factor [28].

Our considerations focused on three factors which seemed essential in determining paste properties. They are (i) the susceptibility of a starch of a particular origin to swelling, (ii) the availability of water to cause swelling and (iii) the thermodynamic compatibility of the starch and GG. Thermodynamic compatibility of the components of the blends would depend on their molecular weight [average molecular number (M_n), average molecular weight (M_w)], polydispersity, and amylose content in starches.

According to Lii *et al.* [29] PS granules swelled much more readily than CS and TS granules. Unfortunately, relevant data for OS granules are not available. Rapid swelling and exudation of polysaccharides from the granule interior supported viscosity enhancement. According to Funami [30], interactions between GG and exuded amylose could be responsible for the increase in starting viscosity of starch-hydrocolloid blends on heating, whereas GG and exuded amylopectin interactions increased the maximum viscosity values. Table 1 reveals that Funami proposal is valid for CS, but not in general. Amylose content, M_w, M_n and polydispersity (*Pd*) of PS and TS were similar [7]. However, the initial and maximum viscosities of the PS pastes were distinctly higher. The exclusive ionic character of PS could most probably account for this. Moreover, CS swelled more readily than TS [29], meaning that more exudation could be anticipated from CS than from TS granules and, in consequence, a higher initial and maximum viscosity of the paste but experimental data revealed otherwise. Corresponding viscosities for the TS pastes were higher than those of CS pastes.

M_w and M_n, of TS were higher than these of CS but *Pd* of CS was distinctly higher. Funami *et al*. [31] found that, for CS and galactomannans, an increase in maximum viscosity was inversely proportional to the average molecular weight of galactomannan. Low molecular weight of one component facilitated a thermodynamic compatibility with the long chains of the other. In starch — GG interactions, TS of low *Pd* appeared to be more beneficial for developing viscous pastes.

Apparently, the water availability for all starch varieties should be equally dependent on the concentration of GG in the blend. Khanna and Tester [32] discussed the starch — hydrocolloids interactions in terms of the sequestering effect of hydrocolloid, which restricted the amount of water available for starch gelatinization. Mutual interactions of exudations from starch granules with GG could influence the quantity of amylose leached during pasting and controlling the viscosity of the environment and water availability [33]. The initial viscosity, η_0, given in Table 1 could reflect this type of interactions and, simultaneously, presents contribution to the viscosity from elevated dose of GG to the solution prior to pasting. The onset temperature, T_0, for the PS sol initially increased after admixture of 10 % GG in order to decrease with increasing dose of GG in the blends. The high susceptibility of PS granules to swelling heading to a rapid increase in the viscosity of sol could be responsible for this effect. For other starches, an admixture of GG resulted in a decrease in T_0. Such trend in changes of T_0 might indicate that water deficiency, at this stage is insignificant. An increase in the concentration of GG in blends even facilitated pasting initiation. Thus, an increase in η_o could most probably be associated with some sort of interaction of GG with granules facilitating their swelling. This interaction can be assumed to involve exudations covering the surface of granules [34]. Stimulated by interactions with GG, exudation material could pass into solution, thus increasing viscosity. The surface of granules and channel into granule hilum became more accessible to water.

The changes in viscosity in the blends of particular starches, especially in the case of PS was irregular in respect to changes of concentration. In pastes with PS these changes were irregular. As a rule, measured η values for blends containing 30 % GG were much lower than corresponding values for other blends. The same effect was observed by Shi and BeMiller [2] for the PS: GG ratio of 9:1, at the total concentration of polysaccharides of 4 wt. %, and by Sikora and Kowalski [35], who investigated the 14:1 blends of the total concentration of 3 wt. %. For other starches, except in isolated cases, viscosity rose generally with increasing dose of GG in the blends. Some discrepancies were noted in case of the blends containing 50 % GG. They could stem from the very high viscosity of these blends and hence, a possible non-homogeneity clearly observed already in blends with over 50 % GG. The observed results could be attributed to various factors. Irregularities can result due to a change of the character of pastes from GG in PS through the phase separation into PS in GG. Phase separation could occur in the blend containing around 30 % GG. TS behaved to a certain extent similarly but the suggested phase separation took place at about 20 % admixture of GG.

Chaisawang and Suphantharika [4] observed similar effects, and claimed that an addition of GG turned the system into biphasic in which GG was in the continuous phase. Swelling of the starch granules led to an increase in the viscosity of the mixture. The accompanying shear forces disrupted the swollen granules from causing a reduction in the paste viscosity. The authors clarified also that GG did not envelope TS granules and that the latter gelatinized freely. Kruger *et al*. [36] observed that CS granule swelling during pasting was greatly reduced in the presence of GG due to the lower heating rates and the reduced mobility of water. Funami *et al*. [30] explained the effect of GG upon CS in terms of conformationally simple structure of the amylose chain, taking part in the interactions with GG. The authors claimed that GG with longer chains (M_w above $10 \cdot 10^5$) interacted with amylopectin, and longer GG chains offered stronger interactions. Interactions between GG and amylose could influence an increase in gelatinization onset temperature of starch, and these between GG and amylopectin generated an increase in maximum viscosity during gelatinization.

According to Funami *et al*. [30, 31, 37] other interactions of GG with starch, such as thickening effect of GG influenced pasting of starch, leading to acceleration of short-term retrogradation.

PS and TS sols containing 10 % GG pasted almost at the same rate, but at 96 °C, PS fitted to GG more readily than TS, CS and OS. Within 20 min storage of pastes at the same temperature, fitting PS to GG slowed down to initial rate whereas adjustment TS to GG was significantly obscured and adjustment of GG to CS and, particularly considerably OS, was more efficient. Development of viscosity after cooling to 25 °C was most efficient in the PS blend. Qualitatively, the same sequence of interactions was observed for PS and TS blends with 20 % GG. In the blends of the same composition, OS interacted with GG at 96 °C much stronger than in the former blend, and after cooling to 25 °C OS-GG and CS-GG interactions were very efficient. In the blends with 30 % GG interactions of CS and OS were essentially intensified in all the measured points. In the blends with 40 % GG, interactions with tuber starches were significantly more efficient than with both cereal starches. Enhanced set back viscosity

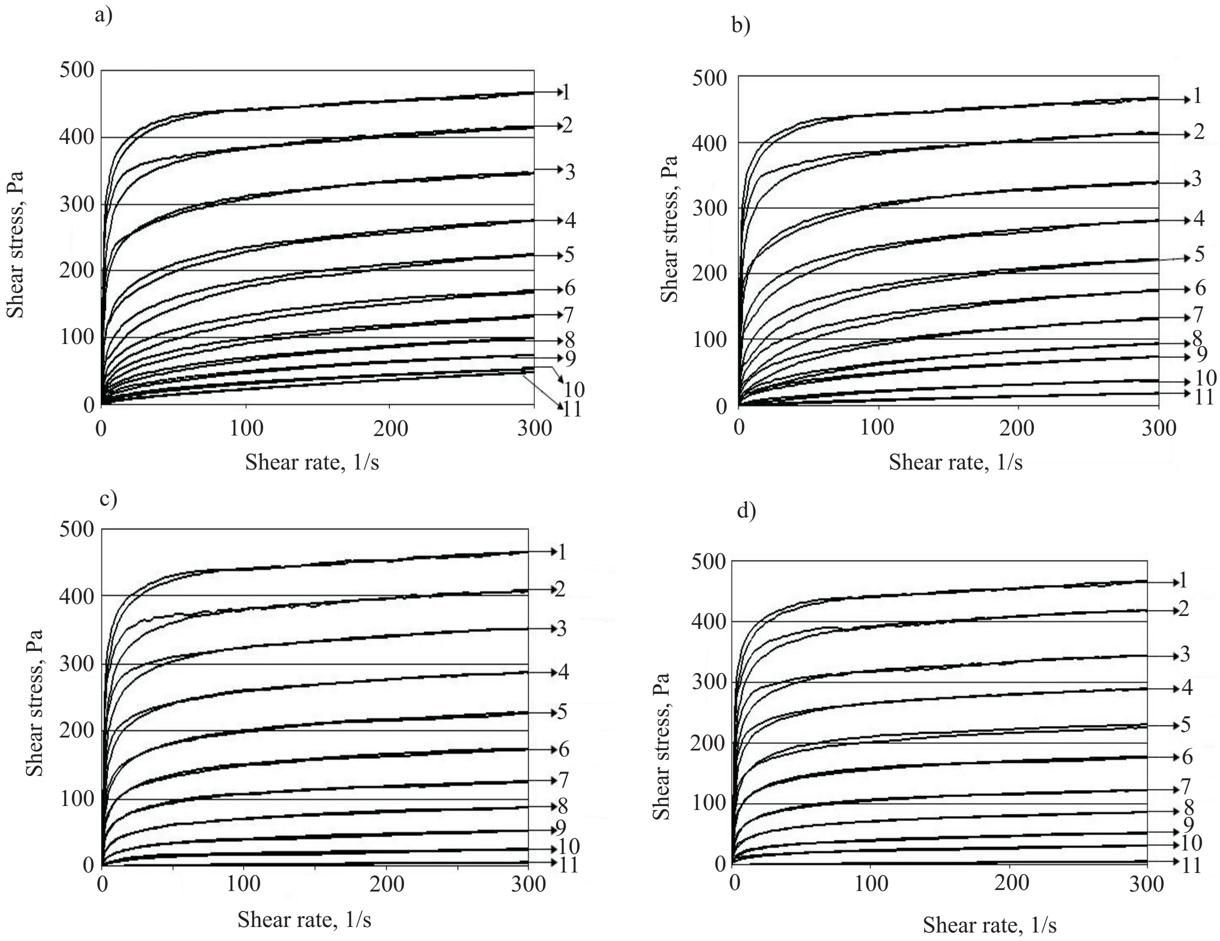

Fig. 2. Flow curves at 50 °C of a) potato, b) tapioca, c) corn and d) oat starches blends with and without guar gum; the numeric marking of the curves correspond to the starch guar gum mass ratio: 1 — 0:10, 2 — 1:9, 3 — 2:8, 4 — 3:7, 5 — 4:6, 6 — 5:5, 7 — 6:4, 8 — 7:3, 9 — 8:2, 10 — 1:1, 11 — 10:0

could be associated with retrogradation. According to Funami *et al*. [37], GG promoted long-term starch retrogradation through an increase in the concentration of amylose in the continuous phase because of its relatively low molecular weight.

A comparison of the data for the OS-GG and CS -GG blends with 30 and 40 % deal of GG suggested that in the latter blends, phase separation could take place. Similarly, phase separation can also occur in PS-GG and TS-GG blends containing 50 % GG.

Results of rheological measurements (flow curves) of 3 wt. % blends of starches with GG of the 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 and 0:10 ration are presented in Fig. 2a—d. Shear thinning of all systems increased with the GG concentration and was more pronounced with tuber starches.

In Table 2, results of fitting of Ostwald de Waele equation to experimental data are presented. That model is used to describe the behavior of non — Newtonian fluids [15].

Consistency coefficient, *K* (Pa · s^n) and flow behavior index *n* (-) in this model measure shear stress at a rate of shear equal to 1 s^{-1} and departure of a fluid from Newtonian flow, respectively [38]. Yield stress (τ_0), represents a finite stress required to achieve flow. Below this parameter a material exhibits solid like characteristics [15]. Additionally, the areas of hysteresis loops were calculated. This area is interpreted as a dimension of energy delivered to the system to break down its thixotropic structure. According to Barnes [39], all liquids with microstructure can show thixotropic behavior, because thixotropy reflects the finite time necessary to move from any state of microstructure to another. It should be noted that in such process shear rate and time vary simultaneously and estimation of the deals of effects of both variables is impossible. Thus, the hysteresis loop can serve, to a certain extent as a parameter for quality control.

The Ostwald de Waele model fitted very well (R^2), but as the dose of GG in these blends increased, the correlations turned slightly worse, most likely because of an increasing non-homogeneity of the solutions. In all blends, very small values of yield stress (τ_0) indicate fluidity of the studied systems. Consistency coefficient, *K*, in the pastes of plain starches decreased in the order: PS > TS > CS > OS. An admixture of increasing portions of GG resulted in an increase in *K*, to which every starch responded differently. The initial order changed to PS > OS

> CS > TS after admixture of the lowest GG dose (10 %) and stabilized later at higher doses of GFG following the order OS > CS > PS > TS practically regardless starch: GG proportion.

T a b l e 2. Rheological parameters for blends of starches with guar gum

Blend composition*)	*K***) Pa · s^{n}	*n* (-)	R^{2}	η_{100} Pa · s	Area of hysteresis loop W · m^{-3}
10:0 PS	1.02^{a}	0681^{i}	0.9999	0.23^{b}	-76.40^{b}
TS	0.22^{a}	0.791^{i}	0.9995	0.08^{a}	-254.80^{a}
CS	0.15^{a}	0.649^{g}	0.9999	0.04^{a}	83.31^{bc}
OS	0.15^{b}	0.660^{f}	0.9999	0.03^{a}	67.05^{b}
9:1 PS	3.05^{ab}	0.505^{h}	0.9999	0.31^{c}	-504.25^{ab}
TS	1.23^{a}	0.614^{i}	0.9980	0.21^{b}	-356.80^{a}
CS	2.98^{a}	0.372^{f}	0.9937	0.17^{a}	-637.90^{a}
OS	7.51^{a}	0.248^{c}	0.9900	0.23^{b}	-199.95^{ab}
8:2 PS	6.61^{bc}	0.427^{g}	0.9997	0.47^{d}	-659.40^{a}
TS	3.90^{ab}	0.495^{h}	0.9973	0.39^{c}	-511.85^{a}
CS	11.18^{b}	0.269^{e}	0.9956	0.38^{b}	-478.40^{a}
OS	13.34^{a}	0.239^{c}	0.9946	0.40^{c}	-197.51^{ab}
7:3 PS	10.94^{c}	0.389^{f}	0.9996	0.66^{e}	-949.25^{a}
TS	8.29^{b}	0.432^{g}	0.9966	0.62^{d}	-563.40^{a}
CS	25.02^{c}	0.166^{bc}	0.9992	0.70^{c}	-210.55^{abc}
OS	27.87^{c}	0.201^{e}	0.9901	0.71^{d}	-69.11^{ab}
6:4 PS	17.98^{e}	0.351^{e}	0.9992	0.91^{f}	-1678.00^{d}
TS	15.64^{c}	0.380^{b}	0.9956	0.92^{c}	-1131.65^{d}
CS	45.55^{d}	0.179^{c}	0.9907	1.06^{d}	-343.75^{ab}
OS	46.04^{d}	0.176^{d}	0.9818	1.05^{e}	-325.75^{ab}
5:5 PS	29.10^{d}	0.310^{b}	0.9985	1.23^{a}	-2496.50^{c}
TS	20.06^{d}	0.339^{f}	0.9955	1.26^{f}	-2104.50^{bc}
CS	67.25^{e}	0.168^{bc}	0.9809	1.48^{e}	-699.30^{a}
OS	77.93^{e}	0.147^{b}	0.9690	1.56^{f}	-624.45^{a}
4:6 PS	50.82^{d}	0.263^{b}	0.9950	1.75^{a}	-2727.00^{c}
TS	47.32^{c}	0.276^{e}	0.9943	1.73^{g}	-2328.50^{b}
CS	99.52^{f}	0.147^{bcd}	0.9723	1.98^{f}	-395.80^{ab}
OS	108.75^{f}	0.131^{b}	0.9602	2.01^{g}	-1849.00^{d}
3:7 PS	91.14^{f}	0.196^{d}	0.9918	2.28^{g}	-1719.00^{d}
TS	88.41^{f}	0.207^{d}	0.9898	2.36^{h}	-1867.00^{c}
CS	145.30^{g}	0.122^{abd}	0.9540	2.58^{g}	278.95^{c}
OS	158.90^{g}	0.109^{a}	0.9318	2.67^{h}	680.50^{c}
2:8 PS	166.75^{g}	0.131^{c}	0.9664	3.06^{h}	-453.10^{ab}
TS	153.05^{g}	0.143^{c}	0.9716	3.01^{i}	-621.70^{a}
CS	198.95^{h}	0.104^{ad}	0.9216	3.22^{h}	1133.00^{d}
OS	201.25^{h}	0.097^{a}	0.9017	3.16^{i}	813.10^{c}
1:9 PS	244.10^{h}	0.097^{a}	0.9075	3.82^{i}	1905.50^{f}
TS	244.15^{h}	0.050^{a}	0.9287	3.84^{j}	1972.50^{f}
CS	248.95^{i}	0.090^{a}	0.8824	3.79^{i}	1566.50^{d}
OS	252.40^{c}	0.093^{a}	0.8887	3.88^{j}	1125.65^{c}
0:10***)	284.45^{j}	0.090^{a}	0.8859	4.38^{j}	1117.90^{e}

*), **), ***) — See Table 1.

This sequence indicated a much higher sensitivity of cereal starches to interaction with GG. As the dose of GG in the blends increased, differences between reaction of starches to it become insignificant. Increasing the dose of GG reduced the flow behavior index values. In plain starch pastes its value decreased in the order TS > PS > OS > CS. After admixture of GG that order changed to TS > PS > CS > OS and was maintained regardless the level of the GG admixture until the 1:9 ratio was reached, and then no differences between *n* for particular pastes was observed. Thus, blends with the most and least TS and OS resembled Newtonian fluids, respectively. The viscosities at 100 s^{-1}, η_{100}, distinct for each plain starch paste, after admixture of GG turned more uniform regardless the starch variety. The numerical values and their uniformity increased with the level of admixed GG.

PS and TS pastes were characterized by negative values of hysteresis loop areas, which was attributed to

T a b l e 3. Two-factorial ANOVA analysis

	GG conc.	η_{max}	η at 96 °C	η after 20 min at 96 °C	η_{min}	η after cooling to 25 °C	*K*	n	η at 100 s^{-1}	Area of hysteresis loop
GG concentration, %	1.000									
η_{max}, B.u.	0.912	1.000								
η at 96 °C, B.u.	0.900	0.959	1.000							
η after 20 min at 96 °C, B.u.	0.932	0.930	0.982	1.000						
η_{min}, B.u.	0.922	0.931	0.980	1.000	1.000					
η after cooling to 25 °C, B.u.	0.953	0.875	0.922	0.973	0.972	1.000				
K, Pa · s^{n}	0.917	0.618	0.749	0.845	0.841	0.898	1.000			
n (-)	-0.830	-0.720	-0.529	-0.628	-0.847	-0.725	-0.726	1.000		
η at 100 s^{-1}, mPa · s	0.970	0.888	0.927	0.970	0.961	0.985	0.983	-0.766	1.000	
Area of hysteresis loop, W · m^{-3}	0.516	0.805	0.654	0.587	0.545	0.480	0.288	-0.314	0.399	1.000

the formation of the antithixotropic structures induced by shearing, whereas corresponding values for pastes of both cereal starches were positive. The order of these values was TS < PS < OS < CS. The admixture of GG within the range of starch: GG proportions from 9:1 up to 4:6 invariantly resulted in developing highly negative hysteresis loops which meant that in the presence of GG, generated shearing ordered structures more readily. Starting from proportions 3:7 up to 2:8, corresponding pastes with tuber starches retained negative values of the hysteresis loop areas, though these values showed a steady tendency towards turning positive. Actually, at the 1:9 proportion they were highly positive. In the range of the proportions from 3:7 up to 1:9, relevant values for both cereal starches were already positive and they increased with the dose of GG in the blends (Table 2).

A two-way ANOVA analysis of the rheological parameters is presented in Table 3 with only parameters of essential correlations given.

Correlations involved concentration of GG, viscosity parameters from the Brabender characteristics of gelatinization, parameters of the Ostwald de Waele equation and area of the hysteresis loop within the whole set of the blend compositions. Correlations of the viscosities and the consistency parameter with the concentration of GG in blends were average but the flow behavior index, *n*, correlated less satisfactorily.

The latter correlated negatively with all involved indices. Generally, all correlations involving Ostwald de Waele parameters and area of the hysteresis loop were worse than the correlations with viscosity indices. The collected results confirm the involvement of all factors specified in our former paper [6] in controlling rheology of binary hydrocolloid blends. However, the significance of particular factors in the studied blends varied, therefore at this stage of research, prediction of properties of the blends can only be made qualitatively.

CONCLUSIONS

— Increasing the guar gum content in starches increased Brabender viscosity of composites, and this phenomenon was more pronounced in tuber starches.

— Synergism is more common in guar gum — cereal starch blends than in corresponding tuber starch blends.

— The addition of guar gum increased viscosity after cooling to 25 °C and shear thinning effect of composites.

— Changes in measured parameters for a given starch were not proportional to the concentration of admixed guar gum. Depending on concentration of guar gum, irregularities in increase in viscosity are observed in whole range of rheograms.

— At this stage of study, prediction of properties of the blends can be made solely qualitatively because the importance of earlier specified factors controlling rheology of binary hydrocolloid blends, though essential, change from one blend into another.

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LITERATURE

1. Closs C. B., Conde-Petit B., Roberts I. D., Tolstoguzov V. B., Escher F.: *Carbohydr. Polym.* 1999, **39**, 67.
2. Shi X., BeMiller J. N.: *Carbohydr. Polym.* 2002, **50**, 7.
3. Mandala I., Michon C., Launay B.: *Carbohydr. Polym.* 2004, **58**, 285.
4. Chaisawang M., Suphantharika M.: *Food Hydrocoll.* 2006, **20**, 641.
5. Pongsawatmanit R., Temsiripong T., Suwonsichon T.: *Food Res. Int.* 2007, **40**, 239.
6. Kowalski S., Sikora M., Tomasik P., Krystyjan M.: *Polimery* 2008, **53**, 457.
7. Sikora M., Kowalski S., Tomasik P.: *Food Hydrocoll.* 2008, **22**, 943.
8. Kalichevsky M. T., Ring S. G.: *Carbohydr. Res.* 1987, **162**, 323.
9. Lii C. Y., Tomasik P., Hung W. L., Lai V. M. F.: *Pol. J. Food Sci. Nutr.* 2002, **11**(4), 29.
10. Brown J. C., Livesey G.: *Am. J. Clin. Nutr.* 1994, **60**, 956.
11. Van Nieuwenhoven M. A., Kovacs E. M. R., Brummer R.-J. M., Westerterp-Plantenga M. S., Brouns F.: *J. Am. Coll. Nutr.* 2001, **20**, 87.
12. Owusu-Asiedu A., Patience J. F., Laarveld B., Van Kessel A. G., Simmins P. H., Zijlstra R. T.: *J. Animal Sci.* 2006, **84**, 843.
13. De Cassia Freitas K., Amancio O. M., Novo N. F., Fagundes-Neto U., de Morais M. B.: *Clin. Nutr.* 2006, **25**, 851.
14. Paton D.: *Starch/Stärke* 1977, **29**, 149.
15. Steffe J. M.: "Rheological methods in food process engineering", 2nd ed., East Lansing, MI, USA: Freeman, 1999, p. 328.
16. Elandt R.: "Mathematical statistics applied in agricultural experimental art", PWN, Warszawa 1964, p. 140—194 (in Polish).
17. Ikeda S., Nitta Y., Kim B. S., Temsiripong T., Pongsawatmanit R., Nishinari K.: *Food Hydrocoll.* 2004, **18**, 669.
18. Muzimbaranda C., Tomasik P.: *Starch/Stärke* 1994, **46**, 469.
19. Tomasik P.: "Food 3" (Special issue 1) (Ed. Teixeira da Silva J.), Global Science Books (ISSN 1749-7140), New York 2009, p. 45.
20. Lai V. M.-F., Huang A.-L., Lii C.-Y.: *Food Hydrocoll.* 1999, **13**, 409.
21. Dea I. C. M.: "Polysaccharide in food" (Eds. Blanshard J. M. V., Mitchell I. R.), Butterworth and Co. (Publisher) Ltd., London, UK 1979, p. 229.
22. Alloncle M., Lefebvre J., Llamas G., Doublier J. L.: *Cereal Chem.* 1989, **66**, 90.
23. Abdulmola N. A., Hember M. W. N., Richardson R. K., Morris E. R.: *Carbohydr. Polym.* 1996, **31**, 65.
24. Alloncle M., Doublier J.-L.: *Food Hydrocoll.* 1991, **5**, 455.
25. Eidam D., Kulicke W. M., Kuhn K., Stute R.: *Starch/Stärke* 1995, **47**, 378.
26. Kulicke W. M., Eidam D., Kath F., Kix M., Kull A. H.: *Starch/Stärke* 1996, **48**, 105.
27. Liu H., Lelievre J.: *Cereal Chem.* 1992, **69**, 597.

28. Biliaderis C. G., Arvanitoyannis I., Izydorczyk M. S., Prokopowich D. J.: *Starch/Stärke* 1997, **49**, 278.
29. Lii C. Y., Tomasik P., Hung W.-L., Lai V. M.-F.: *Int. J. Food Chem. Technol.* 2003, **38**, 677.
30. Funami T., Kataoka Y., Omoto T., Goto Y., Asai I., Nishinari K.: *Food Hydrocoll.* 2005, **19**, 15.
31. Funami T., Kataoka Y., Omoto T., Goto Y., Asai I., Nishinari K.: *Food Hydrocoll.* 2005, **19**, 1.
32. Khanna S., Tester R. F.: *Food Hydrocoll.* 2006, **20**, 567.
33. Christianson D. D.: "Food Carbohydrates" (Ed. Lineback D., Inglett G.), AV Publishing Co., Westport 1982, p. 399.
34. Starzyk F., Lii C. Y., Tomasik P.: *Pol. J. Food Nutr. Sci.* 2001, **10**(4), 27.
35. Sikora M., Kowalski S.: "Starch: Recent Achievements in Understanding of Structure and Functionality" (Eds. Yuryev V. P., Tomasik P., Bertoft E.), Nova Science Publishers, Inc., New York 2007, p. 107.
36. Kruger A., Ferraro C., Zaritzky N. E.: *J. Food Eng.* 2003, **58**, 125.
37. Funami T., Kataoka Y., Omoto T., Goto Y., Asai I., Nishinari K.: *Food Hydrocoll.* 2005, **19**, 25.
38. Rao M. A.: "Rheology of fluid and semisolid foods. Principles and applications", Aspen Publishers, Inc., Gaithersburg, Maryland 1999, p. 11.
39. Barnes H. A.: *J. Non-Newtonian Fluid Mech.* 1997, **70**, 1.

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