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Starch polysaccharide hydrocolloid gels

Summary — Studies on the formation of gels from 5 % w/w suspensions of potato, cassava, corn, and oat starches in 0.05 or 0.2 % w/w aqueous solutions of one of Arabic, carob, guar, karaya, or xanthan gum, and κ-carrageen shed light on the rules governing rheological properties of resulting gels. Avoiding phase separation in a plant gum — starch solution is crucial for a high viscosity of gels formed. Partner of anionic starch in the gel should be nonionic unless the partnering plant gum has low M_w and/or high polydispersity (*e.g.* karaya gum). Nonionic starches combine with gums regardless they are anionic or neutral. Usually, Arabic and xanthan gums and κ-carrageen provided less viscous mixed gels with starches. Amylose and exceptionally high lipid contents in starches could also be essential factors influencing gelation. Admixture of plant gums into starch gels reduced elasticity of the mixed gels.

Key words: plant gums, starch, gelation, Brabender viscography.

HYDROKOLOIDALNE ŻELE SKROBIA/POLISACHARYD

Streszczenie — Przeprowadzono żelowanie 5 % mas. zawiesin skrobi ziemniaczanej, tapiokowej, kukurydzianej i owsianej (tabela 1) w 0,05 i 0,2 % mas. wodnych roztworach gumy arabskiej, karob, guarowej, karaja i ksantanowej oraz κ-karagenu. Uzyskane wyniki pozwoliły na lepsze zrozumienie roli czynników rządzących reologicznymi właściwościami powstających żeli. W celu uzyskania żeli o większej lepkości, w roztworach gum ze skrobią istotne jest unikanie rozdzielenia faz. Zatem, partnerem anionowej skrobi, jaką jest skrobia ziemniaczana, powinna być guma niejonowa, chyba że guma charakteryzuje się małym ciężarem cząsteczkowym i/lub wysokim stopniem polidyspersyjności (co umożliwia odpowiednie dopasowanie termodynamiczne partnerów). Właściwości takie ma np. guma karaja i, do pewnego stopnia, także guma arabska (tabela 2). Pozostałe badane niejonowe skrobie mieszają się z gumami bez względu na ich anionowy bądź obojętny charakter. Zazwyczaj, gumy arabska i ksantanowa oraz κ-karagen ze skrobiami dają mieszane żele o mniejszej lepkości (tabele 3—6). Zawartość amylozy w skrobiach oraz wyjątkowo duża zawartość lipidów również mogą okazać się istotnymi czynnikami wpływającymi na przebieg żelowania. Dodatek gum roślinnych do żeli skrobiowych zmniejsza elastyczność takich żeli w stosunku do elastyczności kleiku z samej skrobi (rys. 1 i 2).

Słowa kluczowe: gumy roślinne, skrobia, żelowanie, wiskografia Brabendera.

Mixed gels of polysaccharides play a role in texturing of foodstuffs. Plant gums admixed to starch influence its pasting and, then, viscosity and retrogradation of resulting gels [1—4]. The thermodynamic compatibility of polysaccharides in mixed gels is, perhaps, the key factor controlling results of the blending. Polysaccharides, for instance amylose and amylopectin, can stay in pastes forming separated phases [5, 6] but waxy corn starch forms with agarose a bicontinuous gel of the structure dependent on the components ratio [7]. In that case, energy benefit resulting from intermolecular, molecular (supramolecular) and intersupramolecular interactions among polysaccharides in pastes [8] — a driving force for the polysaccharides to orient in respect to one another — was insufficient to form one continuous phase. In case of starches, such mutual orientation results in the formation of hydrogen-bond supported networks leading to crystallization called retrogradation [9]. In gels consisting of two anionic polysaccharides, interpretation of the interactions controlling gel properties is more difficult.

Further complications occur when starch is one of the polysaccharide partners in the mixed gels. A full gelation of starch is unlikely because of deficiency of water in the starch granule environment. The susceptibility of starch granules to swelling, which initiates gelation, is dependent on both the granule size and botanical origin [10]. In the gels, some granules remain non-gelated (see, for instance, gelation of waxy corn starch in agarose [7]). Thus, gels have a form of either (i) suspension of swollen starch granules in a gel of another polysaccharide [1], (ii)

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separated diphase system [11], (iii) common gel network [11], (iv) system in which floccules were formed in a bridged manner [12], or (v) system of the structure formation of which is governed by depletion (osmotic) flocculation [12].

Natural components of starches, such as lipids and/or proteins, also influence the structure and properties of mixed gels. Polysaccharide – polysaccharide interactions in gels depend on molecular sizes of the components and the lengths of the polysaccharide chains [13]. The latter are certainly essential for the formation of native helical and surface complexes with lipids and proteins, respectively [14].

Mixed gels are cheap and biodegradable materials suitable for application as fillers, ceramic binders, composite materials, surface coatings or sizes for paper and textiles [15—18]. Numerous studies on the properties of the mixed gels [19] let understand of the phenomena governing the gelation and structures of the gels but they did not result in any theory allowing prediction of the properties of the gels.

In this paper, studies on the characteristics of gelation and dynamic rheology of gels prepared from potato, cassava, corn, or oat starches with Arabic, carob (locust bean), guar, karaya, and xanthan gums and κ-carrageen are presented. The factors controlling rheological properties of mixed gels are identified.

EXPERIMENTAL

Materials

— Potato starch was isolated in our laboratory from potatoes of the Glada variety collected from the experimental farm in Wegrzce at Cracow, Poland. Cassava starch was purchased from National Starch & Chemical GmbH in Hambourg, Germany. Corn starch (HZ 44810/28/95) was purchased from Dia-Cel in Lodz, Poland. Oat starch was isolated from oat according to Paton [20]. Properties of those starches are collected in Table 1.

T a b l e 1. Chemical compositions and solubility of starches investigated

Starch variety	Total P a) (mg/100 g)	Dry residue b) (%)	Amylose c) (%)	Lipids d) (%)	Solubility e) in water (%, dry residue) at		
					80 °C	90 °C	95 °C
Potato	125.35±0.23	85.45±0.05	24.03±0.23	0.09±0.04	12.88±0.25	18.26±0.44	—
Cassava	27.29±0.27	86.85±0.04	21.42±0.03	0.12±0.00	34.9±0.76	44.19±1.53	—
Corn	37.9±0.66	86.24±0.04	20.72±0.06	0.40±0.08	4.86±0.10	4.28±0.06	14.77±1.48
Oat	76.7±0.56	89.09±0.02	11.88±0.09	1.23±0.00	2.6±0.28	4.2±0.14	12.3±0.28

a) According to Marsh [21]. b) According to Polish Standards [22]. c) According to Morrison and Laignelet [23]. d) According to Richter [24]. e) According to Leach [25].

— Arabic gum, carob gum, guar gum, karaya gum, xanthan gum and κ-carrageen were purchased from Sigma St. Louis, MO, USA.

Methods of testing

Determination of average molecular weight

Sample preparation

a) starches (0.025 g) were suspended in 2 % aqueous dimethyl sulphoxide (DMSO) solutions (2 cm^3) and agitated at 70 °C for 22 h followed by admixture of 0.005 M aqueous solution of Na_2CO_3 (2 cm^3) and 1 h agitation at room temperature.

b) gums (0.025 g) were added into 0.005 M aqueous solutions of Na_2CO_3 (5 cm^3) and agitated for 24 h at room temperature.

Chromatography

The 0.005 M aqueous solution of Na_2CO_3 used as the eluent was pumped with peristaltic pump (Pharmacia LKB-Pump P-1) from a container through a dosimeter (VICI Valco Instruments Co. Inc.) into a column system. The flow rates were 27 and 7.7 cm^3/h for starches and gums, respectively. For starches, the following columns' system was used:

— 16 mm × 470 mm column packed with „Sephacryl/Pharmacia/S-200" gel,

— 16 mm × 940 mm column packed with „Sephacryl/Pharmacia/S-200" gel,

— 16 mm × 860 mm column packed with „Sephacryl/Pharmacia/S-500" gel,

— 16 mm × 830 mm column packed with „Sephacryl/Pharmacia/S-1000" gel.

For gums the system of two columns was used:

— 16 mm × 380 mm packed with „Sephacryl/Pharmacia/-200" gel,

— 16 mm × 460 mm packed with „Sephacryl/Pharmacia/S-500" gel.

Columns were thermoinsulated with a polyurethane jackets.

The samples (1 cm^3) were injected into the columns and after elution the eluate was collected as 131 fractions, each of 5 cm^3 volume.

Pullulans — P-10, P-50, P-200, and P-800 of 12 200, 48 000, 186 000 and 853 000 Da (2 mg/cm^3) were used as the standards (Showa Denko K. K., Japan).

Fractions of eluate (samples and pullulans) were analyzed according to Morris [26]. Thus, a sample (1 cm^3) was treated with 0.2 % solution of anthrone in concentrated H_2SO_4 (2 cm^3) and maintained for 10 min in a boiling water bath. Then, the sample was cooled to room temperature and its absorbance was measured in 10 mm quartz cell at 540 nm using a M 42 Specord instrument (Carl Zeiss, Jena, Germany).

Characteristics of gelation

Aqueous suspension of starch (5 % w/w calculated for dry residue) was agitated at 800 rpm with a mechanical stirrer. After 20 min, samples were transferred into a Brabender viscograph (Brabender GmbH & Co. KG, Duisburg, Germany) set for heating to 96 ^oC with 1.5 ^{o}/min rate at 75 rpm, maintaining at 96 ^oC for 20 min followed by cooling to 25 ^oC with continuous agitation with the same rate as during heating.

Samples of the blends of starches with gums designed for identical measurements, contained either 0.05 % w/w gum and 4.95 % w/w starch or 0.2 % w/w gum and 4.8 % w/w starch. All measurements were replicated.

Dynamic rheology

A „RheoStress RS 1" (Gebruder Haake GmbH, Karlsruhe, Germany) rheometer was equipped with a cone/plate C60/2^o Ti system. The slit was 0.105 mm. The measurements were carried out for 2 cm^3 samples of the identical compositions as those for the viscographic studies. Blends of starch with gum were mechanically stirred at 450 rpm for 20 min then 20 min pasted at continuous stirring at 90 ^oC in case of blends with cassava or potato starches and at 95 ^oC in case of blends with corn or oat starches. Pasted samples were transferred into the measurement system kept at 25 ^oC then equilibrated for 30 min. The oscillation mode included taking the mechanical spectrum in the range of 0.1—10 Hz, change of the storage modulus (G') within 24 h at constant 1 Hz frequency, and repeating the mechanical spectrum at 0.1—10 Hz after 24 h. All runs were carried out at 1 % deformation fitting to the range of linear viscoelasticity. Measurements were run for 5 % gels containing 0.2 % of gum. The measurements were three times repeated.

X-ray powder diffraction

The measurements were carried out using a Phillips type X'pert diffractometer involving 0.154 nm CuK_α radiation. The operation setting for the diffractometer was 30 mA and 40 kV. The spectra over the range of 5.0—60.0^o 2θ were recorded at 0.02 2θ/s scan rate.

Statistics

Statistica 6.0 software was used. Multifactor analysis of variance was carried out with the Duncan test at the $p < 0.05$ confidence level.

RESULTS AND DISCUSSION

In this paper, interactions between four varieties of starches and six polysaccharide gums, each taken at two different proportions in respect to starch, are discussed. Among the starches, only potato starch was anionic because of the phosphate groups located in its amylopectin component. The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and polydispersity (*Pd*) of those starches (Table 2) declined in the following order, respectively:

$\overline{M}_n$ — cassava starch > corn starch > potato starch > oat starch

$\overline{M}_w$ — potato starch > cassava starch > oat starch > corn starch

Pd — corn starch > oat starch > cassava starch > potato starch.

Table 2. Molecular weight and polydispersity of polysaccharides under study

Polysaccharide	$\overline{M}_n \cdot 10^{-7}$	$\overline{M}_w \cdot 10^{-5}$	Polydispersity (*Pd*)
Starches			
Cassava	1.25	4.86	24.49
Corn	1.20	1.63	75.00
Oat	1.10	1.95	57.89
Potato	1.18	5.65	21.05
Gums			
Arabic	1.99	81.2	2.45
Carob	1.65	39.1	7.21
κ-Carrageen	0.83	7.9	11.00
Guar	0.42	4.52	9.78
Karaya	0.053	0.015	339.70
Xanthan	1.36	14.0	9.70

Six gums used in this study vary in their structures:

— Arabic gum is a branched anionic polysaccharide of fairly differentiated structure.

— Carob (locust bean) gum, a regular neutral, non-anionic polysaccharide has short side-chains.

— κ-Carrageen is the linear anionic gum. Anionic properties of this gum results from dissociation of the sulphate group.

— Guar gum is a non-anionic, slightly branched polysaccharide. Its structure strongly resembled that of carob gum. The differences are in the location of branching points in the molecule of main chain composed of 1 → 4 bound β-D-mannopyranose (Man*p*) units.

— Karaya gum is a strongly anionic, highly branched polysaccharide of not quite clear structure.

— In xanthan gum — a semi-synthetic, anionic, branched, bacterial polysaccharide — the number of the anionic sites located in the side chains is limited and they can be fairly well hidden within the polysaccharide structure. Approximately 40 % molecules of that polysaccharide has 6-CH_2OH and 4-OH groups of the mannopyranose units in the side-chains acylated with the pyruvic acid moieties. Such treated 6-CH_2OH group additionally could undergo cyclization with 4-OH group within the same mannopyranose unit.

T a b l e 3. Brabender characteristics of gelation of 5 % aqueous suspensions of potato starch and its blends with gums*)

Added gum and concentration (%)	T_o**) (°C)	η_{max} (B.u.)	T at η_{max} (°C)	η_{96} (B.u.)	$\eta_{96,20}$ (B.u.)	T at η_{min} (°C)	η_{min} (B.u.)	η_{25} (B.u.)
None	63 ab	4600 fg	70 a	1650 c	1135 cde	84 abc	1075 cde	2060 cde
Arabic								
0.05	63 abc	3200 d	71 ab	1840 cde	1045 cd	84 abc	995 cd	2060 cde
0.2	62 a	890 a	71 ab	705 a	405 a	91 ef	405 a	865 a
Carob								
0.05	63 ab	4685 g	72 bc	1675 c	1180 de	86 bcd	1170	2250 ef
0.2	63 ab	5065 h	74 cd	2490 g	1720 g	88 cde	1705 g	3045 g
Carrageen								
0.05	63 ab	1145 b	96 g	1145 b	955 c	91 ef	935 c	1860 bc
0.2	64 bc	850 a	96 g	745 a	745 b	93 f	740 b	1675 b
Guar								
0.05	63 abc	4505 f	74 cd	1950 def	1320 ef	90 bcd	1275 ef	2230 ef
0.2	63 ab	4120 e	76 e	2145 f	1420 f	86 bcd	1360 f	2430 f
Karaya								
0.05	63 ab	4640 fg	69 a	1695 c	1055 cd	89 de	1005 cd	2875 g
0.2	63 ab	3345 d	75 de	2050 ef	1325 ef	88 cde	1245 ef	2460 f
Xanthan								
0.05	64 abc	1930 c	84 f	1785 cd	1220 def	81 a	1145 cde	2130 de
0.2	65 c	1220 b	96 g	1095 b	1160 cde	83 ab	1125 cde	1880 bcd

*) Parameters measured are: T_o — onset temperature, η_{max} — maximum viscosity, T at η_{max} — temperature at maximum viscosity, η_{96} — viscosity after reaching 96 °C, $\eta_{96,20}$ — viscosity after 20 min storage of the gel at 96 °C, T at η_{min} — temperature at minimum viscosity, η_{min} — minimum viscosity, η_{25} — viscosity after cooling to 25 °C.

**) Parameters in columns denoted with the same letters (a, b, *etc.*) do not differ statistically at the level of confidence $p < 0.05$.

T a b l e 4. Brabender characteristics of gelation of 5 % aqueous suspensions of cassava starch and its blends with gums*)

Added gum and concentration (%)	T_o**) (°C)	η_{max} (B.u.)	T at η_{max} (°C)	η_{96} (B.u.)	$\eta_{96,20}$ (B.u.)	T at η_{min} (°C)	η_{min} (B.u.)	η_{25} (B.u.)
None	67 a	875 b	80bc	585 c	375 c	91 bc	350 c	915 b
Arabic								
0.2	69 ab	645 a	78 a	380 a	250 b	69 a	245 b	610 a
Carob								
0.2	68 ab	1185 c	80 bc	520 b	185 a	90 b	140 a	1265 f
Carrageen								
0.05	67 a	865 b	82 c	610 cd	400 cd	91 bc	385 d	885 b
0.2	69 ab	925 b	82 c	665 de	420 d	94 c	410 d	1000 de
Guar								
0.05	69 ab	915 b	80 bc	655 de	395 cd	93 bc	385 d	1050 cd
0.2	67 a	1150 c	79 bc	740 f	475 e	93 bc	465 e	1240 ef
Karaya								
0.2	68 ab	1210 c	78 a	745 f	485 e	94 c	470 e	1515 g
Xanthan								
0.2	68 ab	895 b	81 bc	675 e	470 e	94 c	455 e	1030 c

*) See Table 3. **) See footnote at Table 3.

Corresponding orders of $\overline{M}_n$, $\overline{M}_w$, and Pd of those gums (Table 2) were as follows:

$\overline{M}_n$ and $\overline{M}_w$ — Arabic > carob > xanthan > κ-carrageen > guar > karaya

Pd — karaya >> κ-carrageen > guar ≥ xanthan > carob > Arabic.

The gums differed also in viscosity of their solutions [27]. At the same, 1 % concentration, Arabic gum produced the least viscous solution of 50 cP, and solution of guar gum was the most viscous (4800 cP).

In Tables 3—6 Brabender characteristics of gelation of 5 % aqueous suspensions of potato, cassava, corn, and oat starches are presented, respectively.

The ability of gums to produce thick solutions was in no relation to any of the parameters of the characteristics of gelation of mixed starch – gum blends. Gelation of starches was controlled first by the swelling ability of granules. Among several starches, potato starch swelled exceptionally well [6]. In case of gelation of granules in plant gum solutions, swelling could be obscured by a

T a b l e 5. Brabender characteristics of gelation of 5 % aqueous suspensions of corn starch and its blends with gums*)

Added gum and concentration (%)	T_o**) (°C)	η_{max} (B.u.)	T at η_{max} (°C)	η_{96} (B.u.)	$\eta_{96,20}$ (B.u.)	T at η_{min} (°C)	η_{min} (B.u.)	η_{25} (B.u.)
None	87 a	448 bc	96 a	413 bc	415 b	96 b	415 a	1143 bc
Arabic								
0.2	86 a	—	—	290 s	325 a	—	—	955 a
Carob								
0.2	69 bc	855 g	96 a	760 f	850 f	96 b	845 f	2030 g
Carrageen								
0.05	85 a	445 bc	96 a	430 bc	430 b	94 b	430 ab	1185 bc
0.2	82 d	420 b	96 a	390 b	415 b	96 b	415 a	1080 ab
Guar								
0.05	85 a	490 cd	96 a	485 cd	490 c	96 b	490 bc	1285 cd
0.2	69 b	1140 h	96 a	870 g	1115 g	87 a	1090 g	1750 f
Karaya								
0.2	86 a	630 a	96 a	615 e	595 d	96 b	595 d	1565 e
Xanthan								
0.5	71 c	540 d	96 a	530 d	550 d	96 b	540 cd	1245 cd
0.2	68 b	745 f	96 a	700 f	740 e	89 a	705 e	1345 d

*) See Table 3. **) See footnote at Table 3.

T a b l e 6. Brabender characteristics of gelation of 5 % aqueous suspensions of oat starch and its blends with gums*)

Added gum and concentration (%)	T_o**) (°C)	η_{max} (B.u.)	T at η_{max} (°C)	η_{96} (B.u.)	$\eta_{96,20}$ (B.u.)	T at η_{min} (°C)	η_{min} (B.u.)	η_{25} (B.u.)
None	90 f	365 a	96 b	345 abc	330 a	89 a	310 a	1320 ab
Arabic								
0.2	64 a	585 c	75 a	505 cde	1135 d	96 a	490 b	2040 d
Carob								
0.2	85 c	1115 e	96 b	475 cd	795 c	90 a	775 d	2790 e
Carrageen								
0.05	89 def	365 a	96 b	310 ab	380 ab	96 a	350a	1115 a
0.2	87 cdef	—	—	305 a	398 ab	—	—	1055 a
Guar								
0.05	90 ef	475 b	96 b	470 bcd	408 ab	92 a	395 a	1550 b
0.2	86 cd	693 d	96 b	640 e	833 c	96 a	685 c	1660 bc
Karaya								
0.2	90 ef	1140 e	96 b	405 abcd	935 c	90 a	910 e	1925 cd
Xanthan								
0.5	87 cde	400 a	96 b	380 abc	395 ab	96 a	380 a	1180 a
0.2	81 b	520 bc	96 b	550 de	545 b	92 a	390 a	1080 a

*) See Table 3. **) See footnote at Table 3.

poor water availability. Deficiency of water should elevate onset temperature, and possible increase in water activity would decline that temperature.

In case of potato starch, the plant gums, except xanthan gum, did not influence gelation temperature. Xanthan gum slightly but significantly elevated that temperature by 2 °C. It pointed to deficiency of water in the granule environment and, logically, this effect becames more remarkable as the gum concentration increased. Plant gums significantly increased gelation temperature of cassava starch and essentially decreased that temperature of corn and oat starches. Both, potato and cassava starches readily gelatinized and, therefore, water availability was essential for the process. For cereal starches which gelatinized less readily, activity of water molecules could be more crucial. Their gelation temperatures declined with increase in the gum concentration.

Structures and properties of resulting mixed gels could be controlled by thermodynamic compatibility of starches and gums. Branching of gums and their molecular weights should be taken under consideration. For mixed gels with naturally anionic potato starch, anionic properties of gums (Arabic, carrageen, karaya, xanthan) could also be essential.

Indeed, maximum viscosity values of mixed gels of potato starch with Arabic, karaya, and xanthan gums, and κ-carrageen were lower than that of starch gel (Table 3). At that stage, water deficiency effect could cooperate with repulsion of negative charges in gum and starch. Maximum viscosity was always achieved at temperature higher than that recorded for starch gel. It was observed particularly for κ-carrageen and xanthan gum. At 96 ^{o}C, viscosity of mixed gels composed of potato starch and one of Arabic or xanthan gums and κ-carrageen remained lower than that of starch gel, whereas the mixed gel from karaya gum and starch was already more viscous than starch gel. After 20 min mixed gels maintaining at 96 ^{o}C only these made of starch in κ-carrageen or Arabic gum remained less viscous than starch gel. Mixed gels with gums after cooling to 25 ^{o}C obviously changed their viscosity but these with κ-carrageen, Arabic or xanthan gum remained less viscous than potato starch gel. Thus, one could assume that anionic character of partners maintained the phase separation in the mixed gels. Evidently, the anionic character of karaya gum did not inhibit formation of viscous gel and that fact could be rationalized in terms of much lower $\overline{M}_n$ of that gum facilitating its thermodynamic compatibility with starch. In case of Arabic gum with very high molecular weight (Table 2), to reach the compatibility was rather impossible.

Parameters of the gelation characteristics of mixed gels of potato starch with non-ionic carob and guar gums were consequently higher than these for starch gel.

In case of mixed gels with cassava starch, anionic character of gums was clearly not essential (Table 4). Only gel with Arabic gum was invariantly less viscous in all points recorded, showing that also in that case Arabic gum and starch gel could form separated phases.

Possible effect of water deficiency on gelation could be recognized by slightly elevated temperature of gelation and viscosity maximum. Lower viscosity of the mixed gel with carob gum at 96 ^{o}C could suggest that the gum slowly released water allowing more extended gelation of starch granules. A contribution of κ-carrageen and xanthan gum to the viscosity of mixed gels was not too significant. That contribution could originate either from poor compatibility of the gums with starch or, rather, from obscured swelling and gelation of starch granules.

The same observations were valid for mixed gels containing corn starch (Table 5) and partly for mixed gels with oat starch (Table 6). Unexpectedly, Arabic gum produced essential increase of the viscosity during gelatinization with oat starch. That starch distinguished from the other starches with the highest lipids' content and the lowest amylose content. Consequently, mixed gels of κ-carrageen and xanthan gum with that starch had viscosity below that of Arabic gum blends with oat starch. Again, inhibition of extended gelation of starch granules could be involved. The results qualitatively correspond to those observed by Chaisawang and Suphantharika [28] for the blends of cassava starch with guar and xanthan gums.

At constant concentration of aqueous solution of a plant gum and starch, the following conditions provided a mixed gel of high viscosity: (i) gel components should not form a gel of separated phases, and (ii) starch granules should fully gelatinize. If starch was anionic (*e.g.* potato starch) the plant gum partner should be non-ionic unless the partnering plant gum has low $\overline{M}_n$ and/or high polydispersity (*e.g.* karaya gum). Low $\overline{M}_n$ of the gum gives thermodynamic compatibility with a starch. Non-ionic cassava, corn or oat starches combined with gums regardless their anionic or non-ionic characters.

In case of both tuber starches (*e.g.* potato, cassava), availability of water at onset temperature, T_o, was crucial for swelling of starch granules. In case of cereal starches more resistant to swelling and gelation (*e.g.* corn and oat starches), water activity seemed to be more important.

Usually, Arabic gum, xanthan gum and κ-carrageen give less viscous mixed gels with starches. One could assume that these gums kept water more efficiently. Hence, they produced more pronounced water deficiency at gelation and, consequently, less starch granules could gelatinize. Viscosity of mixed gel with Arabic gum and oat starch violated that rule. As it was mentioned, among starches under study, oat starch distinguished from the other starches with distinctly lower content of amylose and exceptionally high lipids' content. Thus, both these parameters could also be taken into account as essential factors.

There are several factors co-governing the gel viscosity at various points of the Brabender characteristics of gelation. Therefore, it was not surprising that there are no correlations between viscosity and $\overline{M}_n$, $\overline{M}_w$, and *Pd* of the gel components, and the contents of amylose and lipids in starches.

The small deformation rheology study (Fig. 1) showed that storage modulus *G'* of 5 % potato starch gel

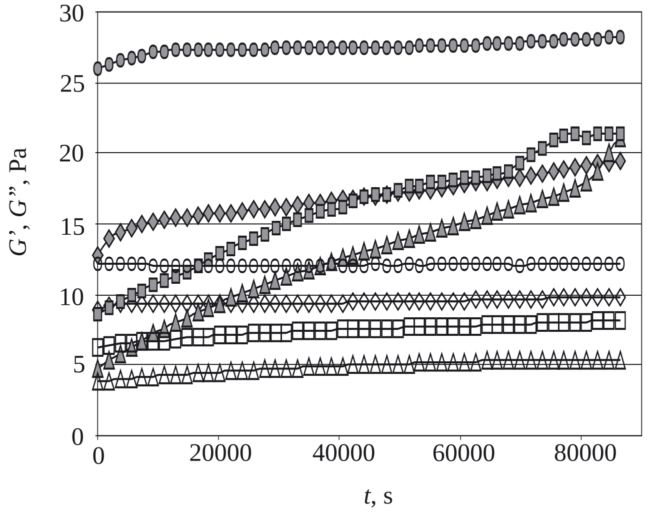


Fig. 1. Time dependence of G' storage modulus (solid points) and G" loss modulus (open points) of 5 % potato starch gel (●) and its blends containing 0.2 % of Arabic (▲ and △), carob (♦ and ◇) or karaya (■ and □) gums

was practically constant in time. A small decrease in the modulus (a drop in viscosity and increase in elasticity) could be noted after 24 h. It could result from amylose — amylopectin phase separation in the starch gel.

Addition of a gum to starch gel always decreased G' and G'' moduli of gels of pure starch (Fig. 1). Thermodynamically advantageous complex structure was more readily reach with more mobile, lower molecular weight karaya or Arabic gums as expressed by G' values. Among three gums investigated, Arabic gum produced initially the most pronounced decrease in G' whereas the effect of addition of carob gum was, relatively, least significant. However, with time, in contrast to pure starch gel with its almost time independent G', G' values of the blends increased in time. The strongest and the weakest increase was found for the blends with Arabic and carob gums, respectively. The blend with karaya gum performed slightly worse than that with Arabic gum but the final value of G' was slightly higher than that for the blend with Arabic gum.

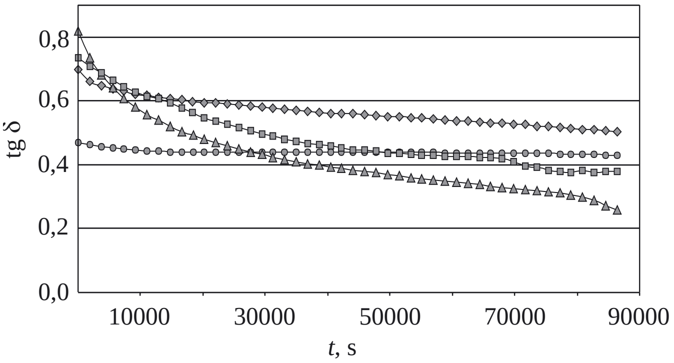


Fig. 2. Time dependence of viscoelastic behavior (tg δ values) of pure 5 % starch gel (●) and its blends with 0.2 % of Arabic (▲), carob (♦) or karaya (■) gums

Shear loss modulus (G'') for pure starch gel and its blends with gums were almost independent on time. Decreasing effect on G'' arranged the gums in the order: none > carob > karaya > Arabic, that is the same order as initial effect of those gums on G'.

Fig. 2 presents changes of $G'/G'' = \operatorname{tg}\delta$ in time for pure 5 % starch gel and its blends with the gums. The ratio chracterizes viscoelastic behavior of the gels. By definition, very diluted, amorphous gels exhibited relatively high tg δ, and glassy, crystalline gels exhibited low tg δ.

The course of changes of tg δ — time function showed that viscoelasticity of pure starch gel was practically constant. Admixture of the gums initially damage the original structure of starch gel but, gradually, gels took more arranged structure. Arabic and carob gums performed the best and the worst, respectively.

Examination of X-ray powder diffractograms of those gels did not reveal any increase in the crystallinity degree of the lyophilized samples on storage. Gelatinized starches and xanthan gum, were amorphous and the products of their blending also remained fully amorphous (Fig. 3).

CONCLUSIONS

— At a given concentration of aqueous solution of a plant gum and a starch, highly viscous mixed gels are formed if no phase separation takes place and starch granules possibly fully gelatinize.

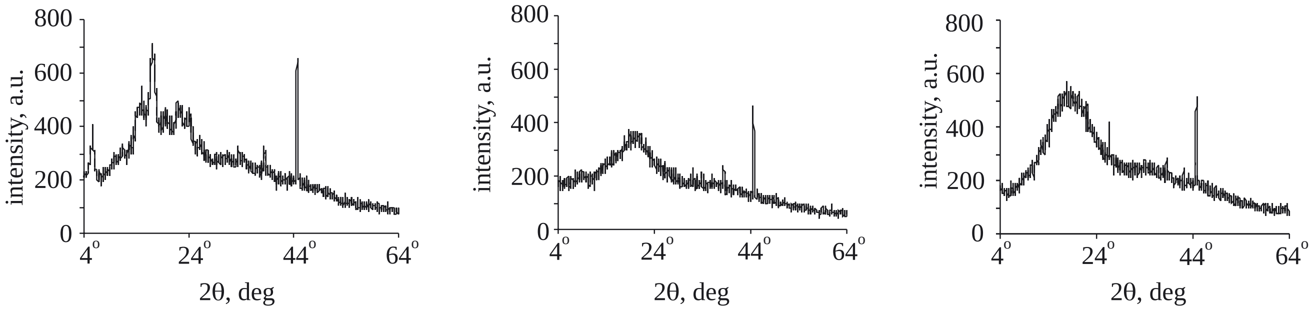
— If starch is anionic (*e.g.* potato starch) the plant gum partner should be non-ionic unless the partnering plant gum has low $\overline{M}_n$ and/or high polydispersity (*e.g.* karaya gum). Low $\overline{M}_n$ of the gum facilitates achieving thermodynamic compatibility with starch.

— Non-ionic starches (cassava, corn and oat starches) combine with gums regardless their anionic or neutral characters.

— In case of both tuber starches (*e.g.* potato, cassava), availability of water at temperature of beginning of gelation (onset temperature, T_o) is crucial for swelling of starch granules.

— In case of cereal starches (*e.g.* corn, oat), more resistant to swelling and gelation, water activity seems to be more important.

— A lower content of amylose and exceptionally high lipids′ content in starch could also be essential factors.



a) b) c)

Fig. 3. Diffractograms of a) non-gelatinized potato starch, b) xanthan gum, c) potato starch/xanthan gum blend after gelation

— Admixture of plant gums into starch gels results in increase in the viscosity and reduction of elasticity of the gels in respect of these values for starch gels.

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