HANNA M. BARANOWSKA[1], MAREK SIKORA[2)*], MAGDALENA KRYSTYJAN[2], PIOTR TOMASIK[3]

Analysis of the formation of starch — hydrocolloid binary gels and their structure based on the relaxation times of the water molecules

Summary — The formation of gels in the blending of cassava, corn, oat and potato starches with κ-carrageenan, guar and xanthan gums and some of their selected properties have been studied. 0.2 % admixture of xanthan gum, significantly decreased the spin-lattice T_1 relaxation time, whereas similar admixtures of guar gum and κ-carrageenan had a relatively weak influence upon starch gelatinization providing, however, a slight increase in T_1 with an increase in temperature. The two latter hydrocolloids decreased gelatinization onset temperature by approximately 5 °C and made gelatinization more diffuse in time. The presence of hydrocolloids influenced also spin-spin T_2 relaxation times. Initially, up to the onset gelatinization temperature, T_2 was most effectively suppressed by xanthan gum. On cooling, T_2 varied inconsistently. As a rule, T_2 in binary gels was higher than in those of plain starch. In all the studied blends both relaxation times monotonously declined with temperature. The activation energy of water molecules in binary gels on cooling was estimated.

Keywords: cassava starch, cornstarch, guar gum, κ-carrageenan, oat starch, potato starch, xanthan gum.

ANALIZA POWSTAWANIA I STRUKTURY PODWÓJNYCH ŻELI SKROBIOWO-HYDROKOLOIDOWYCH NA PODSTAWIE CZASÓW RELAKSACJI CZĄSTECZEK WODY

Streszczenie — Badano powstawanie dwuskładnikowych żeli w wyniku mieszania skrobi kukurydzianej, owsianej, tapiokowej bądź ziemniaczanej z κ-karagenem, gumą guarową lub ksantanową oraz określano wybrane właściwości tych żeli. 0,2-proc. dodatek gumy ksantanowej wyraźnie skracał czas relaksacji spinowo-sieciowej, T_1, podczas gdy dodatek takiej ilości gumy guarowej lub κ-karagenu miał niewielki wpływ na żelowanie skrobi, powodując jednak wraz z rosnącą temperaturą niewielki wzrost T_1. Oba te hydrokoloidy obniżały jedynie, o ok. 5 °C temperaturę początku żelowania, a samo żelowanie było rozciągnięte w czasie. Hydrokoloidy wpływały także na czasy relaksacji spinowo-spinowej, T_2. Początkowo, aż do rozpoczęcia żelowania, czas T_2 ulegał skróceniu, najwyraźniej w układzie z gumą ksantanową (rys. 1, 3, 5, 7). W trakcie chłodzenia wartość T_2 zmieniała się nieregularnie. Na ogół w żelach podwójnych czasy T_2 były dłuższe niż w żelach ze skrobi bez dodatków, a we wszystkich badanych żelach dwuskładnikowych czasy relaksacji jednostajnie się zmniejszały wraz ze spadkiem temperatury (rys. 2, 4, 6, 8). Wyznaczono także energie aktywacji cząsteczek wody w czasie chłodzenia żeli (tabela 1).

Słowa kluczowe: skrobia tapiokowa, skrobia kukurydziana, guma guarowa, κ-karagen, skrobia owsiana, skrobia ziemniaczana, guma ksantanowa.

The functional properties of starch — hydrocolloid binary mixtures has evoked considerable interest as structure providers in food production, modifiers of gelatinization, viscosity, flow and retrogradation [1, 2 and references therein]. The predictive theory for blending starch with hydrocolloid gums has been attempted with limited qualitative success [1]. Further knowledge is complex nature of some effects beginning from the swelling of starch granules through their gelatinization and thermodynamic compatibility of the blend components has necessitated the need to better recognize and quantity them in order to provide adequate knowledge towards a predictive theory of polysaccharide blending. At the present more research and data are being gathered in order such to be able to formulate theory.

The behaviour of water molecules at particular stages of the formation of binary polysaccharide gels might

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[1] University of Life Sciences, Department of Physics, ul. Wojska Polskiego 38/42, 60-637 Poznań, Poland.

[2] University of Agriculture, Department of Carbohydrate Technology, ul. Balicka 122, 30-149 Krakow, Poland.

[3] University of Agriculture, Department of Chemistry & Physics, ul. Balicka 122, 30-149 Krakow, Poland.

[*] Author for correspondence; e-mail: rrsikora@cyf-kr.edu.pl

shed light on key dynamic processes and structure of gels. In our former paper [2] studies on the relaxation time of water molecules in binary potato starch gels with arabic, carob, guar, karaya, and xanthan gums as well as ι- and κ-carrageenans were presented. They revealed that the molecular dynamics of water molecules in such blends initially increased with temperature reflecting a progressive disorder up to the gelatinization temperature, after which it gradually decreased as a consequence of the immobilization of these molecules within the formed gel. Depending on their structure and ionic character, gums specifically influenced swelling, gelatinization and structure of the gel network. The mediating role of water depended on its availability and activity. The application of low field nuclear magnetic resonance to study the relaxation of water molecules in binary gels appeared to be the right method for the investigation of the dynamics of the formation of the gel network and its time dependent changes in a noninvasive and non-destructing manner.

The former studies were limited to one anionic starch — potato starch and has now been extended to the binary mixtures obtained from other non-ionic starches and three non-starchy hydrocolloids.

EXPERIMENTAL

Materials

Cassava, corn, oat and potato starches, κ-carrageenan, guar and xanthan gums have been characterized in our former paper [1, 2]. The characteristics of gelatinization of these materials separately and in blends were also provided [1, 2].

Samples preparation

The studies were carried out on the samples of 5 wt. % aqueous suspensions/gels composed of 4.8 wt. % starch and 0.2 wt. % hydrocolloid. Aqueous binary suspensions of the components were either subjected to experiments, in which they were heated from 20 to 90 °C and then cooled to 20 °C, or were heated on stirring at 90 °C for 1 h.

Methods of testing

The measurements of relaxation time spin—lattice (T_1) and spin—spin (T_2) were conducted on a pulse spectrometer ^{1}H NMR (ELLAB, Poznań, Poland), operating at 15 MHz, equipped with integral temperature control system.

Aqueous suspensions of starch and non-starchy hydrocolloids (0.3 mL) were placed in sealed tubes. The measurements were conducted at increasing temperature from 20 to 90 °C, maintaining the maximum temperature for 1 h, and then at lowering it to 20 °C, at 10 °C intervals after a 20 min stabilization period.

— For measurements of spin—lattice (T_1) relaxation time the inversion-recovery pulse sequence 180_x-TI-90_x-TR was used [3]. The periods between impulses (TI) varied from 50 to 5000 ms at low temperatures and from 130 ms to 12 000 ms at high temperatures. The repetition time (TR), was 35 s. During each relaxation time (T_1) measurement 32 signals of free induction decay (FID), and 110 points on each FID were collected. The CracSpin program was used for the calculations of T_1 values [4].

— For spin—spin relaxation time (T_2) measurements, a series of Carr-Purcell-Meiboom-Gill (CPMG) 90_x-(TE/2-180_y-TE)$_n$ [5, 6] pulses were used. The period between spin echoes (TE) was 6 ms at low temperatures and 15 ms in high temperatures. The amplitudes of 100 spin echoes were recorded. 5 signal accumulations were applied with TR of 35 s.

Selected parameters of the inversion-recovery and CPMG sequences depended on temperature measurements. The values of T_2 were fitted to the spin echo amplitudes to obtain Eq. (1):

$$M_{x,y} = M_\infty \exp\left(\frac{-TE}{T_2}\right) \quad (1)$$

where: M_∞ — *equilibrium value of magnetization,* $M_{x,y}$ — *value of spin echo amplitude taken at time TE.*

RESULTS AND DISCUSSION

As earlier described [7] and illustrated in Fig. 1, on gelatinization of cornstarch as an example, the spin-lattice relaxation time (T_1), increased with an increase in temperature to a break point related to the onset of gelatinization. At this point T_1 temporarily decreased only to rise again after an increase in temperature by approximately 5 °C. T_1 increase therefore in two stages, *i.e.* initially to the onset of gelatinization, and then after a brief decrease, to the final measurement temperature. In

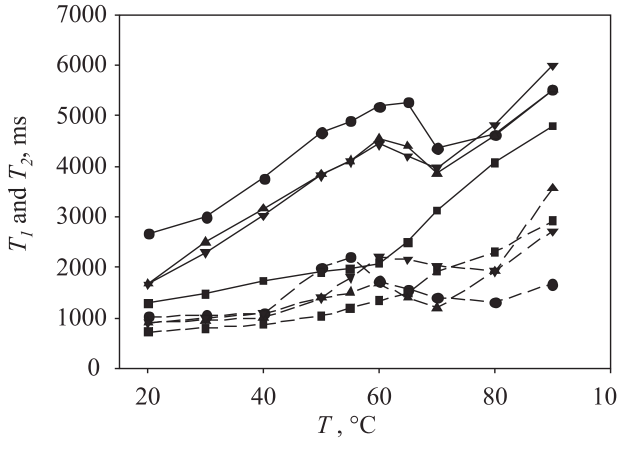

Fig. 1. Changes of T_1 (solid lines) and T_2 (broken lines) in the heating from 20 to 90 °C gels of cornstarch (circles ●) and its binary mixtures with xanthan gum (boxes ■) guar gum (triangles up ▲) and κ-carrageenan (triangles down ▼)

the presence of 0.2 % admixture of either xanthan gum, guar gum or κ-carrageenan, a decrease in the values of T_1 was observed. Xanthan gum appeared to be the most efficient in this respect. Admixtures of guar gum and κ-carrageenan provided, to a certain extent, a similar pattern of increase in T_1 as the function of temperature specific for the plain cornstarch suspension. This indicates, that these components exhibit a relatively weak influence on starch gelatinization. At this stage of gel formation water deficiency can be regarded as a factor controlling swelling and onset of gelatinization. Likewise, hydrocolloid demand for water of hydration did not produce any significant water deficiency which would affect swelling and onset of gelatinization of starch granules. The gelatinization onset temperature decreased for both hydrocolloids by approximately 5 °C and made gelatinization more diffuse with time.

The final value of T_1 obtained for the binary gel with κ-carrageenan was higher than the values for plain cornstarch gel and its blend with guar gum, so it can be assumed both polysaccharides bind water and at 90 °C have a tendency to separate. In the presence of xanthan gum the value of T_1 of the binary blend was remarkably lower. It slowly increased up to 65 °C above which is began to rise rapidly. This effect could be associated with the anionic structure of xanthan gum which favors the formation of a five-fold helical structure of the macromolecule immobilizing water molecules and producing a water deficiency required for the swelling starch granules. The gum is resistant to desiccation and at low concentrations unusually forms viscous gels [8—10]. The lack of a characteristic minimum of the relaxation times implied that water was not bound in the course of the formation of the polymeric network.

The presence of hydrocolloids also influenced T_2 relaxation times. Initially, up to the onset gelatinization temperature, T_2 was suppressed most efficiently by xanthan gum. However, above this temperature water mobility in that gel appeared to be almost the highest. This could indicate that starch and xanthan gum gels exhibit separate and independent water releasing systems. The cornstarch — guar gum structure released water as temperature rose above 70 °C indicating that this gel network was the least stable and therefore, the dynamics of water molecules could be intensified. Below 70 °C, this binary mixture, just as other binary gels retains water most efficiently (Fig. 1). In the κ-carrageenan gel, T_2 increased above 60 °C because of the strong internal polymeric network formed in which intramolecular predominated over intermolecular interactions. Both components also formed separate gel networks.

In the cooling process, T_1 for all cornstarch binary blends were lower than T_1 for plain gel in general, T_1 for starch — κ-carrageenan it exceeded T_1 for plain starch gel only in the 90—75 °C temperature range. This should indicate that a binary gel network did not exist yet in this temperature range. The effect of hydrocolloids on T_1 in the binary gels decreased in the order: none hydrocolloid > κ-carrageenan > guar gum > xanthan gum (Fig. 2).

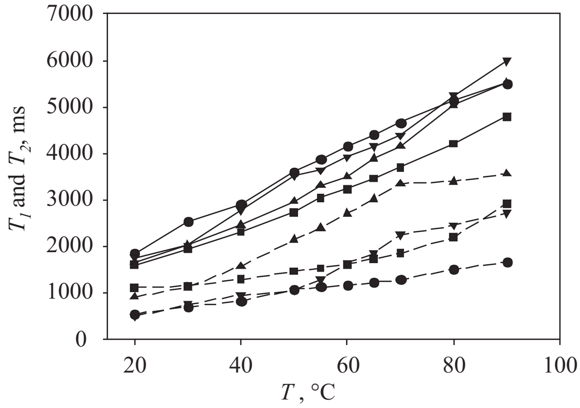

Fig. 2. Changes in T_1 (solid lines) and T_2 (broken lines) on cooling cornstarch — hydrocolloid gels from 90 to 20 °C. See Fig. 1 for notation

T_2 varied inconsistently on cooling. These variations indicated also the formation of dynamic binary systems in which the conformation of polysaccharide chains fluctuated in order to attain an energetically feasible arrangement. As a rule, T_2 in cornstarch binary gels was higher than in the gel of plain starch. This should indicate that in the mixed gels water was not immobilized, and that most likely, both components formed separated gel structures. The order of decreasing water mobility depended on temperature (Fig. 2). In the cornstarch — xanthan gum gels T_1 decreased while T_2 increased as compared to the parameters for plain starch gel. This should mean that on the formation of the gel, the amount of bound water and its mobility increased. This it could be possible when intramolecular interactions dominated over intermolecular interactions.

The effect of the added hydrocolloids upon T_1 on heating in binary mixtures and gels of oat starch were qualitatively similar to that observed for cornstarch. All hydrocolloids reduced T_1 values with xanthan gum being the most efficient. The essential difference was observed in case of T_2 which was remarkably decreased by hydrocolloids and all three exhibited a quite similar, slightly temperature dependent effect (Fig. 3). In the cooled gels, hydrocolloids always decreased T_1 and T_2 indicating limited hydration of the gels and that the effect of each colloid was almost identical, especially below approximately 75 °C (Fig. 4).

In the studies with cassava starch, all three hydrocolloids decreased T_1 on heating and xanthan gum was the most efficient. Xanthan gum stabilized the system up to 55 °C and T_1 remained practically unchanged. At higher temperatures, T_1 rose sharply. The course of temperature dependent changes in T_1 in binary mixtures with guar gum and κ-carrageenan was similar and guar gum most willingly formed a binary gel as manifested by changes at

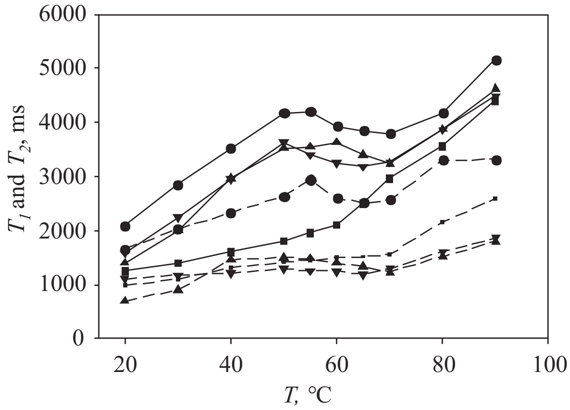

Fig. 3. Changes of T_1 (solid lines) and T_2 (broken lines) on heating from 20 to 90 °C gels of oat starch and its binary mixtures with xanthan gum, guar gum and κ-carrageenan. See Fig. 1 for notation

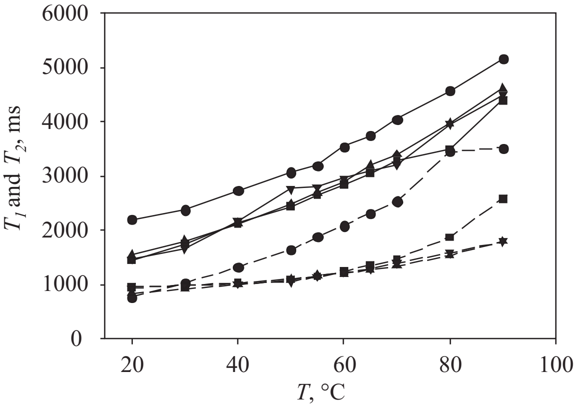

Fig. 4. Changes in T_1 (solid lines) and T_2 (broken lines) on cooling of oat starch — hydrocolloid gels from 90 to 20 °C. See Fig. 1 for notation

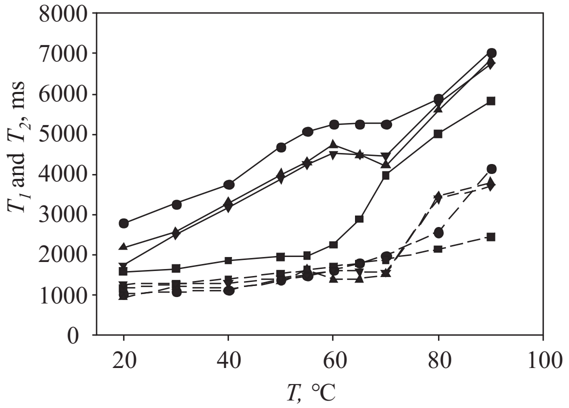

Fig. 5. Changes of T_1 (solid lines) and T_2 (broken lines) on heating from 20 to 90 °C gels of cassava starch and its binary mixtures with xanthan gum, guar gum and κ- carrageenan. See Fig. 1 for notation

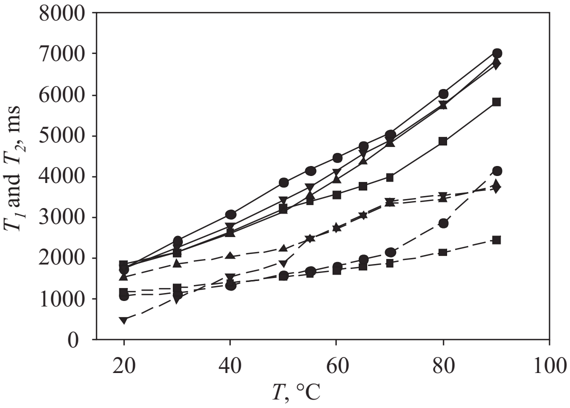

Fig. 6. Changes in T_1 (solid lines) and T_2 (broken lines) on cooling of cassava starch — hydrocolloid gels from 90 to 20 °C. See Fig. 1 for notation

the break point typical for gels with corn and oat starches. The effect of hydrocolloids on T_2 was negligible at temperatures up to 60 °C. At higher temperatures the effect of xanthan gum was related to maintering a low water mobility. The T_2 values obtained for guar gum and κ-carrageenan decreased slightly up to 70 °C, but after the network was developed, rose sharply to a value slightly below that for gel of plain starch (Fig. 5). During cooling, T_1 for binary gels was only slightly lower than T_1 for plain starch gel, particularly below 60 °C, T_2 also varied inconsistently. Xanthan gum exhibited a low, almost stable water mobility in the whole temperature range whereas in the range between 85 and 20 °C T_2 in the gel with guar gum was essentially higher as observed in the case of the gel with κ-carrageenan in the range of 85—35 °C. Below 35 °C T_2 sharply decreased indicating an efficient water molecule retention in the gel (Fig. 6).

In the case of the admixture of hydrocolloids with potato starch a fairly negligible effect on gelatinization was observed. On heating, guar gum and κ-carrageenan caused an upward shift in the onset of gelatinization temperature by approximately 10 °C and in the binary mixture with xanthan gum gelatinization was not observed. Admixture of hydrocolloids to potato starch retained a temperature profile dependent changes in T_2. Guar gum and κ-carrageenan caused an upward shift in the break point by almost 10 °C, but the reverse was the situation with xanthan gum by approximately 5 °C (Fig. 7). On cooling, the profile of temperature dependent changes in T_1 was very similar as also observed like one another and such was for T_2 only that the effect of guar gum was slightly stronger than that of other hydrocolloids (Fig. 8). Such behaviour of T_1 and T_2 might suggest that both components formed either independent networks which mutually interpenetrated or coupled, common networks were formed.

In all the studied blends both relaxation times monotonously declined with temperature. In biological systems, temperature changes of T_1 proceed according to the Arrhenius type relationship (2) [11]:

$$R_1 = \frac{1}{T_1} \approx \exp\left(\frac{\Delta E}{RT}\right) \qquad (2)$$

where: R_1 — *spin-lattice relaxation rate,* ΔE — *the energetic barrier for a reorientation of whole molecule or a group of molecules [12],* R, T — *gaseous constant and temperature in K, respectively.*

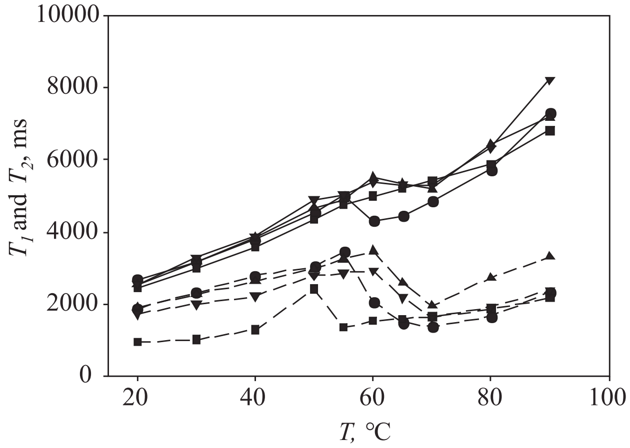

Fig. 7. Changes of T_1 *(solid lines) and* T_2 *(broken lines) on heating from 20 to 90 °C gels of potato starch and its binary mixtures with xanthan gum, guar gum and κ-carrageenan. See Fig. 1 for notation*

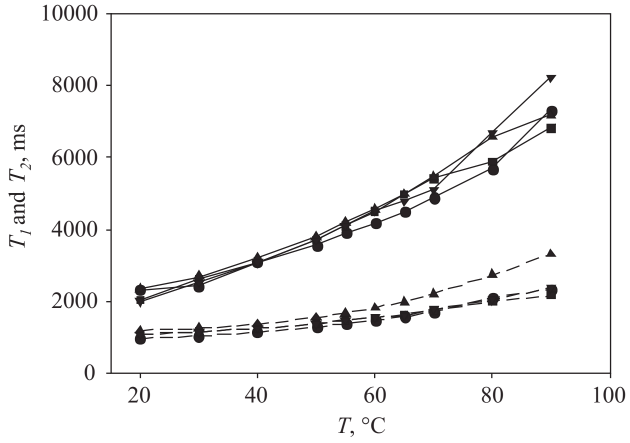

Fig. 8. Changes in T_1 *(solid lines) and* T_2 *(broken lines) on cooling of potato starch — hydrocolloid gels from 90 to 20 °C. See Fig. 1 for notation*

Applying Eq. (2) activation energy (ΔE), of water molecules in binary gels on cooling could be estimated. The error in the calculated ΔE values was minimal (below 3 %). The values presented in Table 1 were determined with an maximum accuracy of ±0.4 kJ/mol.

Cassava and oat starch showed the highest and the lowest energetic barrier of the rotation of the water molecules, respectively. In binary systems with xanthan gum and κ-carrageenan, potato starch gels in which the barrier of rotation of water molecules was highest while oat starch produced with these hydrocolloids systems in which the barrier of rotation of the water molecules was lowest. It should be noted that in these systems with the highest rotation barrier of the rotation of the water molecules both polysaccharide components were anionic. Neutral guar gum in combination with cassava starch produced the gel in which the barrier of rotation for the water molecule was the highest and, invariantly, oat starch gave the system with the lowest rotation barrier for water.

Table 1. Activation energy (ΔE), of water molecules in cooled binary gels calculated from Eq. (2) involved spin-lattice relaxation times

Starch	ΔE, kJ/mol			
	hydrocolloid added			
	none	xanthan gum	guar gum	κ-carrageenan
Corn	13.62	13.82	15.48	15.64
Oat	11.05	13.35	13.81	14.11
Cassava	16.88	14.01	17.16	16.88
Potato	14.38	15.24	14.73	17.14

CONCLUSIONS

1. 0.2 % admixture of either xanthan gum, guar gum or κ-carrageenan influenced the gelatinization of cornstarch weakly. Xanthan gum exhibited the most significant effect among the investigated hydrocolloids. Cornstarch and xanthan gum gels formed separate systems releasing water independently of one another. The cornstarch — guar gum gel network was the least stable but it retained water most efficiently. In the gel with κ-carrageenan a strong internal polymeric network was formed in which intramolecular interaction predominated over intermolecular interactions. Both components also formed separate gel networks.

2. The effect of the added hydrocolloids on gelatinization of oat starch was similar to that observed for cornstarch. The role of hydrocolloids in binary gels of oat starch was qualitatively identical to that observed for cornstarch. These gels seem to be poorly hydrated.

3. In the case of cassava starch, the effect of xanthan gum upon gelatinization was the most remarkable. Guar gum formed a binary gel most easily. The gel with κ-carrageenan most efficiently retained water molecules at temperatures below 35 °C.

4. The admixture of hydrocolloids to potato starch had fairly negligible effect on gelatinization. κ-carrageenan and guar gum formed either independent networks which mutually interpenetrated or coupled, common networks were formed.

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