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Influence of xanthan on the rheological properties of aqueous starch–emulsifier systems

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Abstract

Interactions between potato starch and complex-forming emulsifiers in the presence of xanthan, and their consequences on the rheological properties, were investigated. The aqueous starch–xanthan–emulsifier systems were prepared by mixing the separately dispersed components or by heating the components together. The amount of leached amylose and the formation of starch–emulsifier complexes were determined by amperometric iodine titration. The viscoelasticity was measured with small-deformation oscillatory tests. The results show that while the incompatibility between starch and xanthan does not affect the formation of starch–emulsifier complexes, it does hinder the gelation process induced by starch complexation and reduce the firmness of the resulting gels. The combination of starch with small amounts of an incompatible biopolymer like xanthan and a complex-forming emulsifier allows the generation of different gel structures.

Introduction

Starch is widely used as a thickener and gelling agent in different food products. Small amounts of starch are often replaced by non-starch hydrocolloids to impart the desired textural characteristics to the products as well as to provide processing advantages (1,2). Contrary to other hydrocolloids, starch is composed of two distinct polymer fractions: amylose and amylopectin. Furthermore, starch polymers are packed as spherocrystalline granules, which swell by heating in water while maintaining the granular integrity up to a certain point, depending on the gelatinization conditions. Thus, starch dispersions may be described as suspensions of swollen granules rich in amylopectin dispersed in a continuous amylose matrix. The functional properties of starch are modified by the incorporation of non-starch hydrocolloids, the major practical advantages being an enhancement of the viscosity (3–6), a modified flow behaviour (7), a reduced setting time (8), a reduced tendency for syneresis and a better freeze–thaw stability (9,10). The viscosity enhancement achieved by combining starch with different hydrocolloids was originally attributed to the development of stable starch–hydrocolloid associations during pasting (3). More recent studies conclude that the viscosity increase is essentially due to thermodynamic incompatibility leading to mutual exclusion of the polymers (4,8), although exceptions of specific intermolecular interactions are found, as is the case for starch–ι-carrageenan mixtures (8). In the most common situation, the dissimilar polymers exclude each other from its polymer domain, so that the effective concentration of each polymer is raised, which in turn results in an exponential viscosity increase. This is especially the case when the starch granules are not completely disintegrated and the non-starch hydrocolloid is concentrated in the continuous phase (4). Finally, by cooling and aging the starch–hydrocolloid mixtures, the gelation process and the stability of the resulting gels were reported to be affected. Most hydrocolloids interact with amylose, the gelling fraction of starch, and accelerate their gelation. However, the elasticity of the resulting gels is reduced compared with pure starch systems (5,8,11,12). The crystallization of the amylopectin fraction, on the other hand, does not seem to be influenced by admixtures of hydrocolloids, which was shown to be true for starch–xanthan systems (9).

The level of complexity of starch–hydrocolloid systems increases further when emulsifiers are added to the mixture. Emulsifiers, which are incorporated in starch-based foods to improve texture, are known to affect the rheological properties of starch by interacting in two ways. On one side, emulsifiers interact with the surface of the starch granules and preserve the integrity of the granules by retarding the swelling process (13). On the other side, emulsifiers interact with starch at the molecular level, since most emulsifiers are able to form helical inclusion complexes with the amylose fraction. The complexation of starch induces the gelation of low-concentration starch systems (2–3%), provided that enough amylose is solubilized, the swollen starch granules are not completely disintegrated, and the amylose is saturated with emulsifier. The gelation induced by complexation is a consequence of the physical aggregation of insoluble amylose–lipid complexes (14,15). Since complexation-induced gelation is a rapid process compared with spontaneous gelation (retrogradation), the complexation of starch is useful for generating foods with a gel-like texture, such as puddings (16).

In the present study, the interactions between starch and a complex-forming emulsifier in the presence of a non-starch hydrocolloid, and their consequences on the rheological properties of the system, were investigated. The interactions were studied in low-concentration systems, which were considered as models for food products where starch is used as a binder, thickener and gelling agent. Native potato starch was chosen since it is almost lipid free and therefore free of pre-existing amylose inclusion complexes. Xanthan was used as the other hydrocolloid. Calcium stearoyl-lactyl-2-lactylate (CSL) and glycerol monostearate (GMS) were selected as emulsifiers based on their good complex-forming ability with starch (15).

Materials and methods

Native potato starch was a product from Blattmann & Co. (CH-Wädenswil). Xanthan (Rhodigel) was obtained from Meyhall Chemical AG (CH-Kreuzlingen). CSL (Arthodan CP 80) and GMS (Dimodan PV) were supplied by Grindsted Intercolloid AG (CH-Zug).

For the preparation of potato starch dispersions (3.06 or 2.29 g dry starch/100 g), native potato starch was suspended in deionized water at 25°C in a flask (total 400 g). The suspension was heated in a water bath and held at 96 ± 1°C for 30 min. Stirring was accomplished with an anchor-shaped stirrer at 300 r.p.m. Xanthan dispersions (0.306 or 0.95 g dry xanthan/100 g) were prepared in a similar way. Xanthan powder was carefully dispersed in deionized water in a flask (total 400 g) and heated in a water bath. The dispersion was held at 96 ± 1°C for 30 min and stirred with a magnetic stirrer at 300 r.p.m. The amount of evaporated water of both the starch and xanthan dispersions was determined by weighing and replaced. Potato starch dispersions and xanthan dispersions of lower concentrations were obtained by dilution of the initial dispersions with deionized water, which was also heated to 96°C.

CSL and GMS dispersions (6 g/100 g) were prepared as follows. CSL and GMS were neutralized (pH 6.0–6.5) with 0.1 mol/l NaOH and dispersed in deionized water at 45 and 67°C, respectively, for 30 min. Thereafter, the emulsifier dispersion was cooled to room temperature.

Starch–xanthan–emulsifier systems were prepared by mixing the initial dispersions at appropriate ratios. Systems with only one or two components served as a reference. The components that were left out were replaced by water at 96°C. The temperature of the dispersions before mixing was 96°C for starch and xanthan dispersions, and room temperature for the emulsifier dispersion. The required amount of starch, xanthan and emulsifier dispersion was put into jars (total 30 g). The jars were closed with screw caps, vigorously shaken for 10 s and placed in a 25°C water bath. In one case, the starch–xanthan system was prepared by heating potato starch together with xanthan. Dry starch and xanthan powder were mixed before suspending the mixture in deionized water and heating it. The heat treatment was performed as described above for the pure starch dispersions.

The rheological measurements were carried out 2–3 h after sample preparation using a Controlled Stress Rheometer (Carri-Med CS 100, Carri-Med Ltd, GB Surrey) with an acrylic cone-plate measuring system (∅ = 6 cm, ∠ = 2°). The measurements were carried out at 25°C. The dynamic viscoelastic properties were determined performing oscillations in frequency ranges between 0.01 and 5 Hz (0.06 and 31.4 rad/s) or at a constant frequency of 1 Hz (6.28 rad/s) and deformation amplitudes between 1.5 and 2.5 mrad (5.7–7.2% strain). At this deformation, the samples were in the linear viscoelastic region.

The iodine binding capacity (IBC) of starch was determined by amperometric titration with Methrom equipment (Methrom AG, CH-Herisau). A sample containing 100 mg of starch was made up to 30 ml by the addition of 1 ml of 1 mol/l HCl and deionized water. The sample was titrated with 0.005 mol/l iodine solution (Titrisol, Merck) with constant stirring and a titration rate of 1 ml/min. The voltage of polarization was 140 mV and the attenuation of the polarizer was set to 5 μA. The IBC was calculated by relating the amount of bound iodine to the amount of starch in the sample. The complexation index (CI) was calculated by relating the IBC of the sample containing emulsifier to that of an emulsifier-free control sample (14). The IBC of xanthan was <0.05 g/100 g xanthan and was therefore neglected in starch–xanthan mixtures.

Results and discussion

In a first step, the interactions between starch and xanthan were investigated. The concentrations of the initial polymer dispersions were chosen so as to obtain systems with similar viscoelasticities. For the preparation of the polymer dispersions, a 30 min heat treatment at 96°C and moderate shear were selected. These conditions allowed most of the amylose fraction to leach out of the starch granules, as measured by iodine titration. The heat treatment did not lead to a complete disintegration of the swollen starch granules, as confirmed by optical microscopy (micrographs not shown). On the other hand, it is known that by heating xanthan beyond the order–disorder transition temperature,

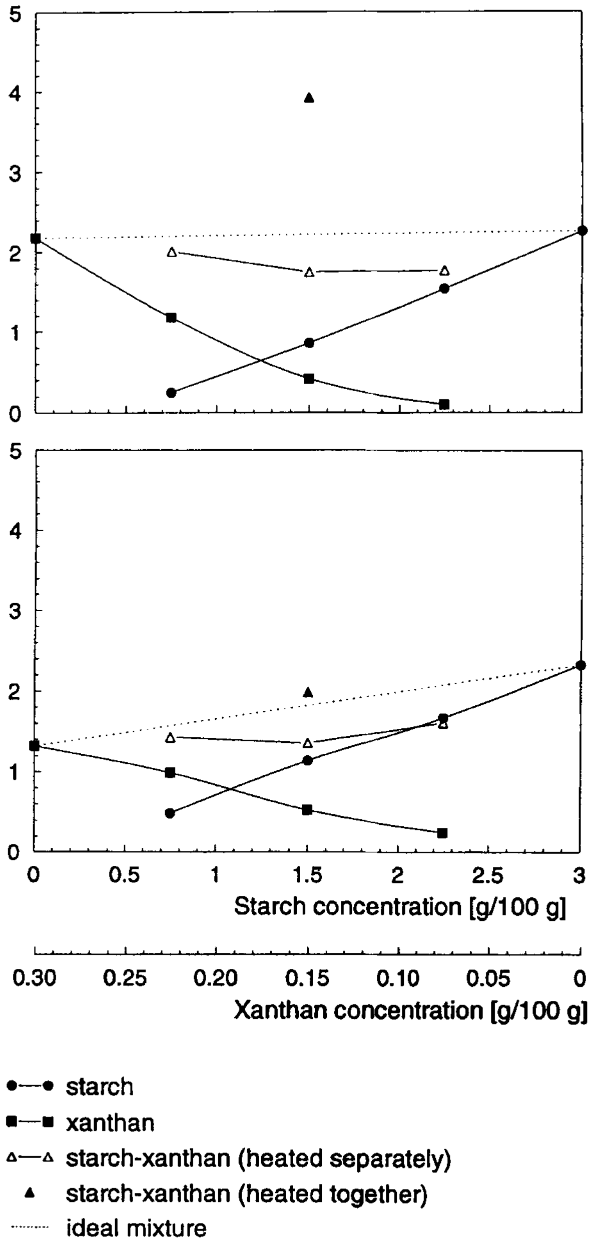

Figure 1 Storage modulus G (1 Hz) and loss modulus G' (1 Hz) of starch and xanthan dispersions, respectively, and of starch–xanthan mixtures prepared by heating the components separately or together. The broken line represents an ideal mixture.

its native ordered form is transformed into a disordered form, which upon cooling leads to a denatured, re-ordered form with a more extended backbone conformation. At low ionic strength, as used in the present study, the transition temperature is <50°C (17).

Figure 1 shows the storage modulus G and the loss modulus G' of pure xanthan and pure potato starch dispersions at different concentrations, as well as of their mixtures prepared by combining the initial starch (3.06 g/100 g) and xanthan (0.306 g/100 g) dispersions at appropriate ratios. Figure 1 also shows the viscoelasticity of a starch–xanthan system, which was prepared by heating both components together. The IBC of selected samples are presented in Table 1.

Table 1 Iodine binding capacity (IBC) of starch (3 g/100 g) dispersion and of starch–xanthan (1.5 and 0.15 g/100 g) mixtures prepared by heating the components separately or together

Sample	IBC (g/100 g starch)
Starch	4.59
Starch–xanthan components heated separately	4.57
Starch–xanthan components heated together	4.07

If the combination of starch and xanthan dispersions were to yield ideal mixtures, where neither interactions nor phase separation occur, their viscoelasticities would be intermediate between the viscoelasticities of the original dispersions and would be linearly dependent on the mixing ratio (dotted line in Fig. 1). However, the viscoelasticity of a starch–xanthan system which was prepared by heating both components together was higher than predicted for an ideal mixture. On the other hand, the IBC of starch was lower when starch was gelatinized in the presence of xanthan. The results on mixtures obtained by combining separately dispersed starch and xanthan show the opposite tendency: the viscoelasticities of the mixtures were slightly lower than predicted for an ideal mixture, whereas the IBC of the starch dispersion was not affected by mixing it with xanthan.

The comparatively high viscoelasticity of the starch–xanthan mixture prepared by heating both components together suggests a synergistic interaction between starch and xanthan. When analysing the causes of this effect, it has to be considered that the rheological properties of a system containing starch strongly depend on the supermolecular structure of starch, which in turn is determined by the conditions of the heat treatment, especially by the amount of shear (18). Although the pure starch system and the starch–xanthan mixture were prepared by the same procedure, the starch–xanthan mixture was not mixed as thoroughly as the pure starch dispersion due to the comparatively high viscoelasticity of the mixture. The effective shear was, therefore, most probably lower for the starch–xanthan mixture, which in turn reduced the leaching of amylose and the disintegration of the starch granules. It is, therefore, concluded that the high viscoelasticity of the starch–xanthan mixture is caused by a lower degree of disintegration of the supermolecular starch structure rather than by interaction between starch and xanthan at the molecular level. This is further supported by the fact that the opposite, i.e. an antagonistic effect, was observed when the starch–xanthan mixtures were prepared by combining separately heated starch and xanthan dispersions. The latter preparation method has the advantage that the swelling state of the starch granules and the amount of solubilized amylose is equal in the initial starch dispersion and in the mixture. Interestingly, the amount of titratable amylose was not reduced by combining starch with xanthan, which confirms

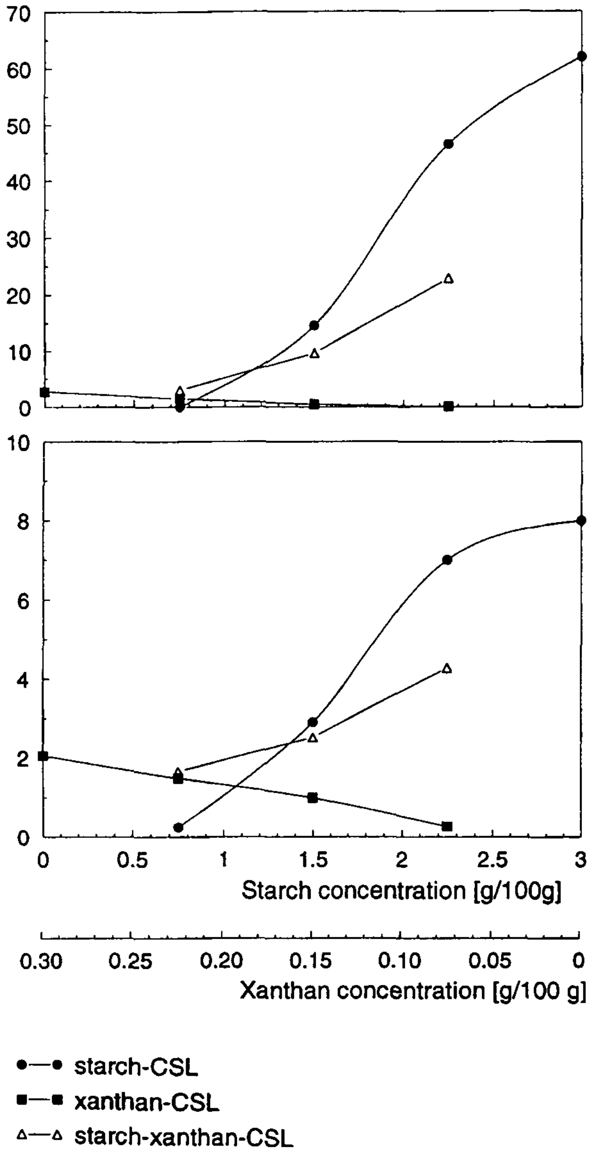

Figure 2 Storage modulus G (1 Hz) and loss modulus G' (1 Hz) of starch and xanthan dispersions, respectively, and of starch–xanthan mixtures with addition of 4 g CSL/100 g starch. In pure xanthan systems, CSL was added at concentrations of 40 g/100 g xanthan. (The different range of scales for G and G' should be noted.)

Table 2 Iodine binding capacity (IBC) and complexation index (CI) of starch (3 g/100 g) dispersions and starch–xanthan (1.5 and 0.15 g/100 g) mixtures without and with addition of 4 g CSL/100 g starch respectively

Sample	IBC (g/100 g starch)	CI (%)
Starch	4.59	0
Starch–CSL	0	100
Starch–xanthan	4.57	0
Starch–xanthan–CSL	0	100

that xanthan did not interfere with the amylose fraction nor did it induce the aggregation of amylose at the concentration level studied. Although the observed antagonistic effect was small, it is an indication of an incompatibility between starch and xanthan, which is not surprising for polymer mixtures. Incompatibilities between various polymers have been reported, including between amylose and amylopectin (19,20), amylose and non-starch hydrocolloids (12), as well as between potato maltodextrin and non-starch hydrocolloids (21). The starch–xanthan systems studied were turbid, but showed no visible signs of phase separation. The polymers may rather have formed microphase-separated domains as a consequence of a demixing process.

A comparison of the results of the present study with the synergistic starch–hydrocolloid interactions reported in the literature (3–5,22) is difficult, since the type of starch and hydrocolloid, their concentrations, as well as the preparation procedure, were not the same. Although synergistic effects cannot be excluded, caused for example by phase separation or specific interactions, it is important to note that some of the reported synergistic viscosity increases may in fact be spurious appearances of synergy, as the experimental design used to study starch–hydrocolloid interactions is not appropriate to assess synergy. This is because viscosities of starch–hydrocolloid mixtures are compared to the viscosities of starch and hydrocolloid alone, the concentrations of the components being the same in the mixture and the pure system (3–5,22). This approach is only admissible if the viscosity of the polymer solutions increases linearly with increasing concentration. Since in reality the concentration dependence of polymer viscosity is exponential, the results may have been interpreted erroneously as synergy.

Based on rheological measurements, it is concluded that incompatibilities exist between starch and xanthan, which probably promote the formation a microphase-separated system, where amylopectin, amylose and xanthan are mutually excluded. The effect of polymer immiscibility on the rheological properties may be masked by an apparent synergistic starch–xanthan interaction, which is observed when the supermolecular structure of starch is better preserved by gelatinizing starch in the presence of xanthan. This latter type of interaction, however, is not comparable to true synergistic interactions like the well-known synergistic xanthan–galactomannan interaction, where evidence for intermolecular binding was found (23).

In order to study the influence of starch complexation on the rheological properties of starch–xanthan systems, a complex-forming emulsifier was added to the mixture. The samples were prepared by combining separately dispersed starch (3.06 g/100 g), xanthan (0.306 g/100 g) and CSL (6 g/100 g) at appropriate ratios. The emulsifier CSL was added at levels of 4 g/100 g starch. As a control, comparable amounts of CSL were added to pure xanthan dispersions (40 g/100 g xanthan). Figure 2 shows the storage modulus G and the loss modulus G' of starch–CSL, xanthan–CSL and xanthan–starch–CSL systems. The IBC and the respective complexation indices (CI) of selected samples are presented in Table 2.

As expected, the IBC of starch-containing systems was reduced from 4.57 to 0 g/100 g starch by addition of CSL, which means that amylose complexes were formed and that the emulsifier concentration was sufficient to saturate the amylose fraction (CI 100%). By adding CSL to the starch dispersions, the development of turbidity was observed, whereas the emulsifier-free samples remained translucent. At starch concentrations >1 g/100 g, the incorporation of CSL at saturation concentrations led to a transformation from a liquid-like to a gel-like texture, as revealed by visual inspection of the samples. The changes took place instantaneously by cooling the samples to 25°C. Accordingly, the storage modulus *G* increased up to 30 times compared to emulsifier-free starch systems, while the loss modulus *G′* increased to a much lesser extent. On the other hand, the addition of CSL did not significantly influence the viscoelasticity of xanthan dispersions. Interestingly, the viscoelasticity of starch–xanthan–CSL mixtures was lower than that of the respective mixtures without xanthan, except for the lowest concentration studied.

As already reported earlier (14), the gelation of starch systems by the addition of CSL occurs as a consequence of the inclusion of emulsifiers into the helical cavity of amylose. The amylose–lipid inclusion complexes possess a low solubility in water, which promotes their physical aggregation. In dilute starch dispersions, the complexes tend to precipitate, lowering the viscosity of the starch system. Above a critical starch concentration, the complexes lead to the formation of an intergranular network and induce the gelation of starch. The resulting system is in fact a filled gel, where the amylopectin-rich starch granules, acting as fillers, are embedded in an aggregated amylose–emulsifier matrix. In the present study, the gels formed by starch complexation were softer when xanthan was added, suggesting that xanthan interferes with the formation of an intergranular amylose–emulsifier network.

To understand better the effect of xanthan addition on the complexation-induced gelation of starch, the rheological properties of starch dispersions (2 g/100 g) with and without the addition of xanthan (0.1 g/100 g) were measured as a function of CSL concentration (0–4 g/100 g starch). Besides CSL, which is an ionic emulsifier, GMS was used in one experiment as an example of a non-ionic emulsifier. Again, all components were separately dispersed and then mixed in order to compare systems having the same supermolecular starch structure. The samples were prepared by combining separately dispersed starch (2.26 g/100 g), xanthan (0.95 g/100 g) and emulsifier (6 g/100 g) at appropriate ratios. Figure 3 shows the storage modulus *G* and the IBC of starch and starch–xanthan dispersions, respectively, at increasing CSL concentrations. Figure 4 shows the storage modulus *G* and the loss modulus *G′* of starch–CSL systems with and without xanthan as a function of frequency. In Table 3, a comparison of the viscoelasticities of starch–xanthan–CSL and starch–xanthan–GMS systems is presented.

As expected, the IBC of starch decreased when CSL was added to the system. The IBC decreased with increasing CSL concentrations in the same manner when xanthan was present, which means that the same amount of complexes were formed in both the starch–CSL and the starch–

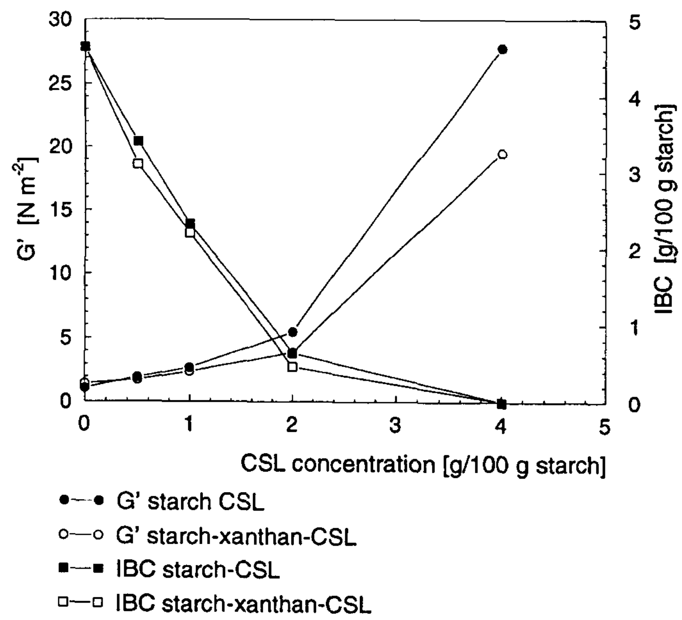

Figure 3 Influence of varying CSL concentration on storage modulus *G* (1 Hz) and iodine binding capacity (IBC) of starch (2 g/100 g) dispersion and starch–xanthan (2 g starch and 0.1 g xanthan/100 g) mixtures.

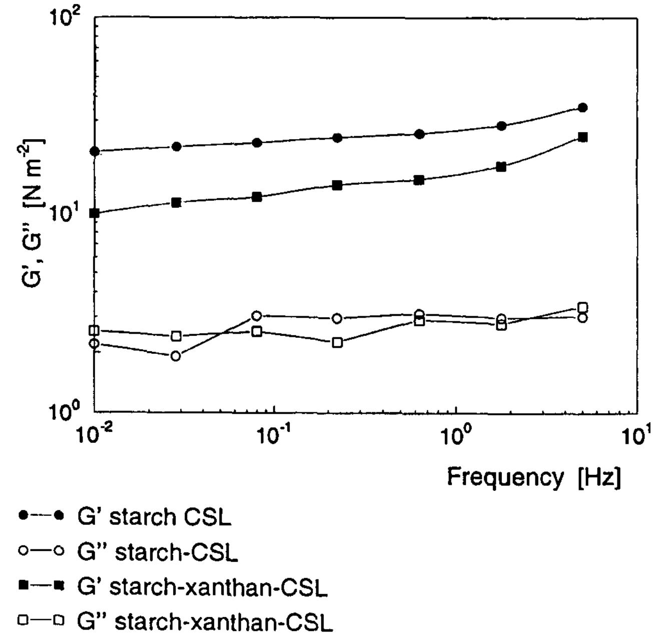

Figure 4 Storage modulus *G* and loss modulus *G′* of starch–CSL (2 g starch/100 g and 4 g CSL/100 g starch) and of starch–xanthan–CSL (2 g starch and 0.1 g xanthan/100 g, 4 g CSL/100 g starch) mixtures as a function of frequency.

Table 3 Storage modulus G, loss modulus G' and complexation index (CI) of starch (2 g/100 g) dispersions and starch–xanthan (2 and 0.1 g/100 g) mixtures with addition of CSL (4 g/100 g starch) or GMS (3 g/100 g starch) respectively

Sample	G (1 Hz) (N/m^2)	G' (1 Hz) (N/m^2)	CI (%)
Starch–CSL	27.8	3.9	100
Starch–xanthan–CSL	19.5	3.6	100
Starch–GMS	18.4	3.7	100
Starch–xanthan–GMS	6.7	2.0	100

xanthan–CSL system. The elasticity of starch–CSL and starch–xanthan–CSL dispersions was comparable up to CSL concentrations of 2 g/100 g starch. At higher emulsifier concentrations, which led to the saturation of the amylose and the gelation of the system, the elasticity of the starch–emulsifier gel was lowered considerably by incorporation of xanthan. The mechanical spectra of starch complexed with 4 g CSL/100 g starch showed only a slight frequency dependence of the storage modulus G in the frequency range of 0.01–5 Hz. Furthermore, the values of the storage modulus G were around 9 times higher than those of the loss modulus G', which is typical for a soft gel. A similar mechanical spectrum was obtained for the respective gel with xanthan, the only difference being the lower elasticity. Basically the same effects were found when GMS was used as emulsifier. GMS also induced the gelation of the starch system, and by incorporation of xanthan the firmness of the gel was reduced. Compared to CSL, lower concentrations of GMS were necessary to saturate the amylose fraction, since GMS has a lower molecular weight. Furthermore, the gels with GMS were generally softer then those formed with CSL.

These results confirm that, while the formation of starch inclusion complexes with emulsifiers was not influenced by the incorporation of another polymer like xanthan, the rheological properties of the resulting gels were affected by the addition of xanthan. Xanthan did not reinforce the amylose–emulsifier network, as could have been expected. On the contrary, a reduction of the firmness of the gels was found. The fact that a decreased gel strength was observed with the ionic emulsifier CSL, as well as with the non-ionic emulsifier GMS, proves that the effect was not due to electrostatic interactions of CSL with the charged polymer xanthan. Most probably, the incompatibility between xanthan and amylose, which is the gel-forming fraction of starch, is responsible for this effect. The results suggest that xanthan interferes with the gelation process of starch induced by amylose complexation and weakens the structure by forming a phase-separated network.

In order to understand how non-starch hydrocolloids affect the rheological properties of starch systems, the location, molecular changes and function of each component have to be considered. Amylopectin is mainly located in the swollen starch granules and acts as filler, while amylose and xanthan form part of the continuous phase. Of the three polymers, only amylose has a strong tendency to aggregate and to induce gelation, which occurs either spontaneously (retrogradation) or may be induced by complexation with a suitable ligand. At low starch concentrations, the time scale for the latter gelation process is about two orders of magnitude smaller than that for spontaneous gelation (24). It can be assumed that by incorporating non-gelling xanthan into starch, the solubility of amylose emulsifiers is further reduced due to mutual exclusion, which increases the aggregation rate of amylose (25). This was shown to be true for spontaneously gelled starch systems, where the addition of hydrocolloids significantly reduced the gelation time (5,8,11). It is hypothesized that two factors contribute to a decreased gel strength of starch–xanthan–CSL systems: first, xanthan weakens the structure as it prevents the formation of a continuous, intergranular amylose–emulsifier network, and second, an increased aggregation rate of amylose promotes the formation of a different, less perfect network structure. On the other hand, the fast gelation process induced by amylose complexation reduces the extent of phase separation, since polymer diffusion is limited by the increase in viscosity during gelation. This would allow the generation of different gel structures with different rheological properties by varying the gelation conditions.

Conclusion

From the practical viewpoint, it may be interesting to replace small amounts of starch by a hydrocolloid with a high thickening power, like xanthan. The rheological properties of the mixture are determined by interactions at two different levels. At the super-molecular level, the granular structure of starch may be better preserved when starch is gelatinized in the presence of a hydrocolloid. At the molecular level, incompatibilities between amylopectin, amylose and xanthan determine the rheological properties of the mixture. Although starch–hydrocolloid incompatibility does not influence the formation of amylose–emulsifier complexes, the mutual exclusion does affect the gelation process induced by amylose complexation and reduces the firmness of the resulting gels. The fact that it is possible to induce the gelation of starch by amylose–emulsifier complexation in the presence of another hydrocolloid could be used for controlled fixation of certain structures created by varying the preparation conditions, i.e. shear rate, time–temperature conditions and order of component addition. Further research, for example visualization of the phase separation and the network structures with microscopic methods, is needed for a better understanding of multicomponent starch–hydrocolloid gels. This would allow the tailoring of the textural and sensorial properties of starch-based foods. For example, starch gels with good flavour-release properties could be produced by inclusion of small droplets of the non-gelling xanthan, which has far better flavour-release characteristics than gelled starch (25).

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