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Effects of Ca- and Na-lignosulfonate on starch gelatinization and network formation

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Abstract

The interaction of lignosulfonates with starches was examined by microscopy and viscosity measurements. 8% starch dispersions with Ca- or Na-lignosulfonate, or with only Ca^{2+} or Na^+, were heated to 97 °C and cooled to 50 °C in a Brabender Viscograph, the gelatinization was followed by light microscopy and image analysis, and the gel network formed after cooling to 4 °C was studied under the transmission electron microscope.

The lignosulfonates (2%) delayed the initial granule swelling in all starches (native maize, waxy maize and waxy barley). The presence of ions enhanced amylose leakage resulting in lower peak viscosity. The viscosity during cooling increased more with Ca-LS than with Na-LS. With a low lignosulfonate concentration the network formed after cooling was homogeneous with fine strands. With Na-lignosulfonate, as well as with Na^+, the network connectivity deteriorated and spherical aggregates formed. Ca-lignosulfonate induced a network with thick strands, but with Ca^{2+} the strands became thinner.

Keywords: Starch; Lignosulfonate; Gelatinization; Viscosity; TEM

1. Introduction

Lignosulfonate is a biopolymer that originates from wood, and is an interesting reaction product of the sulfite pulping process, where lignin reacts with sulfite. The lignosulfonate has a molecular weight of about 5.000–60.000 g/mol and consists of cross-linked phenylpropanoid monomers. It is thought to form a spherical structure with negatively charged sulfonic groups on the surface (Fredheim & Christensen, 2003). Lignosulfonate is water-soluble and has surface-active properties. We have estimated the size of lignosulfonate particles in water to be around 50–60 nm by transmission electron microscopy, micrographs not shown. The size of the particles could make it difficult to penetrate into the granules, so any effect of lignosulfonate on the starch would probably be due to interaction at the surfaces or outside the granules. The great versatility of lignosulfonate makes it suitable for a wide range of products. It is generally used as a dispersant or stabilizer (Gargulak & Lebo, 2000). It has also been used for many years in feed. For humans lignosulfonate is defined as a dietary fibre since it is not degraded in the intestine. The surface-active properties in combination with being a dietary fibre could make it useful as a functional ingredient in foodstuffs. It would then be important to know how it interacts with other components in the food.

Starch is one of the most abundant carbohydrates and used in foodstuffs as a thickener and binder. During heating in water the granules swell, the viscosity increases and amylose leaks out into the solution (Doublier, Llamas, & Le Meur, 1987; Langton & Hermansson, 1989; Richardson, Langton, Bark, & Hermansson, 2003; Steeneken, 1989). The starch gelatinization can easily be altered by other components such as surface-active agents. For example, the interaction with emulsifiers may delay the gelatinization substantially (Deffenbaugh, 1997; Richardson et al., 2003). The effects of lignosulfonate on starch gelatinization have not been examined.

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In the sulfite process, sodium or calcium hydrogen sulfite is used, which gives Na-lignosulfonate or Ca-lignosulfonate. Ion exchange gives lignosulfonates with slightly different properties. Since ions have a low molecular weight, and are loosely bound to lignosulfonate, they are considered to easily diffuse into the amorphous parts of the starch granule along with water (French, 1984). Studies with polarized light on wheat starch granules have shown that the gelatinization can begin both at the centre and on the periphery of the granules, depending on the kind and concentration of added ions (Gough & Pybus, 1973). They also reported that sodium chloride had a slight decreasing effect on the gelatinization temperature, while calcium chloride could both decrease and increase the gelatinization temperature, depending on concentration. The changes in starch granule swelling due to salt addition have been reported by many, e.g. Jane (1993), who measured the enthalpy changes with DSC. On the other hand, in pure amylose gels with added NaCl, $CaCl_2$ or $AlCl_3$, Hermansson, Kidman, and Svegmark (1995) did not observe any major changes in structure except a slightly higher degree of aggregation.

The ions can also affect the viscoelasticity of the cooled gel. Muhrbeck and Eliasson (1987) have shown that the dynamic viscosity and complex modulus of potato starch gels dropped at higher ionic strength, and that divalent cations had a larger effect than monovalent ions. This effect was not seen in cassava starch. Since the two starches differ in phosphate content, they suggested that the ions may block the interactions between phosphate groups on the granule surfaces and hinder cross-linking between the granules.

The objective of this work was to determine the effects of lignosulfonates on starch gelatinization and network formation, and whether these effects could be attributed to the lignosulfonate molecule itself or to the ions that are naturally present. The effects on the different starch components, amylose and amylopectin, were also studied by using starches varying in amylose content.

2. Materials and methods

2.1. Materials

C☆Gel 03401 native maize starch (23% amylose, fat 0.1%, protein 0.3%, moisture 12%) and C☆Gel 04201 waxy maize starch (1–2% amylose, fat 0.1%, protein 0.3%, moisture 13%) from Cerestar Benelux BV, Sas van Gent, Netherlands.

Waxy barley starch (6% amylose) from Lyckeby Stärkelsen, Kristianstad, Sweden.

Ca-lignosulfonate (DP751, 3.6% Ca^{2+}, 1.1% Na^{+}, 6.0% S_0, 2–3% reduced sugars) and Na-lignosulfonate (DP752, 0.4% Ca^{2+}, 6.1% Na^{+}, 5.3% S_0, 2–3% reduced sugars) from LignoTech, Vargön, Sweden.

NaCl and $CaCl_2\cdot 2H_2O$ (p.a.) from Merck, Darmstadt, Germany.

2.2. Starch paste preparation and microscopy

A starch suspension was prepared with 8% (w/w) starch and 0.001 or 2.0% Ca^{2+}- or Na^{+}-lignosulfonate in deionized water. $CaCl_2$ or NaCl was also added to dispersions with 0.001% lignosulfonate in an amount corresponding to that in 2.0% lignosulfonate, i.e. 0.072% Ca^{2+} (as with DP751) or 0.122% Na^{+} (as with DP752).

The suspension was heated in the Brabender Viscograph (Duisburg, Germany) at 75 rpm with a temperature increase of 1.5 °C/min. Viscograms were recorded with a 500 cmg measuring box. The suspension was heated to 97 °C, held at this temperature for 30 min and cooled down to 50 °C. Samples for microscopy were collected at several temperatures, depending on starch type. The paste was held at the desired temperature 1 min before withdrawal and 2 min afterwards, to attain the right temperature. The samples were smeared onto an object glass. After drying, the samples were stained with Lugol's iodine solution and examined with the Nikon Microphot FXA microscope (Japan) and a 20× objective (N.A. 0.5). Images were taken with a Hamamatsu 3CCD camera C6157. All heating experiments were performed at least twice.

After heating for 30 min at 97 °C, some paste was stored in small cylinders for 1 h at 4 °C. One cubic millimetre cubes were cut out of the gels and fixated with 2.5% glutaraldehyde and 0.2% ruthenium red in 0.1 M phosphate buffer of pH 7 over night. Dehydration steps with increasing ethanol concentration (50, 75, 95 and 99.5%) were followed by embedding in polybed (TAAB 812). Thin sections (100 nm) were cut by using an ultramicrotome and collected on formvar-coated grids. The sections were stained according to the thiosemicarbazide–silver proteinate method described by Thiéry (1967). Images were taken with a LEO 906 E transmission electron microscope, TEM (Oberkochen, Germany) at an accelerating voltage of 80 kV.

2.3. Image analysis

Light microscopy images of native maize starch heated to 65 °C, with a low or high concentration of lignosulfonate, were converted into binary images as described previously (Richardson et al., 2003). Several size and shape factors were measured. Only 12–15 images of each sample were measured, and the data was therefore divided into three sets for calculations of the mean value and the standard deviation.

3. Results and discussion

3.1. Maize starch gelatinization with lignosulfonates

The Brabender viscosity of a native maize starch solution was measured during heating with low (0.001%) and high (2%) concentrations of Ca-LS (calcium lignosulfonate)

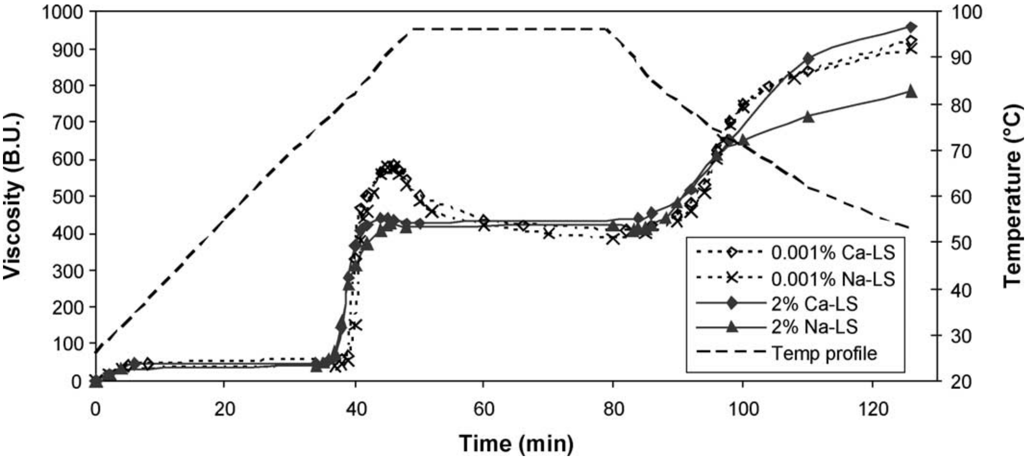

Fig. 1. Brabender viscographs of native maize dispersions with Ca-lignosulfonate (Ca-LS) or Na-lignosulfonate (Na-LS).

or Na-LS (sodium lignosulfonate). The Brabender viscographs for these four pastes are shown in Fig. 1. The viscosity of the low-LS samples followed the general trend for maize starch shown by e.g. Yoshimoto, Takenouchi, and Takeda (2002). It increased rapidly at about 80 °C, reached a peak of 580 B.U. at about 90 °C and decreased to ca 400 B.U. during the 30 min of stirring at 97 °C. During cooling, the viscosity increased once again and reached 900 B.U. at 50 °C. There was no significant difference between the two samples with low Ca-LS and low Na-LS.

When a higher amount of LS (Ca-LS or Na-LS) was added to the paste, the viscosity increase began slightly earlier but the peak viscosity was only 430 B.U. (Fig. 1). The viscosity did not decrease but remained constant during the rest of the heating. There was actually a difference between the effects of Ca-LS and Na-LS during cooling, because addition of Ca-LS resulted in a stronger gel with a viscosity of 960 B.U., while Na-LS gave a weaker gel, 790 B.U.

Images of smears recorded by the light microscope are shown in Fig. 2. The two columns to the left show the images for the low LS pastes. It can be seen that the first large viscosity increase corresponds to an extensive swelling of the granules (a, b, e and f), as also shown in earlier studies (Richardson et al., 2003). At about 80 °C, the granules appear to have become closely packed. At this stage, before granule breakdown, the viscosity is a function of the granule volume fraction (Doublier et al., 1987; Steeneken, 1989). At the peak viscosity the swelling and deformation of the granules are at a maximum (i and j). Some amylose has leaked out, seen as dark areas outside the granules, but the amylopectin parts have not yet begun to dissolve. During further heating the granules begin to rupture and break down into small fragments (m and n), which causes a viscosity decrease. After gel formation (q and r) the paste is quite homogeneous with a well-dispersed amylose phase (small dark dots) and some small granule fragments (brighter objects rich in amylopectin).

In the pastes with a high concentration of lignosulfonate, at low temperatures, the granules actually seemed to be less swollen than with low LS (Fig. 2a–d), but during the rapid viscosity increase amylose began to leak out much earlier (e–h). Amylose in the solution can increase the viscosity somewhat, so the amylose leakage was probably responsible for the earlier viscosity increase. As can be seen in Fig. 2k and l, the granules did not swell to such an extent as with a low LS concentration, which can explain the relatively low peak viscosity, but amylose continued to leak out and formed a concentrated dark phase outside the granules. As there was less swelling and more leakage at an early stage, the effects of further heating were not so pronounced. After heating for 30 min at 97 °C, there was a large degree of inhomogeneity in the pastes with lignosulfonate. Some granules were still extensively swollen, and the amylose phase was more aggregated than in the low LS pastes (m–p). After cooling, the pastes with high LS were still much more inhomogeneous than those with low LS, and amylose and amylopectin seemed to be more separated (q–t). In the images at this magnification, there was no obvious difference between the two pastes with high LS content after cooling, although they had such different viscosities.

These results showed that the addition of lignosulfonate had effects at all stages. Two stages were considered most important and were therefore studied more closely: (1) the early swelling and (2) the gel formation during cooling. These stages will be discussed separately.

3.2. Early stage of swelling

Before the paste viscosity began to increase at about 80 °C, there seemed to be a difference in granule swelling (Fig. 2a–d). To confirm the observations, the granules of native maize at 65 °C were measured by image analysis. The equivalent diameter of granules with high LS added was about 30% smaller than that of granules with low LS added (Table 1), so the swelling was substantially reduced by

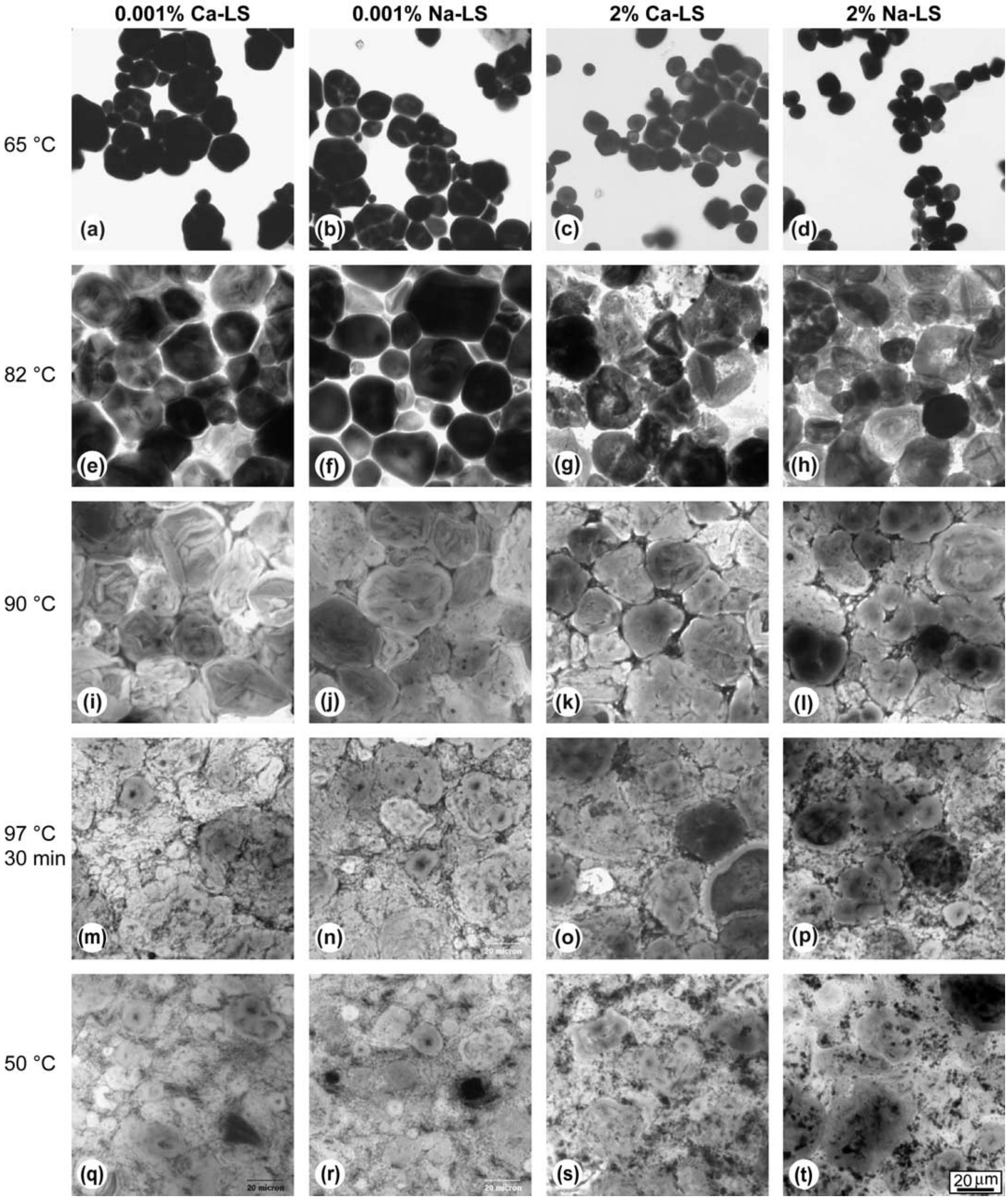

Fig. 2. LM images of native maize smear samples with lignosulfonate at 65 °C (a–d), 82 °C (e–h), 90 °C (i–l), 97 °C and 30 min of heating (m–p) and after cooling to 50 °C (q–t). The samples were stained with Lugol's iodine solution. Amylose is dark and amylopectin brighter.

lignosulfonate addition. The compactness value (based on the relation between area and perimeter) was quite close to 1 in all samples, which means that the granules were still nearly spherical.

The difference in swelling raised the question of whether there could be some interaction between lignosulfonate and any of the starch components (amylose or amylopectin) that hindered swelling. Therefore, pastes with other amylose/amylopectin ratios were also examined: waxy maize (1–2% amylose) and waxy barley (6% amylose). In Fig. 3, images of the three starch pastes with a low and high amount of Ca-LS are shown at 65 °C (maize and waxy maize) and

Table 1
Native maize starch granules heated to 65 °C were measured with image analysis

	Area (μm^2)	Compactness	$D_{\mathrm{equivalent}}$ (μm)
0.001% Ca-LS	227 ± 68	1.14 ± 0.02	15.0 ± 2.1
0.001% Na-LS	226 ± 37	1.19 ± 0.03	15.4 ± 1.3
2% Ca-LS	116 ± 26	1.18 ± 0.05	11.2 ± 1.5
2% Na-LS	105 ± 10	1.15 ± 0.03	10.9 ± 0.4

The granule two-dimensional area, the compactness (1 being completely round) and the equivalent diameter (the diameter of a circle with the same area) were calculated.

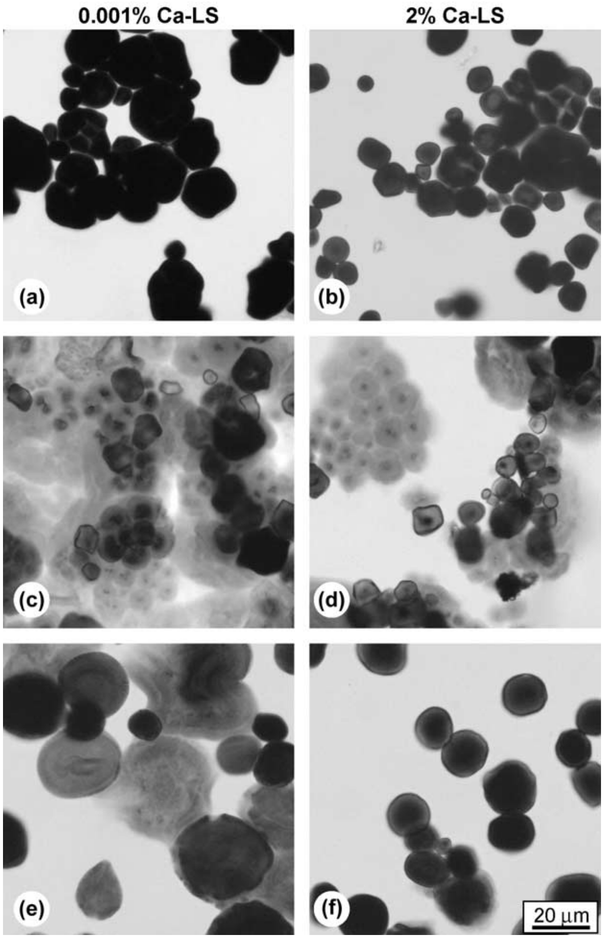

Fig. 3. LM images of native maize (a,b), waxy maize (c,d) and waxy barley (e,f) dispersions with Ca-LS. The samples were heated to 65 °C (a–d) or 60 °C (e,f). To the left are dispersions with 0.001% Ca-LS, to the right dispersions with 2% Ca-LS.

60 °C (waxy barley). There was an obvious delay in swelling in all samples with high Ca-LS. In the waxy maize paste (c and d) a large part of the low Ca-LS granules had begun to rupture at 65 °C, but fewer of the granules with high Ca-LS. With 2% Na-LS the rupture was even more delayed (image not shown). The same trend with a more restricted swelling of the high-LS pastes was seen with waxy barley (Fig. 3e and f).

The delay in swelling was also revealed in the viscosity diagrams. Fig. 4 shows the Brabender viscosity of the three starch pastes with a high and low amount of Ca-LS. Waxy barley had an early viscosity increase at 63 °C and seemed to have two peaks. According to Yoshimoto et al. (2002), these could be related to the amylose/amylopectin content. The first peak corresponds to the melting of amylopectin crystallites. The second peak grows at the expense of the first one as the amylose content in the barley cultivar increases, and is said to be related to melting of amylose–lipid complexes (Kugimiya, Donovan, & Wong, 1980). It was therefore interesting to see that, with addition of Ca-LS to waxy barley starch, the first viscosity increase was smaller (650 B.U. instead of 1450 B.U.) but not the second one. This indicated a delay in the amylopectin crystallite melting. Waxy maize with a low LS-content only had one sharp peak at 69 °C, obviously corresponding to breaking of the amylopectin bonds since there was such a low amylose content. Waxy maize can swell to a greater extent than native starch, which gives a higher peak viscosity, but they also break down more easily resulting in a sharp viscosity decrease (Greenwood & Munro, 1979), also seen in Fig. 4. With addition of Ca-LS, the peak was somewhat delayed and also decreased from 1400 to 1260 B.U.

The experiments showed that the granule swelling was delayed in native maize, waxy maize and waxy barley by addition of lignosulfonate. In the native maize starch, the very first viscosity increase was not delayed although the granules remained smaller with LS. A plausible explanation for this was that amylose was drawn out of the granules, as seen in Fig. 2g and h, and thereby increased the viscosity of the water solution. The peak viscosity was also decreased by lignosulfonate addition. The reason was probably that some

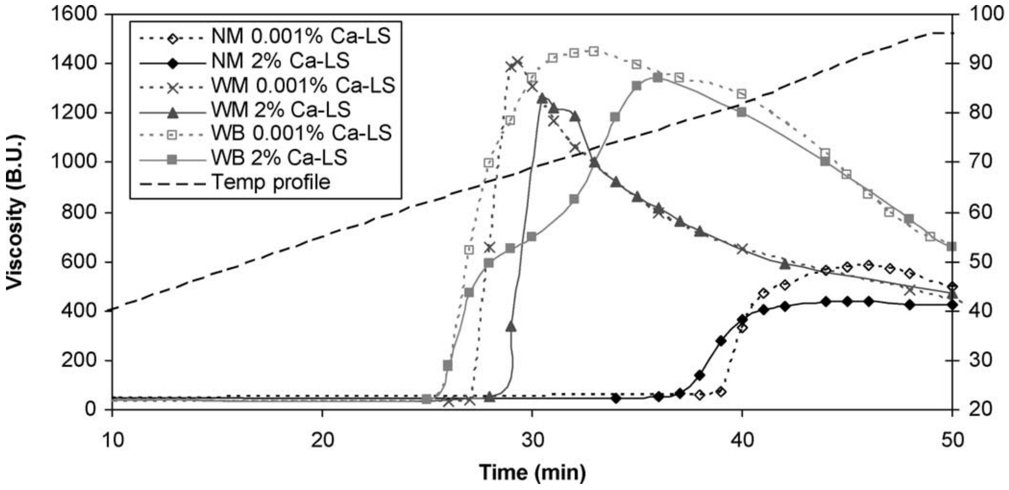

Fig. 4. Brabender viscographs of starch dispersions with Ca-LS during heating (40–97 °C). The starch types are native maize (NM), waxy maize (WM) and waxy barley (WB).

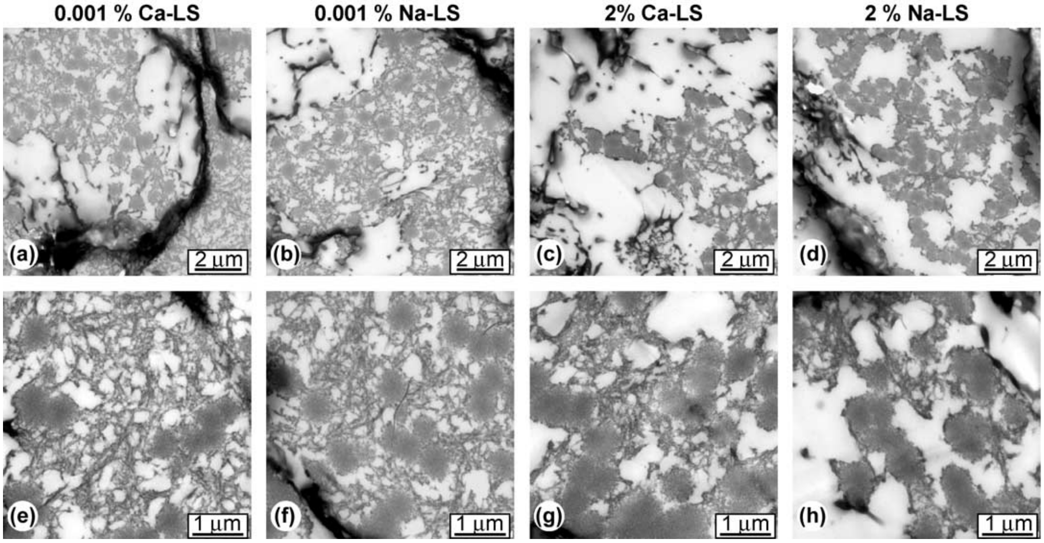

Fig. 5. Native maize starch gels with LS under the TEM, embedded and sectioned after heating at 97 °C for 30 min and cooling in refrigerator during 1 h. Scale bars 2 µm (a–d) and 1 µm (e–h).

of the granules broke into fragments much earlier when LS was added.

Many experiments have shown that most of the interactions between starch and other components involve amylose rather than amylopectin, according to a review by Deffenbaugh (1997), but it has been shown that amylopectin is also capable of reacting with, for example, lipids and proteins (Lundqvist, 2001). In this work, the effects on pure amylopectin were not examined, but there was very little amylose in the waxy maize and still the effects of lignosulfonate were so considerable that the possibilities of interaction with amylopectin, thereby delaying the melting of amylopectin aggregates, could not be excluded. The effect could also be due to molecular adhesion to the granule surfaces, which could hinder transport to and from the granules. Lignosulfonates are surface-active and negatively charged, and would probably interact with the granule surfaces. This did not readily explain the extraction of amylose seen in Fig. 2g and h. The increased dry mass concentration (10% with LS compared to 8% without LS) probably did not influence the swelling at this early stage since the water content was so high.

3.3. Gel formation

During cooling of the paste, the amylose sets into a gel, both in the solution and inside the granules. The increase in Brabender viscosity during cooling is a combined effect of the change in the swollen granules and the formation of an amylose gel network. The amylose aggregation was increased by addition of lignosulfonate, as seen in Fig. 2q–t. The end viscosity became higher when Ca-LS was added and lower when Na-LS was added to the three starch types. To reveal the network structure, the native maize gels were studied under the TEM. Fig. 5 shows the native maize gels heated at 97 °C for 30 min and refrigerated at 4 °C for 1 h. The images show the amylose network strands in the sectioned gels at two magnifications. In the gels with a low amount of LS (a, b, e and f), there was a fine-stranded network interwoven with spherical aggregates that were 400–450 nm in diameter. The composition of the aggregates could not be determined from LM examination, but since amylopectin does not readily form a network and is present at quite high concentrations, the aggregates should at least partly consist of amylopectin. Hermansson et al. (1995) drew a similar conclusion for wheat starch gels that were very similar in appearance to these maize gels. The networks were continuous, covering large areas, and in connection with the non-dissolved granule residues (mainly consisting of amylopectin, according to iodine staining for LM) seen as thick black streaks. There were no visible differences between these two samples (low Ca-LS and low Na-LS).

The gel with 2% Ca-LS had a much more varied structure than the low LS gels. Parts of the network could not be distinguished from the fine network of the low LS gels, but in some areas such as those shown in Fig. 5c and g, the network in this gel was coarser, with fewer and thicker strands. The gel formation was even more dramatically altered by addition of 2% Na-LS to the paste. As shown in Fig. 5d and h, the connectivity deteriorated badly. Fig. 5h shows most clearly that there were almost no amylose strands at all keeping the structure together. The aggregates were spread randomly or aggregated into clusters. There did not seem to be any connection between these poor network areas and the dark granule residues, such as in the lower left corner of Fig. 5d.

These micrographs showed that Na-LS, and to some extent Ca-LS, changed the amylose network formation and the connectivity between the starch components. Na-LS seemed to attach to the surfaces of the spherical aggregates and hinder other molecular connections such as the amylose network, while Ca-LS induced an aggregation of the amylose into thicker strands and also caused extensive inhomogeneity in the gel. This could explain the different end viscosities (at 50 °C) of the gels. Olsson, Langton, and Hermansson (2002) have shown in β-lactoglobulin/amylopectin gels that aggregation into thicker strands increases the gel strength (measured as G'), and bad connectivity between the strands decreases the gel strength. In Fig. 1, the sample with 2% Ca-LS had a high end viscosity (960 B.U.), the low LS samples had an intermediate viscosity of 900 B.U., and the paste with 2% Na-LS had the lowest end viscosity (790 B.U.). These results indicated that the viscosity increase during cooling could be related to the final gel strength.

3.4. Effect of ions and effect of lignosulfonate

The two lignosulfonates that were used in this project differed in ion content, one having mainly Ca^{2+} as the counter ion and the other having mainly Na^{+}. Ions have previously been reported to have an effect on the starch gelatinization (French, 1984; Gough & Pybus, 1973; Jane, 1993). The aim of this work was to study whether the lignosulfonate itself had any effects on the gelatinization, or whether the effects were primarily due to the presence of ions. Therefore, the experiments were also performed with a low concentration of lignosulfonate but with a high ion concentration.

The effects of Ca^{2+} or Na^{+} on the paste viscosity of native maize starch are shown in Fig. 6. In Fig. 6a, the whole temperature cycle is included. The initial stage, up to 90 °C, is enlarged in Fig. 6b. A very interesting effect could be seen

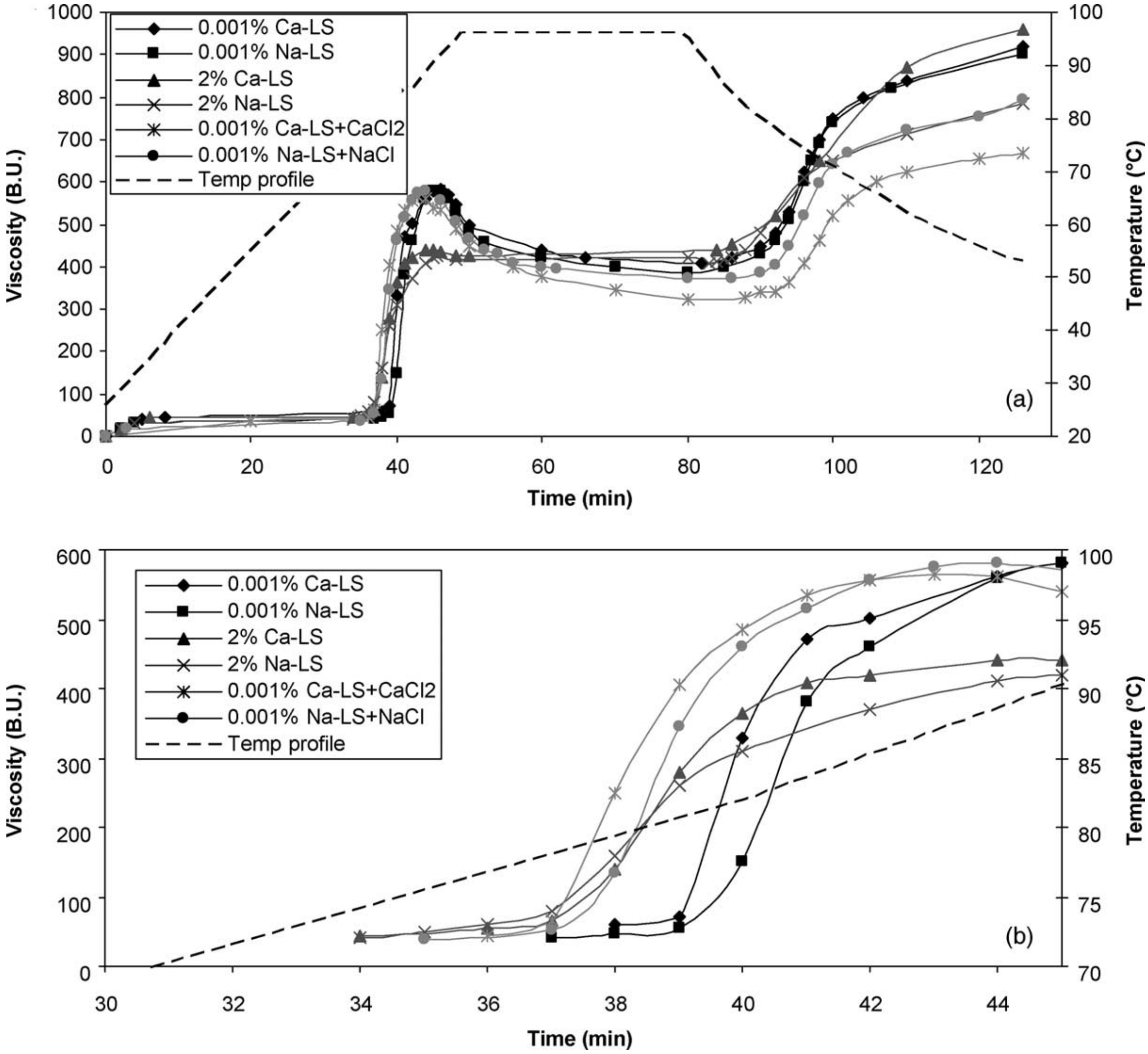

Fig. 6. Brabender viscographs of native maize dispersions with lignosulfonate or ions: (a) overall diagram, (b) the initial stage. The concentrations of $CaCl_2$ and NaCl correspond to the ion concentrations in the 2% lignosulfonates, respectively.

at this early heating. Both the LS pastes and the ion pastes showed an earlier viscosity increase, which is consistent with other works (Gough & Pybus, 1973), but the peak viscosity was only lowered in the pastes with a high concentration of lignosulfonate. As was shown in Figs. 3 and 4, a lower peak viscosity was due to the lignosulfonate delaying the granule swelling. Ca^{2+} and Na^{+} did not affect the peak viscosity and, consequently, did not change the swelling.

The waxy starches did not show an earlier viscosity increase with Ca-LS and Na-LS, such as in native maize, so the earlier increase in pastes with ions present seemed to be coupled to the amylose content. The ions Ca^{2+} and Na^{+} were therefore believed to affect the leakage of amylose out of the granules. This is consistent with earlier studies. For example, French (1984) and Gough and Pybus, 1973 have pointed out that low molecular solutes could penetrate into the amorphous (amylose) phase inside the granules.

The cooling and gel formation stages were also altered by the presence of ions. As seen in Fig. 6a, the gel with Na^{+} had the same end viscosity at 50 °C as the one with Na-LS (790 B.U.). With Ca^{2+}, the final viscosity was even lower (670 B.U.). This was a large difference compared to Ca-LS. A dramatic change was also revealed in the microstructure. Fig. 7 shows the microstructure of starch gels with ions after cooling to either 50 °C or 4 °C, at low magnification in LM (a and b) and at high magnification in TEM (c and d). In the LM images the pastes with ions were quite similar to those with a low LS concentration, with amylose and amylopectin quite well mixed.

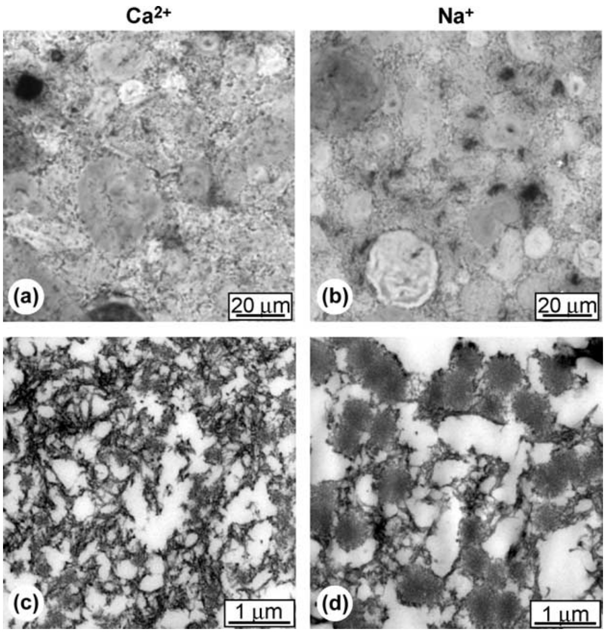

Fig. 7. Images of native maize gels with Ca^{2+} or Na^{+} ions. (a,b) LM images of smear samples, collected after cooling to 50 °C. (c,d) TEM images of embedded gels after heating at 97 °C for 30 min and cooling in refrigerator for 1 h. (a,c) with calcium ions (b,d) with sodium ions.

In the TEM micrographs it could be seen that the amylose network with Na^{+} added (Fig. 7d) was similar to that with high Na-LS (Fig. 5h). Both these gels had many spherical aggregates without any connection and few amylose threads. With Ca^{2+}, there was instead an extremely fine network, and the aggregates were very small (300 nm in diameter, compared to the low-LS samples with about 400 nm). Since this network consisted of very short and thin strands, it was probably more fragile than a network with thicker strands. The apparent strength of the gel, from visual observation, seemed to be related to the increase in viscosity during cooling.

From this microstructural analysis, it was concluded that the Na^{+} ions had about the same effect as Na-LS on gel formation, while Ca^{2+} had an effect that was very different from that of Ca-LS. During the swelling it became evident that the ions had the same influence on the granules whether they were added with lignosulfonate or not, so neither Na^{+} nor Ca^{2+} could be very tightly bound to the LS. In this gelling stage they had completely different effects, Na^{+} hindering network formation and Ca^{2+} promoting a very fine-stranded network. The different appearance of the gel with Ca-LS showed that the lignosulfonate itself also influenced the gel formation. It seemed to impair the network formation and cause greater inhomogeneity throughout the gel, but the exact function could not be determined due to the interaction effects.

4. Conclusions

In this study it was shown that lignosulfonates had effects on starch gelatinization and gel formation. Some of the effects, such as a delayed granule swelling, a more gradual granule breakdown, a lower peak viscosity and greater inhomogeneity of the gel, were due to the lignosulfonate molecule itself. Other effects, such as an earlier amylose leakage during heating and a poor network formation after cooling, could be assigned to the presence of Ca^{2+} and Na^{+} ions in the lignosulfonate. With the right combination of lignosulfonate and ions, different kinds of gel network and thereby rheological properties can be obtained which could be useful in many kinds of applications.

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