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Influence of pH and Ionic Strength on the Viscoelastic Properties of Starch Gels — A Comparison of Potato and Cassava Starches

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SUMMARY

The influence of pH, and of electrolytes, on the viscoelastic properties of potato and cassava starch gels was investigated, using a cone-and-plate rheometer run in the oscillatory mode. The gel strength of the potato starch gels had a maximum around pH 8·5, and was markedly lowered by the addition of even small amounts of electrolytes. This may be due to an electrostatic interaction between potato starch phosphate groups and added cations which blocks the normal phosphate-to-phosphate cross-linking. Neither pH nor electrolytes affected the viscoelastic properties of cassava starch gels. The gelatinization temperature and the gelatinization enthalpy of potato starch, as measured by differential scanning calorimetry, were insensitive to pH and to low electrolyte concentrations.

INTRODUCTION

One of the most important features of starch in food systems is its ability to give structure by the formation of a gel. The rheological properties of starch gels can be controlled by chemical modification, but there are also considerable differences between starches from different sources. A classical method for the investigation of rheological properties is with the Brabender visco/amylograph, where the 'viscosity' in Brabender units is measured. The starch suspension is constantly stirred during a well-defined time–temperature programme, and the result is obtained as a viscogram. The method has several disadvantages: non-Newtonian flow behaviour is not taken into account, and, since the sample is subject to both mechanical and thermal treatment, it is very difficult to relate the results to only one of these parameters. Besides, the mechanical treatment is vigorous, so structures that are built up during the process could easily be destroyed rather than analysed.

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More information about the viscoelastic behaviour of gels, and thus about their structure, is obtained by the use of non-destructive rheological methods. Shear stress relaxation techniques can be used to measure relaxation moduli and relaxation times of starch gels (Chichester & Sterling, 1957), and from such results fundamental knowledge about flow behaviour may be derived (Bohlin, 1980). Oscillatory shear stress measurements give information about the elasticity as well as the viscosity of the substance investigated. This method has been used to investigate the concentration dependence of the viscoelastic behaviour of maize, wheat, potato and cassava (tapioca) starch gels (Evans & Haisman, 1980; Wong & Lelievre, 1981). Neither of these investigations takes into account any influence of pH or of ionic strength on the viscoelastic properties of the gels, although it has been known for a long time that the Brabender viscosity of native potato starch gels is highly susceptible to pH (Nutting, 1952).

In this study, the influence of pH on the viscoelastic properties of potato starch gels was investigated, the oscillatory shear stress technique being used. Furthermore, the influence of electrolytes other than H^+/OH^- was studied. To elucidate the role of the phosphate groups of potato starch, which are believed to play an active part in gel formation (Marsh & Waight, 1982; Putz, 1982), a comparative study was made on cassava starch. This starch has properties which in several respects are similar to those of potato starch (Whistler *et al.*, 1984), but the phosphate present in cassava has been reported not to have the same function as the phosphate groups of potato starch (Moorthy & Ramanujam, 1986).

Differential scanning calorimetry (DSC) was used to study the influence of pH and of electrolytes on the gelatinization behaviour of potato starch.

MATERIALS AND METHODS

Commercial samples of native potato starch (Sveriges Stärkelseproducenters Förening, Karlshamn, Sweden) and of native cassava starch (Lyckeby National, Kristianstad, Sweden) were used. Other chemicals (NaOH, HCl, NaCl, KCl, NH_4Cl, $CaCl_2$, $CdCl_2$) were of analytical grade, and the water used was deionized and distilled.

Sample preparation

For the pH study the starch was slurried in water, and pH was adjusted with NaOH or HCl. The pH range investigated was 5·2–11·9. The starch contents were 2·0 and 4·0% (w/w) for potato and cassava starch slurries, respectively. As for the electrolyte study, the starch was slurried in solutions of NaCl, KCl, NH_4Cl, $CaCl_2$ or $CdCl_2$, of concentrations up to 10·0 mmol litre^{-1}. The pH of these slurries was set to 7·5, and the conductivity was measured with a Kemotron Tetramatic 'mho-meter'. The starch contents were the same as in the pH study.

At least three 2·0 ml samples from each slurry were pipetted into glass test tubes, which were sealed, and then heated in a 90°C water-bath for 120 s. The slurries were stirred throughout the heating stage by the use of a magnetic stirrer, but in the toughest gels stirring was interrupted after *ca* 60 s, due to gel formation. After heating, the test tubes were cooled to 30°C, and kept at this temperature for a minimum of 15 min. No retrograde effects on the viscoelastic properties were observed in samples kept at 30°C, for 90 min, but to minimize such effects the maximum ageing time was 60 min.

Rheological measurements

The measurements were performed on a Bohlin VOR Rheometer (Bohlin Reologi AB, Lund, Sweden) run in the oscillatory mode. A cone-and-plate measurement cell with a 5·4° cone angle and a plate diameter of 30 mm was used. The oscillation amplitude was 0·432°, and the frequency was swept from 0·005 to 1·0 Hz at each run. All measurements were performed at 25°C.

Differential scanning calorimetry

Potato starch slurries in the interval 10–30% (w/w) were prepared. After the pH had been adjusted to 4·2, 7·2 or 9·2, samples of about 5 mg were heated from 25 to 90°C at a heating rate of 10°C min^{-1} in a Perkin Elmer DSC-2. An empty aluminium pan with double lids was used as a reference. The results presented are the mean value and the standard deviation of three runs.

RESULTS

When a viscoelastic material, such as a starch gel, is subject to a sinusoidal shear strain, the generated shear stress is out of phase with the strain by an angle, δ, the loss angle. The definition of this angle is $\tan\delta = G''/G'$, where G'' is the loss modulus and G' is the storage (or elastic) modulus. The viscoelastic behaviour can also be expressed in terms of the complex rigidity modulus, G^*, and the dynamic viscosity, η.

These quantities are defined as $G^* = G' + iG''$ and $\eta = G''/\omega$, ω being the angular frequency of the oscillation (Ferry, 1970).

In this study dynamic viscosity, complex rigidity modulus ('complex modulus') and loss angle were used for the characterization of potato and cassava starch gels. Naturally, when the viscoelastic properties of a starch gel are studied by a non-destructive technique, it is very important to control any structural damage springing from the preparation procedure.

In the present investigation, adjustments of starch concentration and stirring intensity were made to minimize the sedimentation effects during the early stages of heating as well as the mechanical breakdown after the gelatinization and at the transfer from test tube to measurement cell. The variation in dynamic viscosity, complex modulus and loss angle between replicated samples was about 5% for cassava starch gels and about 10% (in some cases nearly 15%) for potato starch gels, where the size distribution of the granules is wider. The gelatinization was considered to be completed after 120 s at 90°C, since further heating did not alter the viscoelastic behaviour of the gels.

At the concentrations used both gels are shear-thinning fluids; their viscosities and complex moduli increase with the shear frequency (Fig. 1) (*cf.* Evans & Haisman, 1980). As mentioned above, the starch concentrations were arbitrarily chosen to give gels that were easy to handle. Since the viscoelastic behaviour of the gels depends not only on the concentration, but also on the size and shape of the starch granules, and on the mechanical treatment, a quantitative comparison of the viscoelastic properties would be of little value. A qualitative comparison is more relevant, however, since potato and cassava starch resemble each other in most respects, while the properties of other starches, e.g. wheat starch, sometimes differ by an order of magnitude (Table 1).

pH study

The viscoelastic behaviour of potato starch gels strongly depends on pH. A viscosity maximum was found around pH 8·5 (Fig. 2). This agrees well with earlier amylograph results (Nutting, 1952), although the considerable differences in methods, concentrations and temperatures exclude any direct comparison of viscosity values.

As shown in Fig. 1, the pH dependence of the complex modulus is comparable with that of the dynamic viscosity, with a distinct maximum around pH 8·5. The loss angle has a minimum at the same pH, though this is of minor significance at oscillation frequencies lower than 0·2 Hz (Fig. 3). This indicates a loss of structure as pH approaches the borders of the interval investigated.

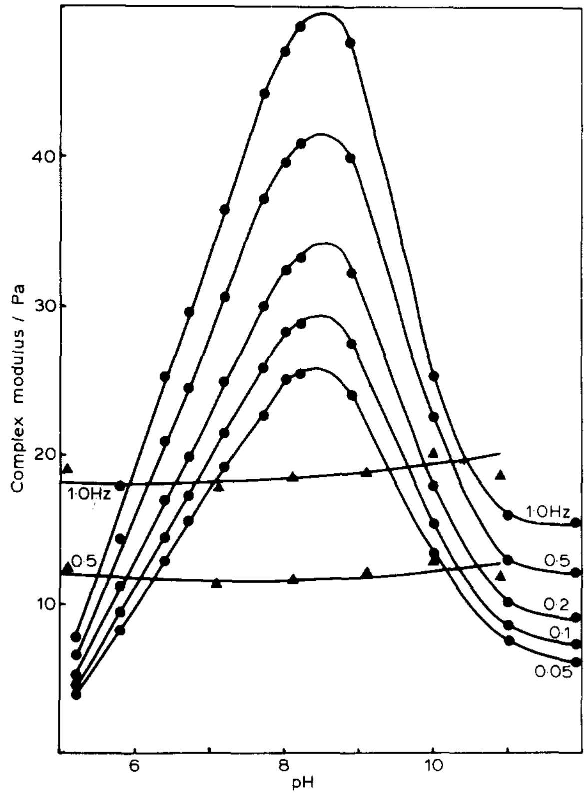

Fig. 1. The complex modulus of potato (●) and cassava (▲) starch gels as a function of pH at different oscillation frequencies.

TABLE 1

Composition and Properties of Starch[a]

	Potato	*Cassava*	*Wheat*
Moisture, %[b]	19	13	13
Ash, %[b]	0.4	0.2	0.2
Protein, %[b]	0.06	0.1	0.4
Lipid, %[b]	0.05	0.1	0.8
Phosphorus, %[b]	0.08	0.01	0.06
Amylose, %[b]	21	17	28
Number of molecules amylose: amylopectin	200	150	1000
Average degree of polymerization	14 000	18 000	3000
Granule diameter/μm	5–100	4–35	1–45
Brabender pasting[c] temperature, °C	61	59	77
Brabender peak[c] viscosity/BU	2500	1400	65

[a] Whistler *et al.* (1984); Swinkels (1985).

[b] Percentage in w/w.

[c] 35 g starch/500 ml water; heating rate 1·5°C min^{-1}.

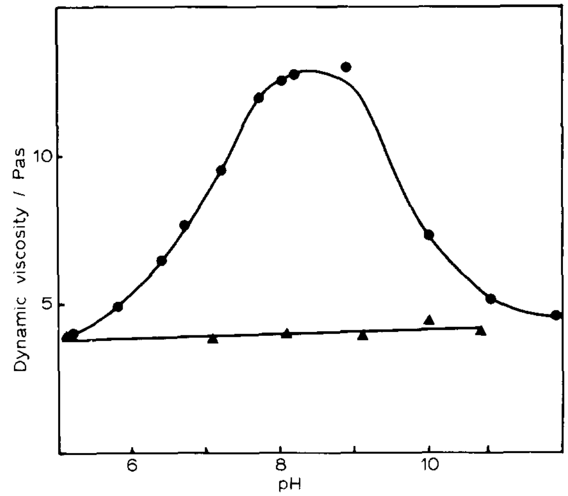

Fig. 2. The dynamic viscosity of potato (●) and cassava (▲) starch gels as a function of pH at an oscillation frequency of 0·2 Hz.

The viscoelastic properties of cassava starch gels were not affected by pH (Figs 1–3).

DSC scans made at pH 4·2, 7·2 and 9·2 on potato starch slurries showed that the gelatinization enthalpy was 17·6 ± 1·0 J g^{-1} independent of pH, and that the peak temperature was 63·0°C ± 0·5°C.

Electrolytes

The addition of electrolytes (NaCl, NH_4Cl, KCl, $CaCl_2$ or $CdCl_2$) to the potato starch slurries also had a considerable effect on the viscoelastic properties of the gels (Figs 4–6). The conductivity of the starch slurries was used as a measure of their ionic strength. Thus, the effects of monovalent and divalent ions could be compared directly, and the surface charge of the starch itself was taken into account. In Fig. 7 the resistivity (defined as conductivity^{-1}) was used to obtain linear relationships. The viscosity, as well as the complex modulus, dropped very steeply at low ionic strengths but levelled off at higher ionic strengths (about 5 mmol litre^{-1} NaCl). The loss angle increased slightly with an increased ionic strength.

Chlorides of divalent cations (Ca^{2+}, Cd^{2+}) had a more pronounced effect on the viscoelastic properties than those of monovalent cations (Na^+, NH_4^+, K^+) at the same ionic strength (or resistivity; Fig. 7).

The viscoelastic properties of the cassava starch gels were not greatly altered by the addition of electrolytes, not even at a NaCl concentration

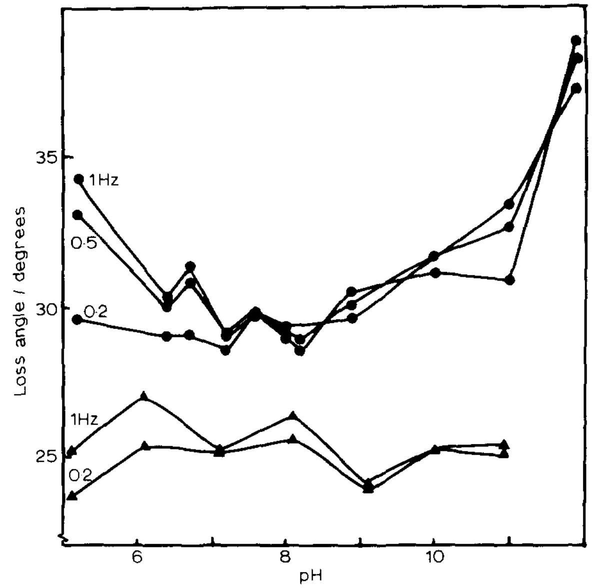

Fig. 3. The loss angle of potato (●) and cassava (▲) starch gels as a function of pH at different oscillation frequencies.

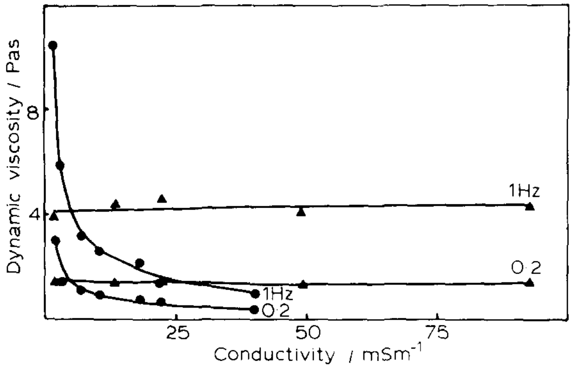

Fig. 4. The dynamic viscosity of potato (●) and cassava (▲) starch gels with added NaCl as a function of the conductivity at 0·2 and 1·0 Hz.

of 10 mmol litre^{-1}, corresponding to a conductivity of 93 mSm^{-1} (Figs 4–6).

The actual low electrolyte concentration did not alter the gelatinization temperature or enthalpy of the starches. This is well in accordance with several studies of the effect of electrolytes upon starch (Gerlsma, 1970; Evans & Haisman, 1982; Oosten, 1982).

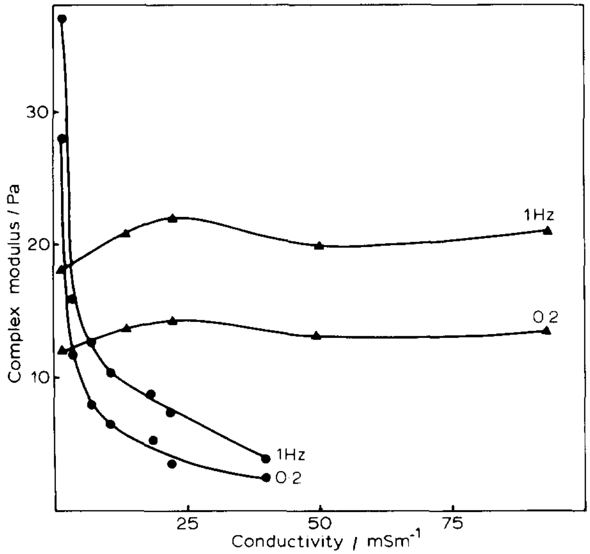

Fig. 5. The complex modulus of potato (●) and cassava (▲) starch gels with added NaCl as a function of the conductivity at 0·2 and 1·0 Hz.

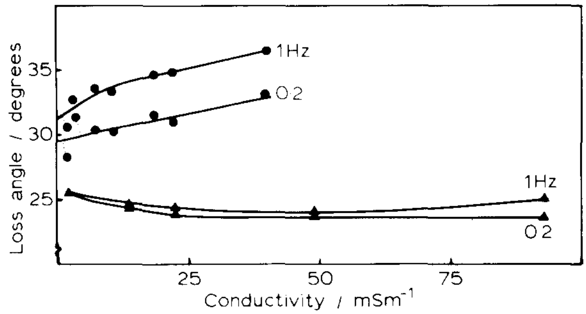

Fig. 6. The loss angle of potato (●) and cassava (▲) starch gels with added NaCl as a function of the conductivity at 0·2 and 1·0 Hz.

DISCUSSION

The present investigation shows that the viscoelastic properties of potato starch gels are strongly dependent on pH and on the ionic strength, while cassava starch gels show no pH or electrolyte sensitivity. As the DSC results do not reveal any involvement of complexing or chemical binding enthalpies, pH or electrolytes are not likely to affect the gelatinization reaction *per se*. Besides, ions of the same charge influence the potato

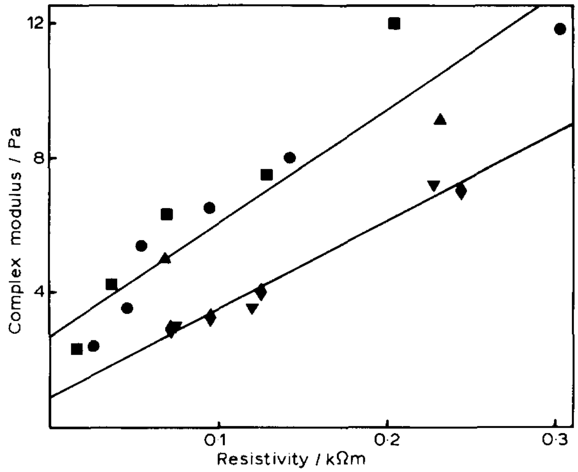

Fig. 7. The complex modulus of potato starch gels with added electrolytes (● NaCl, ■NH_4Cl, ▲ KCl; ◆ $CaCl_2$; ▼ $CdCl_2$) as a function of the resistivity.

starch in the same way regardless of their complexing or chemical binding constants at the possible binding sites (Fig. 7). However it is obvious that the ions present do interfere with the gel formation of potato starch. Nutting (1952) attributes the pH sensitivity of the viscosity to the cations forming a counter-ion layer at the phosphate groups on the surface of the starch granules. These counter-ions would neutralize the electric charge of the starch molecule, thus blocking the formation of crosslinkages between the phosphate groups. Such an interaction between the phosphate groups is affirmed by the results of this study, especially by the gradual loss of structure observed as a slight increase of the loss angle that occurs when the electrolyte concentration is raised (Figs 3 and 6). This interpretation would also support the theory that the phosphate groups of potato starch play an active part in gel formation, which would not be the case with the phosphate present in other starches, such as cassava.

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