



Sulphite and oxidative-reductive depolymerization reactions

Lorna A. Paterson, Sandra E. Hill,* John R. Mitchell & John M. V. Blanshard

Department of Applied Biochemistry and Food Science, The University of Nottingham, Sutton Bonington Campus, Loughborough, UK

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Addition of sulphite at levels between 0.004 and 1% helps to protect the water soluble neutral polysaccharide guar gum from thermal degradation. The greater the amount of sulphite incorporated the more viscous the guar is post-retorting. Starch granules, from a wide range of sources, swell when heated in excess water. The amount of polysaccharide released from the swollen granule after pasting for 60 min at 95°C is increased by the inclusion of low levels (~0.01%) of sulphite. For cassava starch, a pronounced minimum in swelling volume is observed at this sulphite level. This minimum has been related to the pro-oxidant activity of the sulphite in contrast to the antioxidant activity shown for the guar. Intrinsic viscosity data indicates that the action of the sulphite is to degrade the polysaccharides within the starch granule and this can be reduced by scavenging oxygen from the system or by the addition of propyl gallate. It therefore appears that low levels of sulphite protect guar gum from degradation but can cause degradation of the starch polysaccharides. © 1997 Published by Elsevier Science Ltd

INTRODUCTION

Polysaccharides are often added to foods to enhance their eating quality by thickening or gelling the food. During processing, foods are often subjected to high temperatures which may cause degradation of these molecules and therefore a reduction in these functional properties.

At high temperatures and neutral pH degradation is believed to occur through oxidative-reductive depolymerization (ORD) reactions (Wellington, 1983). The presence of transition metals and oxygen is considered critical for the initiation of the reaction. It has been shown that sulphite in combination with the water soluble free radical terminator propyl gallate, will reduce loss of viscosity on heating some neutral biopolymer gums (Mitchell *et al.*, 1991). Guar and locust bean gum, both galactomannans with a backbone of $\alpha(1\rightarrow4)$ linked mannose units with side stubs consisting of single $\alpha(1\rightarrow6)$ linked galactose residues, have been shown to be protected from heat degradation by the presence of this synergistic mixture.

Starch, which is available from a variety of sources, is still the most commonly used thickening agent in food materials. The starch granule contains glucose units linked to form two types of macromolecule; amylose, which is essentially a linear molecule and amylopectin which has a highly ramified structure where the main

chain is composed of $\alpha(1\rightarrow4)$ linked glucose units (as in amylose) plus $\alpha(1\rightarrow6)$ linked side chains. The ratio of these two polysaccharides varies between starch sources, as does the size of the granules they form. On heating in excess water the starch granule undergoes gelatinization. During this complex process the granule imbibes water and swells irreversibly. This increase in volume causes an increase in the viscosity of the system. Amylose is initially lost from the swollen granule and under severe conditions of heat and shear, the granule will lose its integrity. It might be expected that this process of granule disruption would be influenced by changes in the molecular weight of the polysaccharide. For example, a reduction in amylose molecular weight will enhance its ability to reptate (wiggle) out of the granule matrix. It was therefore considered that control of free radical attack by antioxidants might control the viscosity of gelatinized starch systems subjected to severe heat treatment as had been shown to occur for materials such as guar and locust bean gum.

The comparative changes in the viscosity of two polysaccharide systems in the presence of sulphite were therefore investigated. Guar was used as an example of a linear neutral polysaccharide that is readily cold water soluble and known to degrade on heating. Cold water insoluble starches, from a variety of sources, were used to investigate the swelling behaviour of the starch granule during the gelatinization and pasting period. The changes in the fully solubilized starch polysaccharides were also monitored.

*To whom correspondence should be addressed.

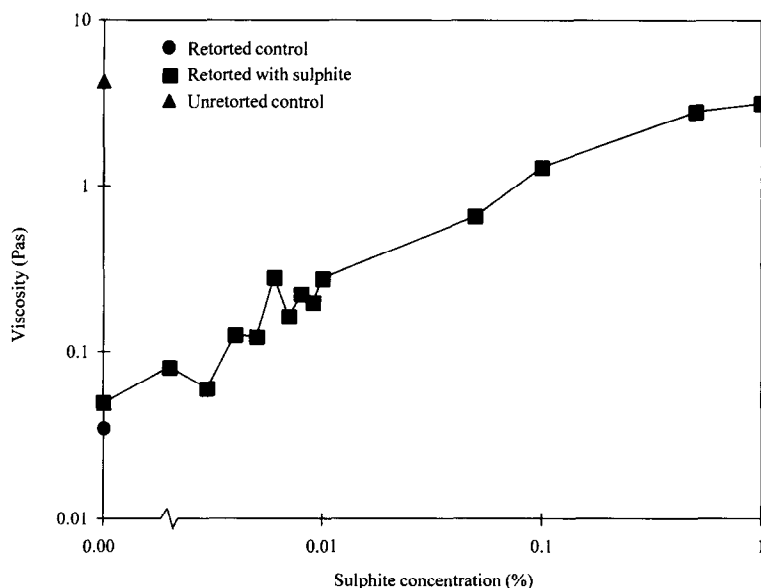


Fig. 1. The effect of sulphite on the viscosity of 0.8% solutions of guar retorted at 121°C for 60 min. Viscosity was measured at 25°C and a shear rate of 1 s⁻¹.

MATERIALS AND METHODS

Maize, potato, wheat and rice starches were purchased from The Sigma Chemical Co. as were the sodium sulphite, propyl gallate and guar. The sago and cassava starches were obtained from Sarawak State, Malaysia and Trivandrum, India, respectively.

Guar suspensions (0.8% w/v) were prepared in pH 7 buffer using a high shear mixer and heated to 60°C to ensure complete solubilization. The samples were then placed in small cans (250 ml) and retorted at 121°C for 60 min. After storage at ambient temperature for 18 h, the viscosity was measured at 25°C over a shear rate range of 1–100 s⁻¹, using a Bohlin CS rheometer with a concentric cylinder geometry (C25).

Starch suspensions (1% w/v) were prepared in distilled water and agitated to ensure complete dispersion, then the samples were gelatinized by shaking in a water bath at 95°C until the starch paste clarity increased (2–3 min). The suspensions were then placed, unstirred, in the water bath for 60 min. Swelling volume was calculated by centrifugation of the pasted samples at 1000 g for 20 min and expressed as ml of sediment/100 ml of pasted (1% w/v) starch suspension. The percentage solubility was determined by drying an aliquot of the supernatant (3 ml) at 105°C overnight.

$$\% \text{ solubility} = \left(\frac{\text{solids in supernatant}}{\text{total solids in system}} \right) \times 100.$$

Intrinsic viscosity determinations were performed by solubilizing and serially diluting the pasted starch samples to concentrations of 1–5 mg/ml in 0.5 M KOH. Flow times were calculated using a U-tube viscometer attached to a Schott Geräte automated measuring system.

Sulphite levels quoted are those assumed through gravimetric determination. However, the actual sulphite

levels present calculated using 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) (Humphrey *et al.*, 1970), were found to be 71% of those cited.

RESULTS AND DISCUSSION

Retorting a 0.8% guar solution in the absence of sulphite resulted in a reduction in viscosity measured at a shear rate of 1 s⁻¹ from 4.26 to 0.035 Pa. Figure 1 shows that the inclusion of sulphite even in the absence of propyl gallate helps to maintain the pre-retorting viscosity. Increases in viscosity above the retorted control samples are observed at low sulphite inclusion levels (~0.004%) and the viscosity increases up to the maximum level (1%) of sulphite incorporation. The protective effect of sulphite on guar degradation has been reported by Rodriguez (1985). The sulphite is considered to act as an oxygen scavenger and thus reduces oxidative–reductive depolymerization (ORD) of the polysaccharide (Wellington, 1983). Protection against free radical attack can be further improved by adding a free radical terminator such as propyl gallate to stop the reaction once it has started.

The action of sulphite in the starch system appears surprisingly different. If high swelling volume equates to high viscosity as would be expected at low volume fractions (Steeneken, 1989), a comparison of Figs 1 and 2 demonstrates the differences between guar and cassava starch. A pronounced minimum occurs in the swelling volume at sulphite levels of 0.01%, this is accompanied by an increase in carbohydrate release from the granule into the supernatant. The difference in the heat treatment for the two systems must be considered. The starch was heated at 95°C compared to 121°C for the guar, the duration for both being 60 min. However, it has been shown that solubility of the polysaccharide for a range of starches increased and the swollen volume

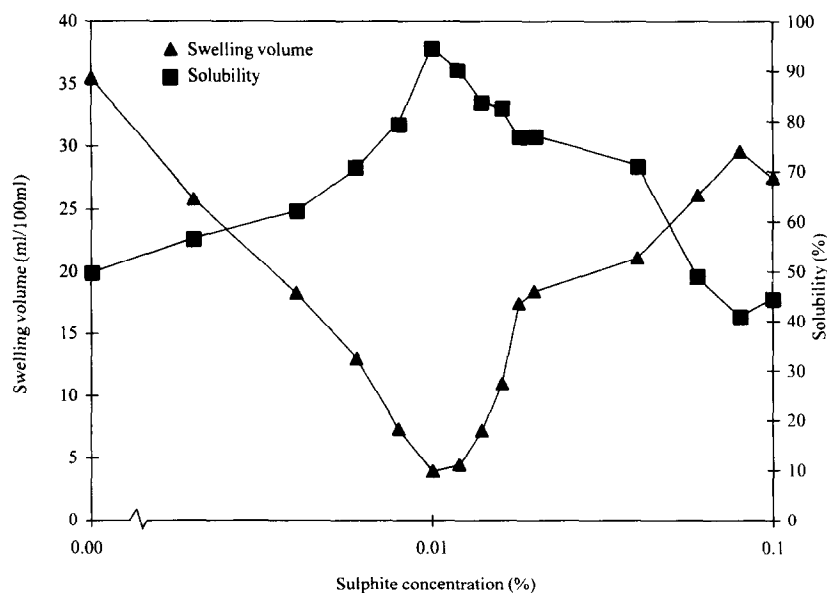


Fig. 2. The effect of sulphite on the swelling volume and solubility of cassava starch pasted at 95°C for 60 min.

decreased on the inclusion of 0.01% sulphite when the starches were treated in excess water at 121°C for 60 min (Paterson *et al.*, 1994).

In Fig. 3 the increase in solubility that occurs on the inclusion of 0.01% sulphite is shown for a range of common commercial starches, it can be concluded that the sulphite's action is common to all the starches tested.

It appears that the sulphite mechanisms for starch at low sulphite levels, acts by promoting oxidative-reductive depolymerization. Oxygen and low levels of sulphite seem to be required for maximum degradation, as higher levels of sulphite allow recovery by scavenging the oxygen present. Supporting evidence for this behaviour is shown when oxygen is bubbled through the mixture, the swelling volume declines to the minimum for 0.01% sulphite and remains at this low level even as the sulphite level is increased (Paterson *et al.*, 1994).

The obvious difference between the starch and guar is that starch occurs in non-cold soluble highly packed

granules. The sulphite action could therefore be concerned with alterations on the granule 'package' rather than on the constituent polysaccharides. To determine whether the action of sulphite alters the starch macromolecules the remains of the granule structure were fully solubilized in 0.5 M KOH post-pasting. The intrinsic viscosities of the resultant soluble polysaccharides were then assessed, as this should relate directly to the molecular weight of the polymers. Figure 4 shows that inclusion of 0.01% sulphite does reduce intrinsic viscosity. There is some recovery in viscosity, and therefore the molecular weight, on the addition of higher (0.1%) amounts of sulphite. The use of propyl gallate with levels of sulphite which have shown maximum ORD nullifies the effect. It has previously been shown that gallate addition reduces the sulphite induced reduction in swollen volume (Mat Hashim *et al.*, 1992; Paterson *et al.*, 1994). These results indicate that the sulphite can act as a pro-oxidant on the starch

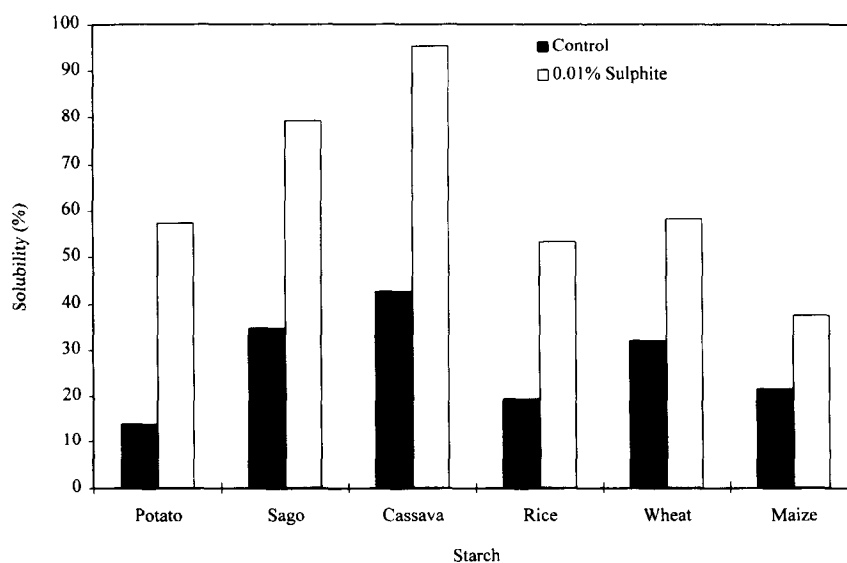


Fig. 3. The effect of 0.01% sulphite on the solubility of a variety of starches pasted at 95°C for 60 min.

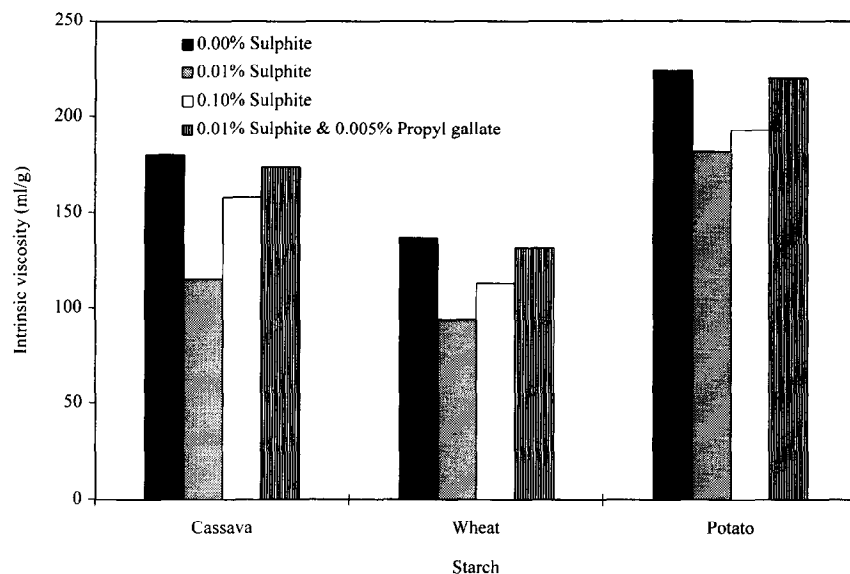


Fig. 4. The effect of sulphite and propyl gallate on the intrinsic viscosity of a variety of starches pasted at 95°C for 60 min.

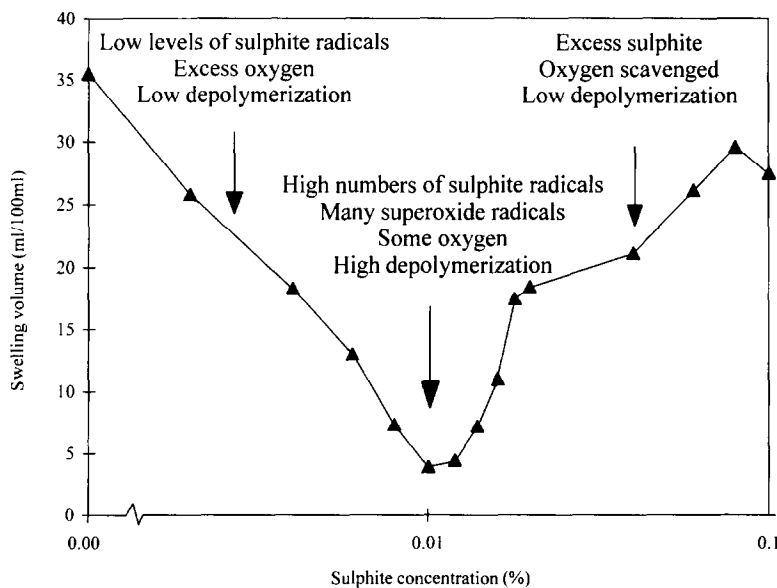


Fig. 5. A hypothesis to explain the action of sulphite on cassava starch.

polysaccharides and it seems that it is the macromolecules within the starch granule which are being attacked and their molecular weight reduced.

CONCLUSION

It would appear that certain levels of sulphite in the presence of oxygen can have pro-oxidant activity which cause a decrease in the molecular weights of the starch polysaccharides. These changes manifest themselves by a decrease in the swelling volume of pasted starch granules and an increase in the amount of carbohydrate released from the granule. A possible explanation of this action is shown diagrammatically in Fig. 5. This pro-oxidant activity was not observed for the water soluble linear polysaccharide, guar.

The pro-oxidant activity of sulphite is stopped by the inclusion of greater amounts of sulphite, presumably as this will reduce the levels of oxygen to below the levels necessary to enter in free radical formation with the sulphite or to form super oxide radicals. The effect is also nullified by the inclusion of propyl gallate, which is known to form stable free radicals and thus terminate the reaction. The combined antioxidant behaviour of sulphite and gallate appears to be the same for the starch and the guar.

REFERENCES

- Humphrey, R. E., Ward, M. N. & Hinze, W. (1970). Spectrophotometric determination of sulphite with 4,4-dithiopyridine and 5,5-dithiobis. *Anal. Chem.*, **42**, 698-702.

- Mat Hashim, D. B., Moorthy, S. N., Mitchell, J. R., Hill, S. E., Linfoot, K. J. & Blanshard, J. M. V. (1992). The effect of low levels of antioxidants on the swelling and solubility of cassava starch. *Starch/Stärke*, **44**(12), 471–475.
- Mitchell, J. R., Reed, J., Hill, S. E. & Rogers, E. (1991). Systems to prevent loss of functionality on heat treatment of galactomannans. *Food Hydrocol.*, **5**, 141–144.
- Paterson, L. A., Mat Hashim, D. B., Hill, S. E., Mitchell, J. R. & Blanshard, J. M. V. (1994). The effect of low levels of sulphite on the swelling volume and solubility of starches. *Starch/Stärke*, **46**(8), 288–291.
- Rodriguez, P. A. B. (1985). Stabilizing polysaccharide-thickened aqueous medium and stable aqueous gel. US Patent No. 4 514 318.
- Steeneken, P. A. M. (1989). Rheological properties of aqueous suspensions of swollen starch granules. *Carb. Polym.*, **11**, 23–42.
- Wellington, S. L. (1983). Biopolymer solution viscosity stabilization—polymer degradation and antioxidant use. *Soc. Pet Eng. J.*, **9296**, 901–912.