The use of anti-oxidants to control viscosity and gel strength loss on heating of galactomannan systems

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SUMMARY

Viscosity loss on autoclaving guar gum solutions can be substantially reduced by the addition of mixtures of the antioxidants, sodium sulphite and propyl gallate. There appears to be a strong synergistic interaction between the two materials with the maximum affect occurring at ratios of sulphite to gallate of about 3:1. Total antioxidant levels required for substantial protection at pH 7.0 are of the order~100ppm. The antioxidant combination is also effective in reducing the loss in gel strength which results from autoclaving mixtures of carrageenan and locust bean gum. The similar optimum ratio of sulphite to gallate to that found with the guar system and the small influence of the antioxidants on carrageenan alone suggests that in this mixed system the antioxidants function primarily by protecting the locust bean gum. The results favour a specific interaction rather then "phase separated" model for the mixed gel system. It is possible some of the reported interactions between polysaccharides and other food ingredients can be understood in terms of the antioxidant properties of the ingredients rather than biopolymer association or phase separation.

INTRODUCTION

Polysaccharides are extensively used as thickeners and gelling agents in heat sterilised foods. It is well established that heat treatment can result in substantial decreases in viscosity and gel strengths the decrease being strongly dependent on pH (Pilnik and MacDonald,(1)).In general viscosity and gel strength loss on heating is far lower at neutral pHs then acid pHs which is indicative of the importance of acid hydrolysis. The exception is pectin where β-elimination dominates. However even at neutral pHs polysaccharides will degrade as a result of oxidative reductive depolymerisation (ORD) reactions. This form of degradation can be controlled by the addition of antioxidant systems. The work that has been carried out has mainly been concerned with the stabilisation of polymers used in oil field applications, e.g. Wellington (2), and little attempt has been

made to extend this approach to food systems using non-toxic antioxidants. Recently, (3) , we have reported some preliminary work which demonstrated that galactomannans, in particular, can be effectively stabilised by low levels of combinations of sodium sulphite and propyl gallate. These materials are allowed as additives in some food products. In this paper we demonstrate that there is a very strong synergism between the two antioxidants and extend the work to the mixed carrageenan/locust bean gum gel systems to determine if the substantial gel strength loss that occurs on autoclaving (Ainsworth and Blanshard (4)) can be prevented.

MATERIALS AND METHODS

Polysaccharides

Guar gum, locust bean gum and carrageenan (described predominantly as kappa) were obtained from the Sigma Chemical Company and used without any further purification.

Other Chemicals

Propyl gallate was obtained from the Sigma Chemical Company. Potassium dihydrogen orthophosphate (SLR grade), disodium hydrogen orthophosphate (SLR grade) potassium chloride (AR grade) and sodium sulphite (AR grade) were obtained from Fisons plc.

Preparation of Solutions and Gels

Unless otherwise stated solutions and gels were prepared in a mixed phosphate buffer of pH 7.0 (9.09 g/l KH_2PO_4, 11.88 g/l Na_2HPO_4). In some cases KCl was added and/or the pH altered by changing the ratio of the two phosphate salts. The anti-oxidants were incorporated into the buffer prior to the addition of the polysaccharide. Guar gum was added at ambient temperature using a high shear mixer to give a concentration (w/v) of 0.8%. Carrageenan and locust bean gum were added to the buffer at a temperature of 80°C to give a total polysaccharide concentration of 0.8%. Cans (diameter 72 mm and height 58 mm) were filled with the guar or carrageenan-locust bean gum mixture and seamed leaving no headspace. Following retorting (120 C for 60 minutes) the cans were water cooled and allowed to stand at ambient temperature for approximately 24 hours prior to viscosity and gel strength measurement. Some measurements were also made on non-retorted controls.

Viscosity

Viscosities were determined at 20°C using a Deer rheometer equipped with cone and plate geometry (cone angle 4°) or concentric cylinder geometry (radius of inner cylinder = 2.8 cm, radius of outer cylinder = 2.9 cm). Measurements were generally

made at five different applied stresses.

Gel Strength

Gel strength measurements were made directly in the can at ambient temperature using a TAXT2 Texture Analyser (Stable Microsytems Ltd, Haslemere, Surrey, England). The lid of the can was removed and a 1.20 cm diameter plunger was used to penetrate the gel at a speed of 2 cm/sec to a distance of 25 mm. The maximum force recorded was taken as the gel strength in Newtons. Following texture measurement, the pH of the gel was recorded.

RESULTS AND DISCUSSION

Figure 1 displays the viscosity of the 0.8% guar solutions following retorting as a function of antioxidant ratio at a total antioxidant level of 200 ppm (0.02%). The data shows very strong synergism between the two additives. It has been reported that the addition of sulphite enhances the thermal stability of guar gum (Rodriguez (5)) but it is clear that the binary system suggested from Wellington's (2) work with xanthan gum is very much more effective. The optimum ratio of the two additives is about 3:1 sulphite to gallate, gallate on its own having little effect.

There is some scatter in Figure 2 but this suggests that the stabilising effect of the additives levels off at concentrations of about 200 ppm. This is consistent with our preliminary work on this system (3) although in the current investigation the maximum viscosity obtained after retorting was about half that of the unretorted control, whereas previously complete stability was claimed. The reason for the difference is that in this case the concentration was well above c* and hence the viscosity will be far more strongly molecular weight dependent then in the previous case where measurements were being made on 0.2% solutions.

It is interesting to compare the effect of the antioxidants on the thermal stability of guar with their ability to prevent the breakstrength loss which occurs on autoclaving mixed carrageenan locust bean gum gels. Figure 3 shows a somewhat similar dependence on additive ratio to that observed for the viscosity of guar gum solutions. There is some suggestion that the sulphite: gallate ratio required for optimum gel strength is higher then that required for control of guar viscosity. Thus replacing 15ppm (0.0015%) of sulphite by gallate in the formulation doubles the gel strength. It is clear that the gel strength can be enhanced by a factor of about 4 compared with the system containing no additives although the strength of the non-retorted system is not achieved.

The effect of total additive concentration at ratios of 17:3 gallate to sulphite is displayed in Figure 4. This set of data implies that retorted gel strength does not reach a maximum

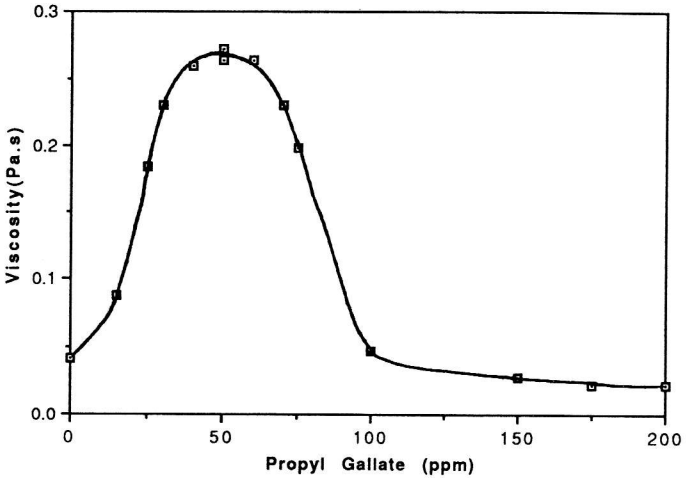

Figure 1. Effect of Antioxidant Ratio on the Viscosity (measured at 20°C and $50s^{-1}$) of a 0.8% Guar Gum Solution at pH 7.0. The Total Antioxidant Concentration (Gallate plus Sulphite) was 200 ppm and Numbers on the Abscissa are the Propyl Gallate Concentration. The Viscosity of an Unretorted Control Containing no Additives was 0.55 Pa.s.

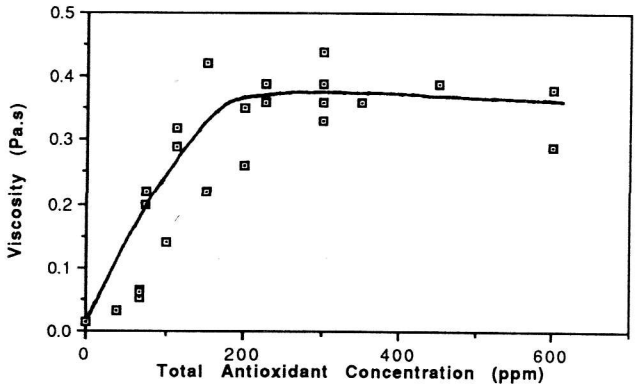

Figure 2. Effect of Total Antioxidant Concentration at a Sulphite:Gallate Ratio of 15:5 on Viscosity of Retorted Guar Solutions. Other Details as in the Legend to Figure 1.

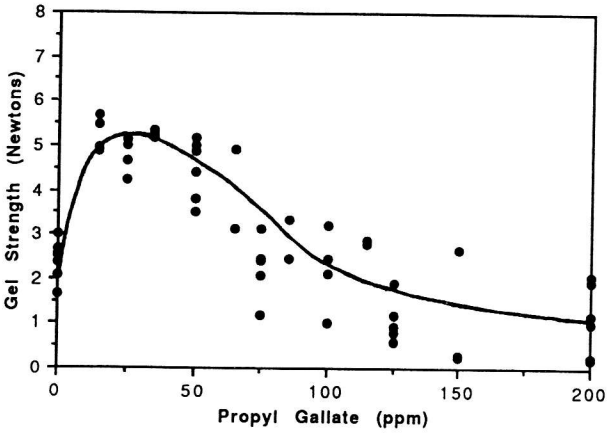

Figure 3. Effect of Antioxidant Ratio on the Strength of Retorted Gels at pH 7.0 Containing 0.4% Locust Bean Gum and 0.4% Carrageenan. The Total Antioxidant Concentration (Gallate plus Sulphite) was 200 ppm and Numbers on the Abscissa Represent the Concentration of Gallate . The Strength of a Retorted Control Containing no Antioxidants was 1.11 N (Five Measurements, Lowest-0.57N, Highest-1.73N) and a Non-Retorted Control with no Antioxidants was 7.0N (6.5N, 7.5N).

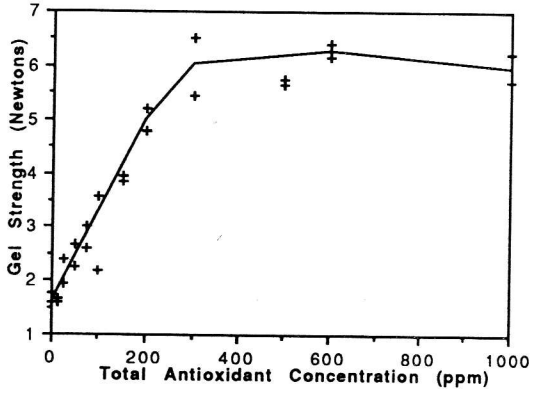

Figure 4. Effect of Total Antioxidant Concentration at a Sulphite:Gallate Ratio of 17:3 on Strength of Retorted Gels. Other Details as in Legend to Figure 3.

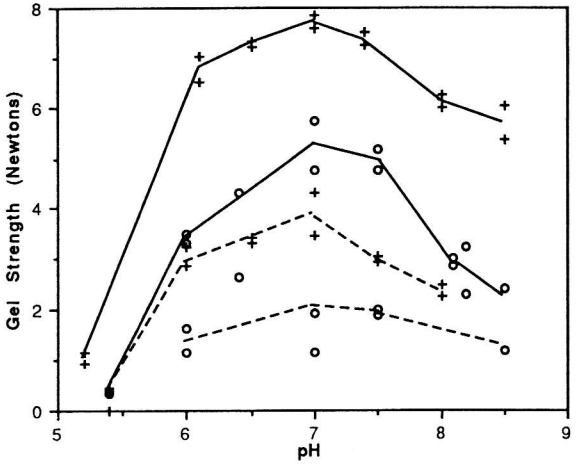

Figure 5. Effect of pH and KCl Addition on the Strength of Retorted Gels. ——— With Antioxidants (200 ppm of Sulphite and Gallate. Ratio 17:3). - - - - Without Antioxidants. ,+, With 0.1M KCl. ,o, No KCl. Other Details as in the Legend to Figure 3.

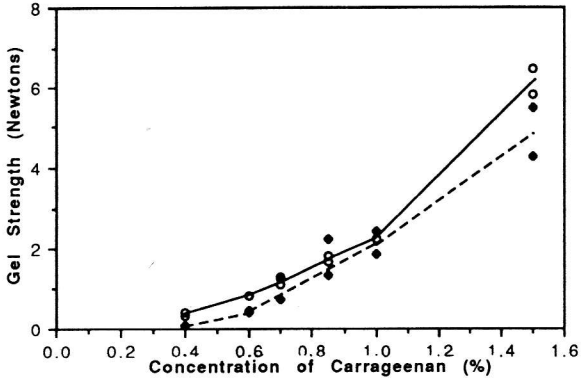

Figure 6. Retorted Gel Strength as a Function of Carrageenan Concentration Alone (pH 7.0, no added KCl). - -◆- - - No Antioxidants. ———o——— With 200 ppm of Sulphite plus Gallate (Ratio 17:3).

until the additive level exceeds 300 ppm although substantial improvement is obtained at far lower levels.

It is well recognised that the strength of these systems is strongly influenced by pH and by K^+ level. Figure 5 shows that gel strength is enhanced by the presence of KCl, however in the presence of KCl the antioxidant systems still have a substantial beneficial affect which in % or ratio terms is comparable to that obtained when there is no added K^+ . Maximum gel strength is obtained near neutral pH and below pH 5 a solid gel is not obtained after retorting whether or not the antioxidants are present. This is presumably because at the lower pHs hydrolysis becomes far important as a degradation mechanism compared with ORD reactions.

Retorted gels containing carrageenan alone are not stabilised to anything like the same extent (Figure 6) compared with the mixed polysaccharide system and this suggests that what is important is the role of the antioxidants in protecting the galactomannans against degradation. This is of course consistent with our original work showing that compared with some other other food polysaccharides these materials are particularly receptive to protection by antioxidants.

A number of models have been suggested to explain the synergistic interaction between carrageenan and locust bean gum. The early suggestions that there was a specific association between unsubstituted regions of the mannan chain and carrageenan junction zones (Dea et al, (6)) have been challenged mainly on the basis that X-ray diffractograms on mixtures can be explained by the addition of carrageenan and mannan patterns and do not reveal a new ordered form (Cairns et al, (7)). A picture where locust bean gum associates with the carrageenan junction zones at only a small number of points on the galactomannan chain with the long flexible galactomannan chains making a small entropic contribution to the modulus but a major contribution to the rupture strength by holding the network together while carrageenan junctions reform on deformation would seem easier to reconcile with the strong dependence of brittleness on locust bean gum molecular weight implied by this work than would be the case for a phase separated picture.

Finally we would wish to make the point that we have shown that in simple aqueous systems very small amounts of antioxidants can drastically effect the "functionality" of polysaccharides. There will be antioxidant activity associated with many natural food ingredients. Some of the interations/synergisms reported between food ingredients e.g. galactomannans and milk, may be explained by the antioxidant capability of the ingredients included with the polysaccharide rather then a "non-chemical" macromolecular interaction.

ACKNOWLEDGEMENTS

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