

thaw treatments. Size exclusion chromatography analysis of the two phases showed that one of the phases contains only dextran, whereas the other one contains both polysaccharides, LBG being highly concentrated. Using FITC-labelled dextran, the phase containing LBG and dextran was examined by fluorescence microscopy: LBG and dextran appeared to be separated inside this phase.

Rheological experiments were performed on the phase containing LBG: mechanical spectra differed dramatically from those expected for macromolecular solutions, suggesting that a weak gel structure was formed. The evolution of the rheological behaviour of a 2% LBG solution, stored at room temperature for several weeks, as a function of time was monitored. Here again, the macromolecular solution evolved steadily into a weak gel structure. These overall results suggest that LBG can self-associate if the concentration of polymer is high enough. This condition was fulfilled in the dextran/LBG mixtures investigated, and these results can provide new insights into the gelation mechanisms of galactomannan-based mixtures.

Reference

Dea, I.C.M., Morris, E.R., Rees, D.A., Welsh, J., Barnes, H.A. & Price, J. (1977). *Carbohydr. Res.*, **57**, 249–272.

THE EFFECT OF GALACTOMANNAN ADDITION ON THE THERMAL BEHAVIOUR OF XANTHAN GUM SYSTEMS

PAULO B. FERNANDES^{a,b} and JEAN-LOUIS DOUBLIER^c

^a*Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, 4200 Porto, Portugal*

^b*Present address: Nestec Ltd Nestlé Research Centre, PO Box 44, CH-1000 Lausanne 26, Switzerland*

^c*INRA-LPCM, BP 527, 44026 Nantes Cx 03, France*

Xanthan gum (XC) is an anionic polysaccharide produced by the micro-organism *Xanthomonas campestris*. The high viscosity of this biopolymer at low solution concentrations is due to both high molecular weight and high structural chain rigidity. Galactomannan polysaccharides occur as reserve materials in a wide range of legume seeds. Locust bean gum (LBG) galactomannan and XG are known to form thermoreversible and synergistic gels when mixed. The interactions observed between LBG and XG have been extensively studied. Recently, Lopes *et al.* (1992) described the role of conformation and acetylation of xanthan on XG/guar gum (GG) galactomannan interactions for total polymer concentrations of 1 and 0.5 g/l. Specific and co-operative interactions between XG and GG were demonstrated. The stability of such interactions increased when the degree of XG acetylation decreased and the conformation of the XG was disordered. Doublier (1994) demonstrated that gelation can occur in XG/GG mixtures (total polymer concentration of 5 g/l) with the xanthan in the ordered state. Dynamic viscoelastic measurements have been carried out with blends of XG and GG in order to characterise their gelation properties.

Oscillatory shear experiments were performed using a Carri-Med CSL-100 controlled stress rheometer fitted with a parallel

plate device (gap 2 mm; plate diameter 6 cm). The gelation phenomena of the XG/GG mixtures were studied by cooling–heating cycles ($70^{\circ}\text{C} > 5^{\circ}\text{C} > 70^{\circ}\text{C}$; frequency 1 Hz; rate $1^{\circ}\text{C}/\text{min}$). The mixing ratios (XG:GG) used were 1:1 at 10 g/l and 1:2 at 15 g/l, in water and 0.1 M NaCl. The characteristics of the XG sample were: intrinsic viscosity 33 dl/g; acetate content 3.7% and pyruvate content 8.6%. The thermorheological behaviour of the XG/GG mixed system was compared to those of XG/LBG mixtures and XG alone.

The XG/GG mixed system (in water) presented systematically a significant increase of the G' and G'' moduli at a temperature of about 22°C . During the temperature sweep experiments the cooling and heating curves of the XG/galactomannan mixed systems were almost superimposable. In general, the synergistic interactions observed between XG and GG increased dramatically when the conformation of the XG molecules was disordered. Of particular interest is the description of viscoelastic properties of XG/GG mixed systems upon varying temperature in order to improve our knowledge of the mechanism of gelation and gel structure of XG/galactomannan systems.

References

- Doublier, J.L. (1994). In *Gums and Stabilisers for the Food Industry 7*, G.O. Phillips, P.A. Williams & D.J. Wedlock, eds. IRL Press, Oxford, pp. 257–270.
- Lopes, L., Andrade, C.T., Milas, M. & Rinaudo, M. (1992). *Carbohydr. Polym.* **17**, 121–126.

THE EFFECT OF TETRAALKYLAMMONIUM BROMIDE SALTS ON THE INTERACTION OF XANTHAN WITH KONJAC MANNAN

P. ANNABLE and P.A. WILLIAMS

Centre for Water Soluble Polymers, The North East Wales Institute, Connah's Quay, Deeside, Chwyd, CH5 4BR, UK

The effect of tetraalkylammonium bromide salts, R_4NBr where $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$ and $t\text{-C}_4\text{H}_9$, on both the conformational behaviour of xanthan and its interaction with konjac mannan (KM) were studied using differential scanning calorimetry (DSC) and small deformation oscillatory measurements.

It was found that as the size of the cation, R_4N^+ increased, the conformational disorder $\rightarrow$ order transition of xanthan was shifted to lower temperatures. In admixture with KM, gels were formed in all cases in the presence of electrolyte (0.04 mol dm^{-3}), however the gel strength, as monitored by the value of G' at 25°C , was found to increase with increasing cation size.

Xanthan/KM gels were also studied as a function of increasing tetrapropyl-ammonium bromide (Pr_4NBr) concentration. It was found that the gel strength (G') decreased as the Pr_4NBr concentration increased ($0.005\text{--}0.02 \text{ mol dm}^{-3}$) however, the onset of gelation remained constant ($\sim 60^{\circ}\text{C}$).

DSC cooling traces of xanthan/KM in Pr_4NBr showed three peaks which were attributed to: (a) xanthan conformational change in Pr_4NBr ; (b) xanthan/KM gelation in Pr_4NBr ; and (c) a peak closely related to xanthan/KM gelation – xanthan conformational change in the absence of electrolyte. The relative areas of these peaks were dependent upon the Pr_4NBr concentration.