## DIRECT OBSERVATION OF KAPPA-CARRAGEENAN AND GALACTOMANNAN MIXTURES BY CRYO-TEM

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It is well known that kappa-carrageenan and galactomannans show strong synergistic effects when mixed in aqueous solution. This gives an enhancement in viscosity or even gelation, below the concentration at which this takes place in either of the pure polymer systems. It has been suggested that the synergistic effect is due to an association of galactomannan chains to carrageenan aggregates (Williams *et al.*, 1993), which possibly also brings about changes in the extent of carrageenan self-aggregation. In this study cryo-Transmission Electron Microscopy is used to investigate the microstructure of the polysaccharide aggregates in the pure and mixed systems.

### Reference

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## STUDIES ON KAPPA CARRAGEENAN–LOCUST BEAN GUM MIXTURES IN THE PRESENCE OF SODIUM CHLORIDE AND SODIUM IODIDE

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The solution properties of kappa carrageenan–locust bean gum mixtures have been studied by small deformation oscillation measurements and differential scanning calorimetry (dsc) in the presence of sodium chloride and sodium iodide. Addition of sodium iodide resulted in a sharp increase in the dynamic viscosity ($\eta^*$) of kappa carrageenan solutions on cooling corresponding to an exothermic peak in the dsc cooling curve. Since both processes were completely reversible with no hysteresis and since gelation was not observed it was concluded that they occurred as a result of the carrageenan molecules undergoing a conformational change i.e. coil → helix.

On addition of sodium chloride, the storage and loss moduli ($G^{1}$, $G^{11}$) increased dramatically on cooling and gelation was observed. The process was reversible but there was pronounced hysteresis indicating molecular aggregation had occurred.

For carrageenan–locust bean gum mixtures (90:10) in the presence of sodium chloride, gelation was observed as noted from rheological and dsc measurements. The gelation temperature $T_{gel}$, was close to $T_{gel}$ for carrageenan in the absence of locust bean gum but $G^{1}$ and $G^{11}$ were markedly enhanced. For similar mixtures in the presence of sodium iodide the data indicated that a conformational change occurred at the same temperature as for carrageenan alone in sodium iodide but there was no gelation. Similar results have been found previously (Piculell *et al.*).

### Reference

Piculell, L., Zhang, W., Turquois, T., Rochas, C., Taravel, F.R. & Williams, P.A. Effect of added galacto and gluco mannans on the nmr of $^{133}$Cs ions in kappa carrageenan gels (in preparation).

## A LIGHT SCATTERING STUDY OF THE POLYMER BLEND CARRAGEENAN/GALACTOMANNAN

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Samples of sonicated k- or i-carrageenan were mixed with galactomannan (carob gum, guar gum) and studied by multi angle laser light scattering (MALLS). The ion specificity of the carrageenans (Piculell *et al.*, 1990) was used to control their conformations, which made it possible to separately study the coil, the double helix or the aggregates' interaction with galactomannan. The studies were done at a total polymer concentration of (0·05% w/w), and the ratio between the two polymers was varied. The Rayleigh ratio was obtained at different angles and an apparent molecular weight was calculated. For k-carrageenan no growth in apparent molecular weight was observed neither in coil nor in double helix conformation. Aggregates of k-carrageenan showed an interaction with carob gum, but not with guar gum, while i-carrageenan showed no extended growth in apparent molecular weight for any conformation. It is suggested that mixed aggregates are formed (Williams *et al.*, 1993), due to a non-specific adsorption of the flexible galactomannan onto the aggregates of k-carrageenan.

### References

Piculell, L. & Nilsson, S. (1990). *Prog. Coll. & Polym. Sci.*, **82**, 198–210.

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## PHASE SEPARATION IN DEXTRAN/LOCUST BEAN GUM MIXTURES

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It is well known that locust bean gum (LBG) develops strong synergism with other polysaccharides such as xanthan gum and $\kappa$-carrageenan. However, the mechanism of gelation of these mixed systems is not yet well understood. Two types of models have been proposed: one assuming the formation of a coupled network through specific junction zones and an other one based on the existence of a phase-separated network. Mixtures of LBG ($M_w \approx 2 \times 10^6$) with dextran ($M_w \approx 5 \times 10^5$) were studied with the aim to investigate the influence of the addition of a polysaccharide on the behaviour of LBG. Dextran/LBG systems exhibited phase separation at room temperature, confirming the incompatibility between the two biopolymers suggested by Dea *et al.* (1977) after freezethaw 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

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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°C > 5°C > 70°C; frequency 1 Hz; rate 1°C/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

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

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The effect of tetraalkylammonium bromide salts, $R_4NBr$ where $R = CH_3$, $C_2H_5$, n-$C_3H_7$ and t-$C_4H_9$, 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 → 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 (0·005–0·02 mol dm$^{-3}$) however, the onset of gelation remained constant ($\sim$60°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.