

## MICROSCOPY OF XANTHAN/GALACTOMANNAN SYSTEMS

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Xanthan gum/galactomannan (guar gum and locust bean gum) mixtures are widely used in the food industry due to the synergistic properties they develop. Despite the molecular mechanisms underlying these synergistic phenomena still being a matter of debate, it is generally considered that these properties arise from specific interactions between xanthan and galactomannan chains. In the present work, light microscopic techniques were used to gain more insight into the structure of such mixtures. 50/50 xanthan/galactomannan mixtures were prepared in aqueous solution (no salt added) and the total concentration ranged from 2 to 4%.

By the use of polarized light microscopy the formation of cholesteric mesophases in xanthan gum was clearly seen as already reported by several authors. In xanthan/galactomannan mixtures, we observed birefringent areas suggesting a concentration of xanthan inside these zones. Moreover these mesophases in the blend appeared more anisotropic than in xanthan gum alone. The same blends were prepared using a fluorescein-labelled galactomannan and were observed using fluorescence microscopy. This labelled-galactomannan also appeared concentrated in definite areas. Clearly, these results indicate that phase separation has occurred in these systems yielding xanthan-enriched and galactomannan-enriched phases. Moreover, xanthan molecules organize themselves as liquid-crystalline mesophases.

## SUPERMOLECULAR ASPECTS OF XANTHAN-LOCUST BEAN GUM GELS BASED ON RHEOLOGY AND ELECTRON MICROSCOPY

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The viscoelastic properties and supermolecular structure of synergistic gels formed by xanthan and locust bean gum (LBG) of two different mannose:galactose ratios (M:G), have been investigated by small deformation viscoelastic measurements and by low angle rotary shadowing transmission for electron microscopy.

The rheological properties at 20°C for mixtures subjected to heating and cooling cycles in the temperature range 30–80°C were found to be dependent on M:G ratio. Mixtures of xanthan and LBG mixed at temperature  $\leq 40^\circ\text{C}$  were found to form true gels with low phase angles. Blends of xanthan and LBG with low M:G ratio showed no increased synergistic effects as the temperature was increased, whilst the mixture of xanthan and LBG with high M:G ratio showed a strong increase in synergistic effects as the temperature was raised above 60°C. A difference in gelation temperature ( $T_g$ ) of  $\sim 13^\circ\text{C}$  was observed between the mixtures of xanthan and the two LBG fractions. ( $T_g$ ) for xanthan with high M:G ratio was  $\sim 53^\circ\text{C}$ , whilst  $T_g$  for mixtures of xanthan and LBG with low M:G ratio was  $\sim 40^\circ\text{C}$ .

Results obtained using electron microscopy showed that the xanthan-LBG network was formed from xanthan super-

molecular strands, and addition of LBG did not influence the xanthan structure. The observed structural features of the gels were independent of heat treatment and LBG fraction. The structural similarities and the rheological differences observed between xanthan and the LBG fractions are discussed in comparison with existing interaction models at the molecular level. Based on these results a speculative network model at the supermolecular level is presented.

## SCREENING FOR SYNERGISTIC INTERACTIONS IN DILUTE POLYSACCHARIDE SOLUTIONS

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A simple viscometric approach has been used to screen for binding interactions between different polysaccharides in very dilute solution where exclusion effects should be negligible. The method involves preparing stock solutions to approximately the same, low, viscosity ( $\eta_{sp} \approx 1$ ), dialysing to identical ionic conditions, mixing in various proportions, and looking for departures from the initial common viscosity.

Mixtures of xanthan or deacetylated xanthan with locust bean gum (LBG) or konjac mannan (KM) show massive enhancement of viscosity, as anticipated from formation of synergistic gels at higher concentrations. However, no viscosity changes on mixing with LBG or KM were observed for other conformationally ordered bacterial polysaccharides (welan and rhamsan) or for alginate and pectin with sufficient  $\text{Ca}^{2+}$  to induce almost complete conversion to the dimeric 'egg box' form, demonstrating that conformational rigidity is not, in itself, sufficient for other polysaccharides to form heterotypic junctions with mannan or glucomannan chains.

Interactions of carrageenans with LBG appear to depend on both conformation and extent of aggregation. Mixtures of LBG with  $\text{K}^+$  kappa carrageenan in 100 mM KCl (which is known to promote extensive aggregation of double helices) gave erratic values for rotational viscosity and showed typical gel-like mechanical spectra under low amplitude oscillation. Disordered carrageenans ( $\text{K}^+$  kappa in water and lambda in 100 mM KCl) showed no evidence of interaction with LBG. Negative results were also obtained for iota carrageenan under ionic conditions believed to promote ordering without significant aggregation (100 mM KCl). However, under conditions where limited aggregation might be expected (iota carrageenan in 90 mM  $\text{CaCl}_2$ ;  $\text{Me}_4\text{N}^+$  kappa carrageenan in 150 mM  $\text{Me}_4\text{NI}$ ) significant reductions in viscosity were observed on mixing with LBG, which may indicate some intermolecular association but without formation of an extended network structure.

## DETERMINATION OF DIFFUSION COEFFICIENTS OF POLYMERS IN GELS USING THE CONFOCAL LASER SCANNING MICROSCOPE

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The development of a photobleaching technique, CFMM (continuous fluorescence multipoint microphotolysis) to