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Letter to the Editor

Reply to 'Role of conformation in synergistic interactions of xanthan.'

In a recent publication (Zhan *et al.*, 1993), we described rheological studies of xanthan–carob mixed gels prepared at different mixing temperatures. It was found that the mixtures all behaved as true gels when cooled to room temperature. The variation in storage modulus (G') (measured at room temperature) with mixing temperature mirrored the degree of disordering of the xanthan molecule, as monitored by optical rotation studies on xanthan solutions of appropriate concentration. Further, the measured G' values decreased with increasing ionic strength mirroring, once again, the increase in helical content for xanthan solutions. From these studies it was argued that disordering the xanthan helix facilitated formation of intermolecular binding between the two polysaccharides and gelation.

However, Morris (1990) has offered an alternative explanation. It was suggested that the increased cohesion after heating and cooling is due to differences in the process of mixing. For cold mixed systems it was argued that the reduction in G' is due to breakdown of the gel structure as it forms during mixing, resulting in a smashed gel or slurry. In a recent study Morris and Foster (1994) have shown that for xanthan–carob mixtures the onset of gelation occurs at ~60°C and, at mixing temperatures below 60°C, some degree of structural disruption will occur on mixing.

Williams *et al.* (1991) noted that the melting temperature (T_g) of xanthan–carob gels was essentially independent of ionic strength. This has been confirmed by subsequent studies (Zhan *et al.*, 1993; Morris & Foster, 1994). Given this fact, it should be possible to prepare mixtures at a mixing temperature above T_g in which the conformation of xanthan is determined by the level of added salt. This experiment should discriminate between the effect of gel disruption and xanthan conformation. Such experiments were described by Zhan *et al.* (1993). Mixing temperatures of 75°C and 90°C were chosen — both greater than the onset of the gelation temperature $T_g = 60°\mathrm{C}$. At these mixing temperatures, the G' values of the gels, measured after cooling to room temperature, were essentially independent of preparation temperature, but decreased with added salt content. This is consistent with added salt increasing the level of ordering of xanthan, thus decreasing the level of interaction on mixing, and decreasing G' on cooling. On the basis of these studies it was concluded that xanthan disordering facilitated gelation. Zhan *et al.* (1983) suggest an equilibrium of the form

$$\mathrm{X\ (helix)} \underset{\mathrm{salt}}{\overset{T}{\rightleftharpoons}} \mathrm{X\ (coil)} \rightleftharpoons \mathrm{XG}$$

Thus the addition of carob galactomannan G will perturb the xanthan helix–coil equilibrium in favour of the more stable XG aggregate. Thus estimates of xanthan ordering from studies on xanthan solutions alone overestimate the helical content present in the mixture. Although for preparation temperatures below T_g disruption of the gel network during mixing will contribute to a lower modulus, the primary factor affecting gelation is the degree of disordering of the helix. Indeed, in the results of Foster and Morris (1994), as discussed by Morris and Foster (1994), on the polytetramer variant of xanthan it is shown that the polytetramer helix is more stable than xanthan, and that there is no evidence of interaction with either locust bean gum or konjac mannan, which, to us, supports the necessity of disordering for interaction. Thus, we do not believe that it is necessary to propose two types of binding, as suggested by Williams *et al.* (1991) and Mannion *et al.* (1992), in order to explain gelation.

Morris and Foster (1994) do suggest an additional factor which they claim could account for the decrease in G' for xanthan–carob gels prepared at a given mixing temperature, but in the presence of increasing levels of salt. The argument advanced is that, with increasing addition of salt, xanthan–xanthan aggregation as demonstrated by Ross-Murphy *et al.* (1983), hinders helix–carob binding and conversion to the new mixed 'heterotypic' structure. Our major criticism of this suggestion is that, although salt is known to induce aggregation of xanthan in the ordered form, the nature of these aggregates are unknown. Furthermore, the helix–coil transition can be successfully explained solely in terms of screening of the polymer charge and there is, to our knowledge, no experimental evidence showing that any xanthan–xanthan aggregation induces any additional stabilisation of the xanthan helix.

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