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Viscoelastic properties of xanthan/galactomannan mixtures: comparison of guar gum with locust bean gum

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The rheological behaviour of xanthan/guar gum systems has been investigated and compared to that of xanthan/locust bean gum mixtures using oscillatory shear and creep-recovery measurements. The total polysaccharide concentration was kept constant at 0.5% w/w, the xanthan/galactomannan ratio ranged from 1/99 to 90/10 and three ionic strengths were studied. As for xanthan/locust bean gum mixtures, strong synergistic phenomena were exhibited by xanthan/guar gum systems. Clearly, the addition of xanthan gum even at a very low level to a guar gum solution induced a transition of the system from a macromolecular solution to a structured system displaying gel-like properties.

The comparison between three guar gum samples with different molecular weights evidenced a strong effect of the molecular weight: the higher this parameter, the stronger the synergistic interaction. At a low xanthan/galactomannan ratio (< 10/90), xanthan/guar gum mixtures and xanthan/locust bean gum mixtures (with comparable galactomannan molecular weights) resulted in similar viscoelastic behaviour. In contrast, at a higher xanthan/galactomannan ratio, a stronger synergism was exhibited with locust bean gum, as expected. The rheological properties were greatly influenced by the presence of electrolyte. In the case of xanthan/guar gum systems, the storage (G') and the loss (G'') moduli were increased when electrolyte was present, in contrast to xanthan/locust bean gum mixtures which exhibited a reverse tendency.

These results provide evidence that xanthan gum plays a major role in the rheological behaviour of the xanthan/galactomannan systems even at a low concentration. Overall, similar results were found with xanthan/guar or xanthan/locust bean gum mixtures. However, differences in the mechanism may exist according to the mannose/galactose ratio of the galactomannan and also to the xanthan/galactomannan ratio and the ionic strength. © 1997 Elsevier Science Ltd

INTRODUCTION

Galactomannans form a family of seed-reserve polysaccharides, based on a (1-4)-linked β-D-mannan backbone substituted with (1-6)-linked α-D-galactosyl stubs, which are present to various degrees according to the botanical origin of the galactomannan. Locust bean gum from *Ceratonia siliqua* has a mannose to galactose ratio of about 3.5–4.0 while this ratio for guar gum, from *Cyamopsis tetragonolobus*, is about 1.8–2.0. It is known that the galactose substituents are clustered mainly in doublets approximately randomly spaced, the 'hairy regions', interspersed by longer regions of unsubstituted mannan backbone, the 'smooth regions' (Courtois & Le Dizet, 1970; McCleary *et al.*, 1984; McCleary *et al.*, 1985). These two types of galactomannans are employed by the food industry as thickeners but they are generally considered not to form gels on their own although LBG does at high concentrations under specific conditions, i.e. at low temperature or upon ageing (Dea *et al.*, 1977; Morris, 1990; Garnier *et al.*, 1995).

The *Xanthomonas campestris* extracellular polysaccharide (xanthan gum), which has found

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widespread technological application, has a cellulose backbone substituted on every second residue with a charged trisaccharide side chain. This side chain consists of two mannose units separated by a glucuronic acid residue. The mannose residue attached to the cellulosic backbone is variably acetylated and the terminal mannose can contain a pyruvate group (Jansson *et al.*, 1975). Xanthan gum, which in itself is non-gelling, undergoes a temperature-induced conformational transition from an ordered helical structure to a disordered one. This transition temperature is strongly dependent on the salt content.

Synergistic properties of locust bean gum with xanthan gum are well known and widely exploited by the food industry. It is noteworthy that gelation occurs from the admixture of these two non-gelling components. Such properties have not been described in mixtures with guar gum. However, in blends of xanthan gum and guar gum an increase in viscosity has been reported (Dea *et al.*, 1977; Tako & Nakamura, 1985; Cairns *et al.*, 1986; Shatwell *et al.*, 1991; Lopes *et al.*, 1992), which suggests that some molecular interaction may arise in xanthan/guar gum systems. Doublier & Llamas (1991) have shown that the presence of xanthan gum at a very low level induces a transition of the system from a macromolecular solution to a structured system.

Much effort has been made to elucidate the properties of xanthan/galactomannan mixtures. Different models have been proposed, mostly for xanthan/locust bean gum (Dea & Morrison, 1975; Dea *et al.*, 1977; Morris *et al.*, 1977) but also for xanthan/guar gum mixtures (Tako & Nakamura, 1985; Shatwell *et al.*, 1991). They all involve the formation of a network through specific junction zones (Dea *et al.*, 1977; Cairns *et al.*, 1986; Cairns *et al.*, 1987; Morris, 1992). The former model assumed the association of unsubstituted regions of the galactomannan with the backbone of the xanthan helix (Dea *et al.*, 1977; Morris *et al.*, 1977). This model was supported experimentally by a decrease in interaction magnitude when galactose substitution increased (Dea & Morrison, 1975). Another model assumed that regularly substituted mannan chains with galactose units located on one side of the backbone are linked with the xanthan backbone. This model would not rule out the former one but provides a means of understanding the interactions of xanthan with highly substituted galactomannans like guar gum (McCleary, 1979; McCleary *et al.*, 1984). In order to improve the knowledge of these systems, attempts have been made to effect enzymatic modification of guar gum. The purpose was to reduce the galactose content of the gum (McCleary & Neukom, 1982; Chidwick *et al.*, 1991; Luyten *et al.*, 1994). The effect of galactose removal from guar gum on its degree of interaction with xanthan gum has been shown by McCleary & Neukom (1982). Chidwick *et al.* (1991) found that the mannose/galactose ratio of guar gum treated with α-galactosidase from *Aspergillus giganteus* could be increased from $\sim$1.8 up to 4.3. The interaction between xanthan and the modified gum led to an increased yield stress compared to the mixture containing unmodified guar gum. Mannion *et al.* (1992) and Fernandes (1995) also observed the increase of the storage modulus of xanthan/locust bean gum systems while the mannose/galactose ratio of the locust bean gum fractions increased. All these observations show that the xanthan/galactomannan interactions are strongly affected by the fine structure of the galactomannan. They do not provide, however, a clear understanding of the mechanism involved. Lundin & Hermansson (1995) proposed that the network would be formed by xanthan superstrands, interconnected by the galactomannan itself adsorbed or linked onto the surface of these superstrands, the strength of which depends upon the mannose/galactose ratio. Other models have been proposed but were quite speculative (Cheetham & Mashimba, 1988; Tako, 1991). The exact nature of synergistic interactions between these different polysaccharides remains still poorly understood, particularly in the case of xanthan/guar gum systems.

In a recent study of glucomannan/xanthan systems in comparison to locust bean gum/xanthan mixtures, it was suggested that gelation of those systems involves heterotypic binding between both components (Goycoolea *et al.*, 1995). This was also an attempt to reconcile the different models assuming binding between xanthan and mannans. The authors argued that similarities in the rheological and thermal behaviour of glucomannan/xanthan and locust bean gum/xanthan systems indicate a similar mechanism of interactions. Therefore, the question arises as to whether a similar mechanism can account for the obvious synergistic properties of guar gum with xanthan.

The aim of the present work was to investigate the properties of xanthan/guar gum mixtures using rheological techniques. The viscoelastic behaviour of these polysaccharide blends has been primarily investigated using oscillatory shear measurements, in comparison with their individual components. Furthermore, a few creep experiments have been performed to obtain a more complete rheological charaterization. The present paper describes the influence of parameters such as xanthan/galactomannan ratio, galactomannan galactose content, molecular weight and ionic strength.

MATERIALS AND METHODS

Materials

A commercial food grade xanthan sample was kindly supplied by Rhône-Poulenc (France). The pyruvate content was 4.5% (70% pyruvated) and the acetate content was 5.2% (fully acetylated). Its intrinsic viscosity in 0.13 M KCl was 6500 ml/g. The galactomannans used were obtained from Meyhall Chemical (Switzerland). Intrinsic viscosities were 1980, 1910 and 1590 ml/g, respectively, for the three guar gum samples (referred to as samples 1, 2 and 3, respectively) and 1490 ml/g for locust bean gum. Using the Mark–Houwink equation (Robinson *et al.*, 1982) the respective viscosity average molecular weights of guar samples were estimated to be 3.3×10^6, 3.2×10^6 and 2.5×10^6. The mannose/galactose ratio, obtained after methanolysis and separation of their methyl glycosides by high performance liquid chromatography (Quemener & Thibault, 1990), were 3.8 for locust bean gum and 2, 1.6 and 1.6, for guar gum samples 1, 2 and 3, respectively. Some experiments on purified galactomannan samples obtained by precipitation in ethanol according to Lopes da Silva & Gonçalves (1990) have also been performed in order to compare with native galactomannan. No change between native and purified galactomannan, neither in their intrinsic viscosity nor in the viscoelastic properties of the galactomannan alone or of the xanthan/galactomannan mixtures, was found. Therefore the major part of the experiments have been performed with unpurified galactomannan samples.

Preparation of solutions and mixtures

Guar gum and locust bean gum were first dispersed at 25°C in water, then heated to 80°C for 30 min. The xanthan gum solution was prepared by dispersion in distilled water, or in KCl at 25°C, with strong stirring for 15 min. Blends of the galactomannan with xanthan gum at 0.5% total polysaccharide concentration were obtained by mixing appropriate amounts of xanthan and galactomannan solutions at 25°C and then at 80°C under magnetic stirring for 30 min. Alternatively, some xanthan/guar gum mixtures have been prepared directly by dispersing the appropriate amount of xanthan and guar gum powder in aqueous solution. The solution was then heated at 80°C for 30 min with magnetic stirring. Similar viscoelastic properties were found as with the previous procedure. The main cause of any difference in viscoelastic properties was the mixing temperature (Schorsch, 1995). The hot mixture was poured into the rheometer and cooled rapidly down to the measurement temperature (25°C). The xanthan/galactomannan ratios used for the mixtures were between 1/99 and 99/1.

Methods

Oscillatory shear measurements

The experiments were performed using a Rheometrics Fluid Spectrometer (RFS II) with a cone-plate device (2.29° cone angle, 50 mm diameter). Measurements were performed after a 30 min ageing period at 25°C. The amplitude of deformation was chosen at 5% strain, in order to remain within the linearity limits of viscoelasticity. The frequency range was mainly between 0.01 and 100 rad/s and the temperature measurement was fixed at 25°C.

Creep-recovery measurements

These experiments were carried out with the CarriMed Rheometer using a cone-plate device (3.58° cone angle, 60 mm diameter). The temperature was fixed at 25°C and measurements were performed after a 30 min ageing period. Different shear stresses were applied, from 0.5 to 3 Pa according to the xanthan/galactomannan ratio of the mixture, for 1 h. The shear recovery upon cancellation of shear stress was recorded for 4 h.

RESULTS

Viscoelastic behaviour of xanthan/guar gum mixtures

Dynamic measurements

Mixtures of xanthan/guar gum (sample 1) at ratios ranging from 1/99 to 99/1 were prepared. The viscoelastic spectrum of a xanthan/guar gum mixture at a 50/50 ratio and at 0.5% total concentration, in 0.13 M KCl, is shown in Fig. 1. At first sight, this is typical of a gel as usually considered since the frequency dependence of the storage modulus G' over the whole frequency range was slight and $G' > G''$. However, there remained some ambiguity since at 0.01 rad/s, $G'/G'' \approx 8.5$ and a slight frequency dependence was observed ($G' \approx 40$ Pa at 10 rad/s and only 25 Pa at 0.01 rad/s). Figure 2 shows the results obtained at a much lower ratio (xanthan/guar = 5/95)

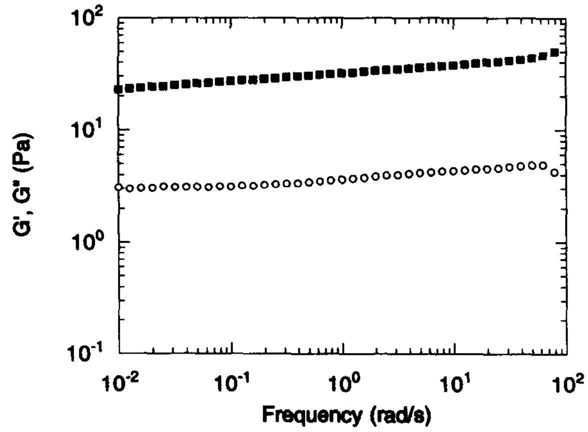

Fig. 1. Viscoelastic spectrum of a 50/50 xanthan/guar gum (sample 1) mixture in 0.13 M KCl (■, G'; ○, G'') (total polysaccharide: 0.5%; temperature: 25°C).

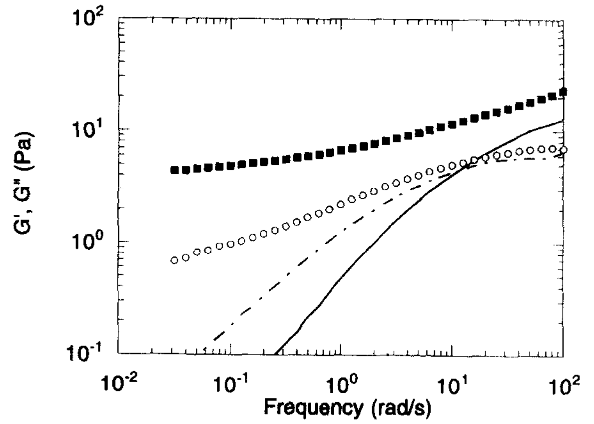

Fig. 2. Viscoelastic spectrum of a 5/95 xanthan/guar gum (sample 1) mixture (■, G'; ○, G'') (total polysaccharide: 0.5%). Comparison with a guar gum solution (continuous line, G'; dashed line, G'') at 0.5% in 0.13 M KCl (temperature: 25°C).

under the same conditions (total concentration: 0.5%, 0.13 M KCl). The behaviour of a guar gum solution at 0.5% is also shown for comparison. While guar gum alone exhibited the classical behaviour of a macromolecular solution with strong G' and G'' dependence upon frequency ($G'' \propto \omega$ and $G' \propto \omega^2$) and a cross-over at high frequency, the 5/95 mixture resulted in a rather different spectrum, with the appearance of a plateau for G' towards the low frequency range. On the other hand, the G'' trace of the 5/95 system tended to mimic the G'' curve of the galactomannan alone at high frequency. Within this frequency range, G' of the guar gum solution was still lower than G' of the mixture, but the traces tended to join each other. Clearly, the viscoelastic behaviour exhibited by such a mixture was solid-like at low frequency but close to that of the guar gum solution at high frequency. Increasing progressively the xanthan content in the mixture yielded similar effects. However, the deviation from the mechanical spectrum of the galactomannan was more and more pronounced, particularly for the G' values at low frequency, which increased continuously. For mixtures at a high xanthan/guar gum ratio ($>60/40$), a quite different tendency was found, as shown in Fig. 3 for a 80/20 ratio. This result is compared to xanthan alone at 0.5% in similar ionic conditions. Overall, a spectrum similar to that obtained in Fig. 1 for the 50/50 ratio is shown. However, the viscoelastic behaviour was not characteristic of a typical gel: the G' and G'' dependency upon frequency was not negligible ($G' \approx 10$ Pa at 0.01 rad/s and ≈ 26 Pa at 10 rad/s) and $G'/G'' \approx 4$ at 0.01 rad/s. This seems to be related to the fact that the role of xanthan predominates.

The rheological behaviour of xanthan/locust bean gum mixtures at 0.5% in 0.13 M KCl and for ratios 5/95, 50/50 and 80/20 is illustrated in Figs 4, 5 and Fig. 6, respectively, for comparison. The solid-like character of these mixtures whatever the ratio was clearly exhibited. Figure 4 illustrates the fact that the presence of xanthan gum at a low ratio (5/95) dramatically changed the properties of locust bean gum, similarly to that observed for xanthan/guar gum systems. Clearly, gel-like properties were exhibited with the appearance of the plateau for G' towards the low frequency range. At 0.01 rad/s, $G' \approx 1.5$ Pa and $G'/G'' \approx 7$. Here again, the presence of a low amount of xanthan induced a transition of the system from a macromolecular solution to a structured system.

The viscoelastic spectrum of the 50/50 xanthan/locust bean gum system (Fig. 5) appeared typical of a gel with $G' > G''$. Moreover, two plateau regions, at low frequency and at high frequency, were evident. These two plateau regions in the G' trace were separated by an inflection point at ≈ 2.5 rad/s. This point coincided

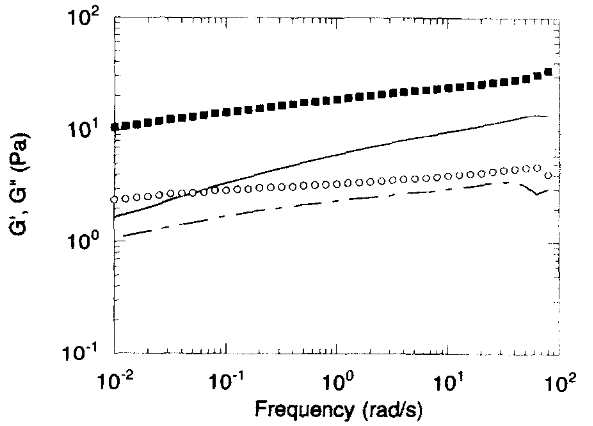

Fig. 3. Viscoelastic spectrum of a 80/20 xanthan/guar gum (sample 1) mixture in 0.13 M KCl (■, G'; ○, G'') (total polysaccharide: 0.5%). Comparison with a xanthan solution (continuous line, G'; dashed line, G'') at 0.5% in 0.13 M KCl (temperature: 25°C).

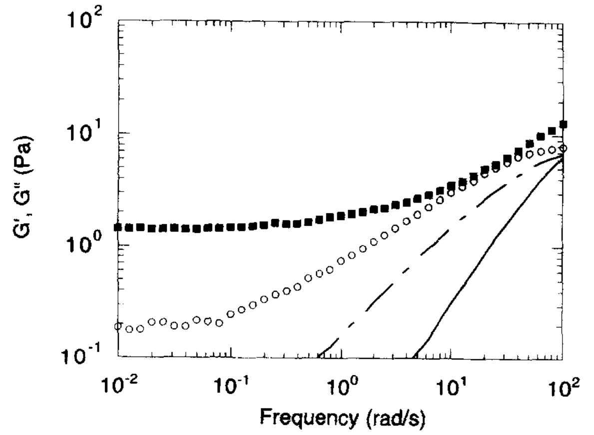

Fig. 4. Viscoelastic spectrum of a 5/95 xanthan/locust bean gum mixture in 0.13 M KCl (■, G'; ○, G'') (total polysaccharide: 0.5%). Comparison with a locust bean gum solution (continuous line, G'; dashed line, G'') at 0.5% in 0.13 M KCl (temperature: 25°C).

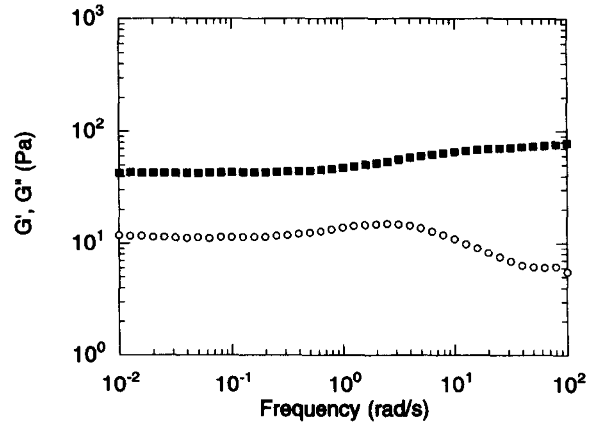

Fig. 5. Viscoelastic spectrum of a 50/50 xanthan/locust bean gum mixture in 0.13 M KCl (■, G'; ○, G'') (total polysaccharide: 0.5%; temperature: 25°C).

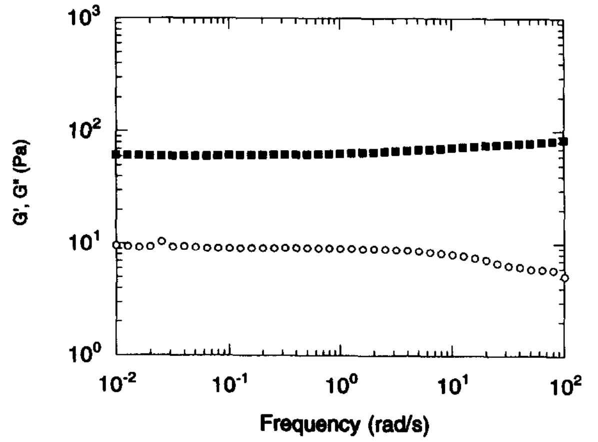

Fig. 6. Viscoelastic spectrum of a 80/20 xanthan/locust bean gum mixture in 0.13 M KCl (■, G'; ○, G'') (total polysaccharide: 0.5%; temperature: 25°C).

with a maximum in the G'' trace. Similar results have been reported by Cuvelier & Launay (1986) for a 70/30 xanthan/locust bean gum mixture. At a 80/20 ratio, as illustrated in Fig. 6, a similar spectrum was obtained. Two plateau regions were still apparent although the difference between them was narrower. The gel properties of the system were clearly seen in contrast to xanthan/guar gum mixtures at the same ratio (Fig. 3).

Transient behaviour: creep-recovery properties

The use of the two types of dynamic and transient measurements is required for a more complete characterization of the viscoelastic properties of gels. Typically, classical dynamic measurements are able to examine a frequency range between 0.01 and 100 rad/s, which corresponds to a time-scale range of about 0.01 to 100 s, while transient methods provide information for time-scales ranging from ~10 s to very long times.

Figure 7 illustrates the creep behaviour of a 5/95 xanthan/guar gum and xanthan/locust bean gum system at 0.5% in 0.13 M KCl. Qualitatively, no strong difference appears between curves of both systems. This suggests that, under these conditions, guar gum and locust bean gum behave in the same way when mixed with xanthan gum. These curves contrasted deeply with those of xanthan gum or of galactomannan alone (Doublier, 1994). A constant value of the compliance J was rapidly reached, showing that no steady shear occurred. As a consequence, the recovery curve almost returned to $J=0$, indicating that the system was completely elastic. Such behaviour is indeed typical of a viscoelastic solid and confirms clearly that, despite the low amount of xanthan, these mixed systems in the presence of guar gum or locust bean gum were gel-like. Moreover, the compliance moduli in the case of guar gum appeared much lower than in the case of locust bean gum. The compliance at $t=60$ min was $J \approx 0.4\,\mathrm{Pa}^{-1}$ for the xanthan/guar gum system, compared to $J \approx 1.4\,\mathrm{Pa}^{-1}$ for xanthan/locust bean gum. This means, as already seen when comparing G' values at low frequency in Figs 2 and 4, that the gels with guar gum were firmer. Such a difference should be ascribed to a difference in molecular weight as will be discussed later.

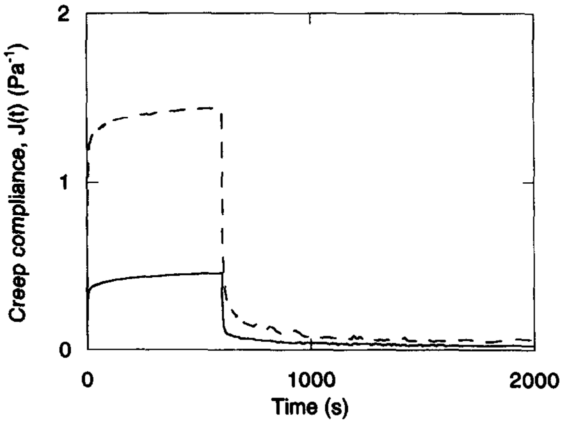

Fig. 7. Creep behaviour of 5/95 xanthan/guar gum (sample 1) (continuous line) and of xanthan/locust bean gum (dashed line) mixtures in 0.13 M KCl (total polysaccharide: 0.5%; applied shear stress: 0.5 Pa; temperature: 25°C).

Figure 8 illustrates the creep behaviour of 50/50 xanthan/guar gum and xanthan/locust bean gum mixtures at 0.5% in 0.13 M KCl. In contrast to the above results, xanthan/guar gum and xanthan/locust bean gum behave in a different way. The recovery curve of the xanthan/locust bean gum mixture returned to $J=0$, indicating again a solid-like structure. The behaviour of the xanthan/guar system appeared more typical of a viscoelastic liquid: the creep curve did not reach a constant value and the recovery curve did not return to $J=0$. Clearly, the recovery was not completed, indicating that steady flow had occurred. However, it should be said that the steady shear viscosity was very high, namely 2.6×10^5 Pa.s, the shear

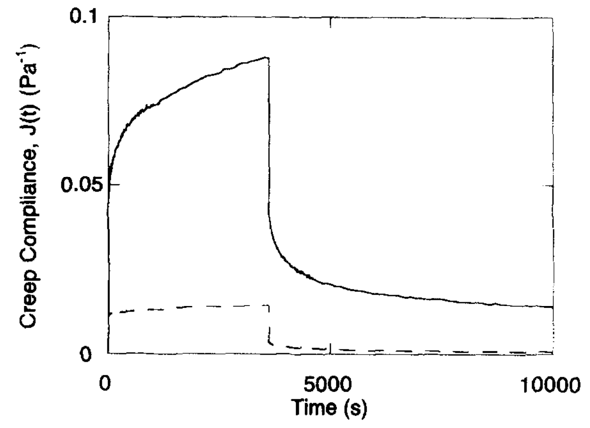

Fig. 8. Creep behaviour of 50/50 xanthan/guar gum (sample 1) (continuous line) and of xanthan/locust bean gum (dashed line) mixtures at 0.5% in 0.13 M KCl (total polysaccharide: 0.5%; applied shear stress: 3 Pa; temperature: 25°C).

rate being $5\times10^{-6}\,s^{-1}$. The creep behaviour of the 80/20 xanthan/galactomannan systems under the same conditions is shown in Fig. 9. Similar curves as those obtained for the 50/50 ratio were obtained. The curve of the mixtures contrasted strongly with that of xanthan gum (not shown). Both recovery curves did not return to $J=0$. Here again, the steady shear viscosity for the xanthan/guar gum mixture was very high, i.e. 2.1×10^5 Pa.s at a shear rate of $4.7\times10^{-6}\,s^{-1}$. In the case of xanthan gum alone, in similar conditions, the steady shear viscosity was only of the order of 10^3 Pa.s at a shear rate of $10^{-3}\,s^{-1}$.

Overall, these results show that a similar tendency appears between xanthan/guar gum and xanthan/locust bean gum mixtures at a low xanthan/galactomannan ratio. It is thus clear that the presence of xanthan even at a low ratio induces a transition of the system from a macromolecular solution to a structured system displaying gel-like properties. However, for mixtures with a high xanthan gum content, differences between xanthan/guar gum and xanthan/locust bean gum systems have been found.

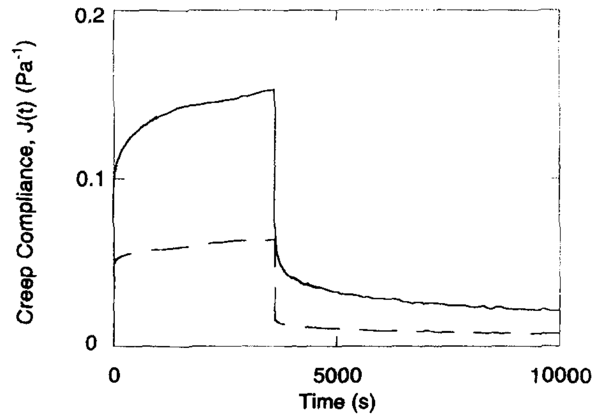

Fig. 9. Creep behaviour of 80/20 xanthan/guar gum (sample 1) (continuous line; applied shear stress: 1 Pa) and of xanthan/locust bean gum (dashed line; applied shear stress: 2 Pa) mixtures in 0.13 M KCl (total polysaccharide: 0.5%; temperature: 25°C).

Comparison of three guar gum samples

The synergistic properties of xanthan/guar gum mixed systems with the three guar samples were compared. Qualitatively, similar effects as those illustrated in Figs 1-3 for sample 1 have been observed with samples 2 and 3. However, the moduli were significantly lower, especially for sample 3 which has the lower intrinsic viscosity value and hence the lower molecular weight. As an illustration, Fig. 10 shows, for these three guar gum samples, the G' variations, at 0.1 rad/s, as a function of the xanthan/guar gum ratio. The traces were qualitatively similar. G' increased with the xanthan/guar gum ratio up to a maximum and then decreased. An optimum was reached for a 40/60 xanthan/guar gum mixture for samples 1 and 2. In contrast, the xanthan/guar gum (sample 3) system did not display any maximum. We noticed instead an almost constant value of G' whatever the xanthan/guar gum ratio. However, such systems exhibited viscoelastic properties qualitatively similar to those obtained with guar gum samples 1 and 2. Only the magnitude of the G' values changed. G' values of the mixtures with sample 3 were significantly higher than those of guar gum alone whatever the ratio, but they remained lower than the G' values of xanthan gum. Synergistic effects in xanthan/guar gum systems thus appear dramatically different from one guar sample to the other. This can be ascribed, at least partly, to differences in molecular weight. However, other

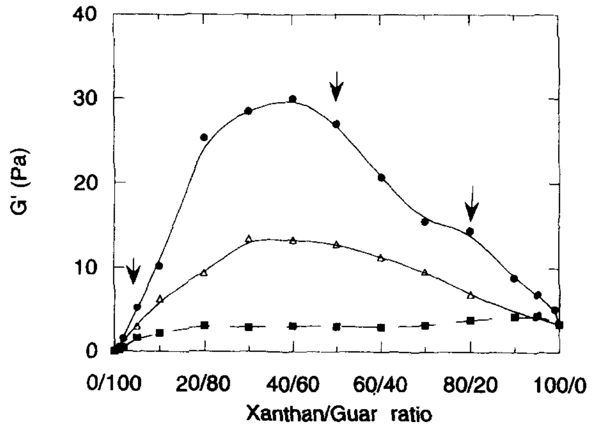

Fig. 10. G' variations of xanthan/guar gum mixtures as a function of the xanthan/guar gum ratio for three guar gum samples (•, sample 1; △, sample 2; ■, sample 3) (total polysaccharide: 0.5%; ionic strength: 0.13 M KCl; temperature: 25°C; frequency measurement: 0.1 rad/s). The arrows show the ratios corresponding to the results illustrated in Figs 1, 2 and 3.

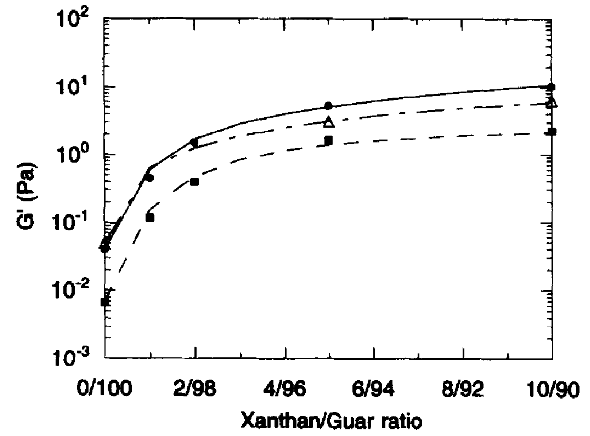

Fig. 11. G' variations of xanthan/guar gum mixtures as a function of the xanthan/guar gum ratio within the range 0/100 to 10/90 for three guar gum samples (•, sample 1; △, sample 2; ■, sample 3) (same results as in Fig. 10).

parameters such as the mannose/galactose ratio might be involved.

Figure 11 illustrates G' variations at 0.1 rad/s in a log–log scale for the same mixtures at ratios ranging from 1/99 to 10/90. This representation allows us to illustrate the dramatic increase of the G' modulus due to the presence of a low amount of xanthan. With respect to guar alone, G' was multiplied by ≈10 for the 1/99 ratio and by more than 100 for the 10/90 ratio. The effectiveness of xanthan gum even at a very low content is evident. On the other hand, this figure confirms the difference between guar gum samples; the synergistic interaction again increased in the order sample 1 > sample 2 > sample 3.

Figure 12 shows the variations of G' at 0.1 rad/s for locust bean gum as a function of the xanthan/galactomannan ratio as compared to guar gum samples 1 and 3. Two main features were evident. First, the curve of the xanthan/locust bean gum mixture showed, as for xanthan/guar gum systems, an increase in G' values as early as at a 1/99 ratio. Then a plateau was reached between the 30/70 and the 40/60 xanthan/locust bean gum ratio. Second, in contrast to xanthan/guar gum systems, an increase of G' was observed beyond the 50/50 ratio, i.e. towards the high xanthan/locust bean gum ratios. An optimum was reached at 60/40 with $G' \approx 70$ Pa. Moreover, xanthan/locust bean gum mixtures exhibited pronounced gel-like properties in this range as illustrated in Figs 6 and 9.

Again, the behaviour at a low ratio from 1/99 to 10/90 has to be considered specifically. Figure 13 shows the viscoelastic spectra of xanthan/locust bean gum and xanthan/guar gum (sample 3) at a 5/95 ratio. These two galactomannan samples have similar intrinsic viscosity values, 1490 and 1590 ml/g, respectively, indicating that the degree of polymerization of the mannan backbone is of the same order. The spectra were almost totally superposed. This suggests that, for a low xanthan content, guar gum and locust bean gum react in the same way. There is no effect of the chemical structure. The more important parameter appears to be the molecular weight. A practical result is that, in this range, stronger synergistic properties can be obtained with guar gum, provided the molecular weight of guar gum is higher.

For higher ratios, ranging from 10/90 to 40/60, as illustrated in Fig. 11, the synergism in xanthan/locust bean gum systems was much stronger than in the case of the xanthan/guar gum, provided the degree of polymerization was comparable (sample 3). At 0.1 rad/s and for the 40/60 ratio, $G' \approx 17$ Pa for the xanthan/locust bean gum mixture and only ≈6 Pa for the xanthan/guar gum (sample 3) system. However, for the same ratios, we found the G' value for the xanthan/guar gum (sample 1 of higher degree of polymerization) systems to be close to that of the

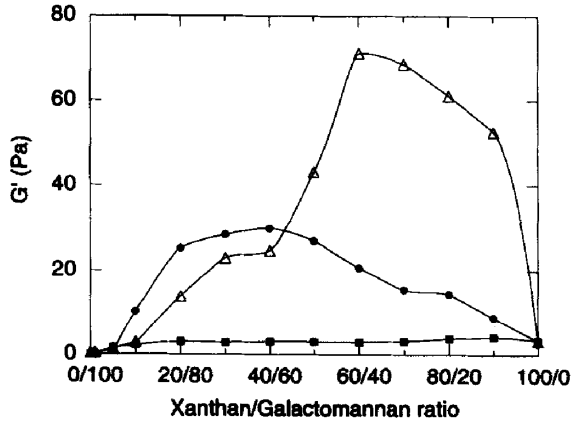

Fig. 12. G' variations of xanthan/guar gum mixtures and xanthan/locust bean gum as a function of the xanthan/guar gum ratio (•, guar sample 1; ■, guar sample 3; △, locust bean gum) (total polysaccharide: 0.5%; ionic strength: 0.13 M KCl; temperature: 25°C; frequency measurement: 0.1 rad/s).

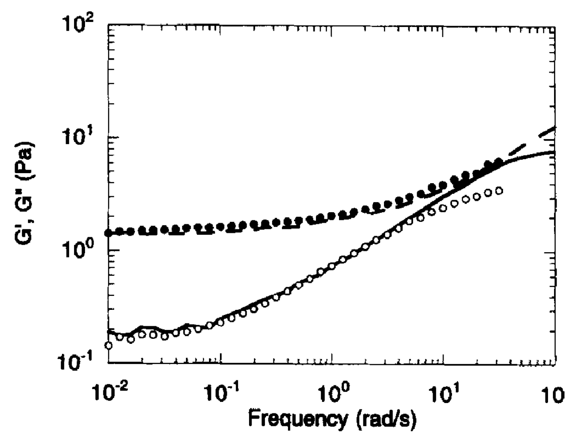

Fig. 13. Viscoelastic spectra of a 5/95 xanthan/locust bean gum mixture (dashed line, G'; continuous line, G'') and of a 5/95 xanthan/guar gum (guar sample 3) mixture (•, G'; ○, G'') in 0.13 M KCl (temperature: 25°C).

xanthan/locust bean gum mixtures and even higher. The effect of the galactomannan molecular weight on the xanthan/galactomannan interaction is thus clearly illustrated.

Additionally, when the content of xanthan in the mixture increased beyond the 50/50 ratio, the synergism with locust bean gum was much stronger than with guar gum whatever the molecular weight of the guar gum sample. This can be explained by the chemical structure of the galactomannan: the higher the content of galactose of the galactomannan, the lower the synergism, as expected.

Effect of ionic strength

The viscoelastic behaviour of xanthan/guar gum systems in the presence or in the absence of electrolyte was investigated. Qualitatively similar spectra were obtained whatever the ionic strength. G' variations as a function of the xanthan/guar gum (sample 1) ratio for three medium conditions (no salt added, 0.013 M KCl, 0.13 M KCl) are illustrated in Fig. 14. In the presence or in the absence of KCl, the G' traces of xanthan/guar gum (sample 1) were quite similar. A maximum was reached at a 40/60 ratio in 0.13 M KCl (as already shown in Fig. 10) and in 0.013 M KCl. If no salt was present, an almost constant value was found for ratios between 20/80 and 60/40. It is clear that the viscoelastic properties were strongly dependent on ionic strength: the higher this parameter, the better the synergism. For example, at a 40/60 ratio, G' values were ~30 Pa in 0.13 M KCl, ~10 Pa in 0.013 M KCl and ~5 Pa without salt. For a guar gum solution no effect of the ionic strength was found whereas for xanthan alone G' was enhanced by the presence of electrolyte. These latter results are consistent with those reported in the literature (Smith *et al.*, 1981; Rochefort & Middleman, 1987). These authors postulated to the fact that xanthan polymer–polymer association is promoted upon increasing salt concentration owing to a reduction in intermolecular repulsion.

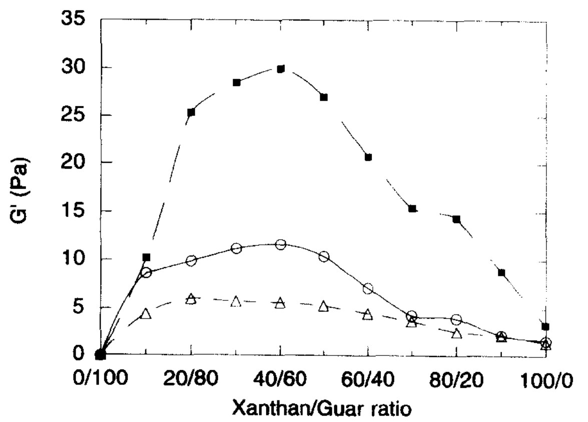

Fig. 14. G' variations of xanthan/guar gum (guar sample 1) mixtures as a function of the xanthan/galactomannan ratio. Effect of ionic strength (△, no salt added; ○, 0.013 M KCl; ■, 0.13 M KCl) (total polysaccharide: 0.5%; temperature: 25°C).

Similar experiments have been carried out on xanthan/locust bean gum systems. The rheological properties (G' and G'' moduli) were strongly influenced by the presence of electrolyte but in the reverse way in comparison to xanthan/guar gum mixtures: G' and G'' were reduced when KCl was present. These results are consistent with those reported by Tako & Nakamura (1984), Tako (1991) and Zhan *et al.* (1993).

DISCUSSION

The term 'gel' has been used so often indiscriminately that it has become ambiguous. This term indeed classically defines a range of systems which exhibit solid-like properties while a vast excess of solvent is present. Such peculiar behaviour arises from the formation of a three-dimensional network which extends itself continously through the whole system. According to Ferry (1948) a gel can be described as 'a substantially diluted system which exhibits no steady-state flow'. This statement excludes viscoelastic liquids and only true solids are accepted by this definition. According to Burchard & Ross-Murphy (1990), 'systems are gels, i.e. they all possess at least one property which can stand as the operational definition of a gel; they possess a plateau in the real part of complex modulus extending over an appreciate window of frequencies'. Another requirement is that $G'(\omega)$ is considerably larger and preferably more than one order of magnitude higher than $G''(\omega)$ in the plateau region to ensure that the system is solid-like. There was no mention of the extent of the frequency window to be taken into account. This extends the definition to viscoelastic liquids which would exhibit flow at times longer than the time-scale accessed in the measurement. Generally, two classes of networks may be distinguished, referred to as 'true gels' and 'weak gels'. A true gel should be free-standing and arise from a three-dimensional network. In contrast, for a weak gel, the 'solid' nature appears less clearly since, when submitted to high enough stress or if time is long enough, it may exhibit flow. Xanthan gum is very often taken as an example of a 'weak gel'. This system behaves indeed as a solid on a time-scale of seconds. Actually, the mechanical spectrum of a xanthan gum dispersion can be regarded as that of a viscoelastic fluid, the cross-point G' and G'' occurring at a lower frequency than those accessible, meaning that the macromolecular chains relax towards long times (Rochefort & Middleman, 1987; Doublier, 1994; Schorsch, 1995). This is due to the high stiffness of macromolecular chains. Moreover, it is easy to show that the system flows freely by transient methods

(Giboreau *et al.*, 1994). Clearly, xanthan gum does not exhibit solid-like properties and therefore does not arise from a three-dimensional network. This clearly illustrates the ambiguity of taking for granted the so-called operational definition of a gel to infer a network through a three-dimensional structure when the accessed frequency window is too narrow.

The present results show that the viscoelastic properties of xanthan/galactomannan systems depend strongly on the xanthan/galactomannan ratio (Figs 10 and 12). As observed in Figs 2 and 4 for the xanthan/guar and xanthan/locust bean gum systems, the presence of xanthan even at a low content induces a transition in the system, although rich in galactomannan, from a macromolecular solution to a structured system displaying gel-like properties. At a low ratio, the presence of an elastic plateau at low frequency, indicating a solid-like behaviour of the system, is evident. The G' modulus seems to exhibit a finite value at zero frequency. This result is confirmed by means of transient measurements. Moreover, no difference between xanthan/locust bean gum and xanthan/guar gum systems at these ratios was observed. Guar gum and locust bean gum samples with similar molecular weight react in the same way (Fig. 13). There is thus no effect of the chemical structure (mannose/galactose ratio). The determining parameter appears to be the molecular weight.

When the content of xanthan gum in the mixture increases, the resulting system exhibits peculiar properties, which vary according to the mannose/galactose ratio. A maximum in the synergistic effect was reached at a 40/60 xanthan/guar gum ratio (samples 1 and 2) and at a 60/40 xanthan/locust bean gum ratio. This latter result is consistent with Cuvelier & Launay's data (Cuvelier & Launay, 1986; Cuvelier & Launay, 1988) on xanthan/locust bean gum mixtures. However, in the case of xanthan/guar gum systems in water (no salt added), Tako & Nakamura (1985) found a 66/33 ratio ($C = 0.2\%$) and Clark (1987) a 60/40 ratio for concentrations ranging from 0.1% to 0.5%.

The solid-like character of xanthan/locust bean gum mixtures (assuming a finite G' value at $\omega \approx 0$) subsists for ratios up to ≈80/20. Moreover, the viscoelastic spectra are in agreement with data reported by Cuvelier & Launay (1986), who observed that the curves $G'(\omega)$ and $G''(\omega)$ displayed a more complex shape than for monocomponent gels. Two elastic plateau zones were evidenced. The authors ascribed this uncommon behaviour to the coexistence of two types of junction zones, with a slowly changing balance between one type and the other. The plateau at low frequency was supposed to arise from stable physical crosslinks whereas the second plateau at high frequency was ascribed to crosslinks which appear to be less permanent. It has been suggested that the low-frequency plateau was induced by xanthan/locust bean gum interactions whereas the high-frequency plateau was related to xanthan/xanthan interactions. However, the existence of these two types of interactions has actually not been demonstrated. In any case, it is clear that xanthan/locust bean gum systems can be considered as true gels following the above-proposed definition.

In the case of the xanthan/guar gum systems, the presence of xanthan gum changes the behaviour of guar gum dramatically. In any case, the xanthan/guar gum system is not just a solution which results from the mere addition of the two polysaccharides. However, in contrast to locust bean gum, the presence of a true elastic plateau at low frequency is more ambiguous, as shown by the creep-recovery results. This system can be regarded as a weak gel, probably due to the fact that the three-dimensional network is less long-lived. Furthermore, these results illustrate that it is necessary to consider the whole viscoelastic spectrum to characterize such systems. The performance of a single measurement at a fixed frequency, as in Tako & Nakamura (1984, 1985), is not enough to describe their viscoelastic properties. Moreover, our results prove the necessity of considering the viscoelastic behaviour of these systems over a long time-scale, the two types of methods, dynamic on one side and transient measurements on the other side, being required for a complete rheological characterization.

The present data show also that the xanthan/galactomannan interaction changes on the addition of electrolyte. Whereas G' and G'' of xanthan/locust bean gum systems are decreased when KCl is present, an opposite phenomenon is found with xanthan/guar gum systems. The results dealing with xanthan/locust bean gum are in agreement with Tako & Nakamura (1984), Tako (1991) and Zhan *et al.* (1993) but in contrast to the data of Cheetham & Mashimba (1988). Williams *et al.* (1991) reported on the independence of the ionic strength (presence or absence of NaCl) on xanthan/locust bean gum mixtures, in contrast to xanthan/konjac mannan systems. In the latter systems, G' and G'' were reduced when electrolyte was present, with divalent cations having a greater effect than monovalent cations. For xanthan/guar gum blends, Clark (1987) found that addition of either sodium ions (at a level $>10^{-3}$ molar) or calcium ions (at a level $>5.10^{-4}$ molar) diminished the interaction significantly. This was related to a conformational change of the xanthan gum molecule, from disordered to ordered, induced by the presence of these cations. According to the author, the conformation of the xanthan molecule largely controls the interaction changes at different ion levels. Similar results have been reported by Lopes *et al.* (1992). However, Goycoolea *et al.* (1995) provided some evidence that xanthan can develop synergistic properties with mannans (glucomannans, locust bean gum) whatever its conformation. This was also observed with xanthan/guar gum in the absence of salt (Schorsch, 1995).

The comparison of guar gum samples has clearly shown that noticeable differences may exist between them. Results with mixed systems implying either guar gum sample 1, sample 2 or sample 3 clearly demonstrate the effect of the molecular weight whatever the xanthan/guar gum ratio. The higher the molecular weight, the stronger is the synergism. These differences in molecular weight give rise, at the same concentration, to various entanglement life-times. Also, it is to be emphasized that classical guar gum samples that are used in the food industry have an intrinsic viscosity of the order of 10–15 dL/g, corresponding to molecular weight spanning from $\sim 1.2\times 10^6$ to $\sim 2.5\times 10^6$. The present result demonstrates that evident synergistic properties are displayed provided the guar sample has a quite high molecular weight, namely higher than 3×10^6. Moreover, the comparison between samples 1 and 2 of comparable intrinsic viscosity, hence of comparable molecular weight, but with a slightly different mannose/galactose ratio, suggests that the synergistic interaction between xanthan and guar gum is also dependent upon this latter parameter: the higher the mannose/galactose ratio, the stronger the synergism.

When the content of xanthan in the mixture is higher than 10/90, synergistic properties are clearly developed with guar gum although they are weaker than with xanthan/locust bean gum at comparable molecular weight. However, it is worth mentioning that this deficit in synergism can be compensated for, at least in the range 10/90 to 50/50, by using a guar sample of high molecular weight, as illustrated in Fig. 12 when comparing guar gum (sample 1) to locust bean gum.

CONCLUSION

The existence of outstanding synergistic phenomena between guar gum and xanthan gum is illustrated. The main parameter involved in the mechanisms is the molecular weight of the galactomannan. Despite differences that are evidently related to the chemical structure, particularly the mannose/galactose ratio, it is likely that the synergistic properties developed by guar gum with xanthan gum originate from a similar basic mechanism as with xanthan/locust bean gum systems. This makes the classical and widely accepted interpretation, or its recent improvements, based on the existence of specific interactions or 'heterotypic junction zones' between xanthan and galactomannan questionable. It at least requires some refinements. A way to improve our understanding of such mechanisms would be to investigate more specifically the behaviour of one of the polysaccharides in the presence of the other. For instance, using polarized light microscopy we showed (Schorsch *et al.*, 1995) that xanthan molecules in xanthan/galactomannan mixtures are prone to organize themselves as liquid-crystalline mesophases. This may suggest a concentration effect of this polysaccharide in a xanthan-enriched phase, which could arise from a phase separation process. However, such a phenomenon has not been evidenced although it is predicted from Flory's theory when rod-like species are mixed with flexible macromolecules (Hefford, 1984). There are many arguments which can be used against this interpretation. For instance, it is difficult to explain why synergistic properties are exhibited at a low polysaccharide concentration as well as at a very low xanthan/galactomannan ratio. However, it may be argued that the same criticism can hold for the other mechanisms. Further work is required on the thermal behaviour of these mixed systems in relation to the fact that xanthan molecules undergo a helix–coil transition at a temperature which depends deeply upon the ionic environment. From a practical standpoint, the use of guar gum instead of locust bean gum, at least for ratios ranging from 1/99 to 50/50, can be worthwhile provided the molecular weight of guar gum is high enough. These synergistic properties can be very useful in the case of stabilization of food emulsions and suspensions and provide the basis of new functionalities resulting in new textural characteristics.

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