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Rheological description at the minimum gelling conditions of kappa-carrageenan/locust bean gum systems*

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Abstract. Kappa-carrageenan/locust bean gum interactions at the minimum gelling concentration have been studied by dynamic and viscosity measurements at 15°C. Both rheological methods used have been shown to be complementary. The existence of a weak network structure exhibiting thixotropic behaviour has been observed. The formation of the weak network is discussed.

Introduction

Kappa-carrageenan (*k-car*) and locust bean gum (LBG) are polysaccharides which form synergistic gels upon mixing (1,2). These synergistic effects have many different technological applications, particularly in the food industry (3). Previous results have been reported on the rheological properties of *k-car*/LBG mixed systems in the vicinity of the sol–gel transition (4,5). From these data, the *k-car* content at which the sol–gel transition occurred was found to be constant whatever the total polymer concentration investigated and was twice as low as in the case of *k-car* alone. Normally the rheological behaviour of *k-car*/LBG blends in the vicinity of the sol–gel transition was gel-like at low frequency whereas it remained close to that of individual galactomannan at high frequency.

The aim of the present work is to describe the rheological properties at the minimum gelling conditions (concentration and mixing ratio) of *k-car*/LBG systems. Dynamic and viscosity measurements have been performed in the semi-dilute domain (0.30 and 0.40%) at different *k-car*/LBG ratios.

Materials and methods

The locust bean gum sample was obtained according to Gonçalves *et al.* (6) and was purified according to Fernandes *et al.* (7). The *k-car* sample extracted from *Eucheuma cotonii* was supplied by SBI (Carentan, France) in the K^+ salt form and was used without further purification (8).

The gels were prepared by mixing solutions of LBG and *k-car*, at 90°C. The hot solution of *k-car*/LBG mixture was poured directly onto the plate of the

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rheometer which was at 40°C and covered with light oil in order to eliminate dehydration problems. Then, it was cooled to 15°C in few minutes. All dynamic and viscosity measurements were performed at 15°C using a Rheometrics Fluids Spectrometer (RFS II, Rheometric Inc., Piscataway, New Jersey, USA) with a cone and plate geometry (2° cone angle and 5.0 cm diameter). Dynamic spectra were obtained from measurements within the frequency range 0.01–100 rad/s at a strain amplitude of 0.05. Viscosity measurements were performed by programming the shear rate from 0 to 1 s^{-1} and then going back to 0.

Results and discussion

We previously showed from viscosity and viscoelastic dynamic measurements that no gelation takes place in the present experimental conditions (15°C) if the *k-car* concentration is <0.5% (5). However, this concentration was lowered to 0.22–0.24% in the case of *k-car*/LBG blends. Gel formation was not observed at the 0.3% total polymer concentration. For a total polymer concentration of 0.4%, gelation occurred at the 54/46 mixing ratio (4,5). Variations of G′ and G″ as a function of time of such a mixture are shown in Figure 1. A slow and continuous increase of both viscoelastic moduli, G′ and G″, was experienced over the 14 h of the experiment. At the beginning of the process, G″ was much higher than G′ in contrast to what was seen with the 14 h-old system for which G′ > G″. Clearly, the system had not reached a steady value at the end of the experiment. These results suggest that the mixture passed progressively from a solution to a gelled system. This point is more clearly illustrated in Figure 2 where the viscoelastic spectrum at t = 0 h was typical of a macromolecular solution, with G″ > G′ and a strong dependency of both moduli upon frequency, as we previously reported for a 0.48% *k-car* system in the same experimental conditions (5). In contrast, at t = 14 h, G′ and G″ varied very slightly with frequency, G′ > G″ all along the frequency range except towards the highest frequency, where both parameters tended to be equal. Moreover, G′ reached a constant value at low frequency. Such a behaviour is typical of a weak gel (9). This spectrum was close to that obtained with *k-car* alone at 0.51%, here too under the same conditions, with G′ at low frequency of the same order (0.2–0.5 Pa). This means that, despite the *k-car* content in the mixture being half that in *k-car* alone, a network is obtained which displays viscoelastic properties relatively close to those exhibited by *k-car* alone, just beyond the gelling concentration (between 0.48 and 0.51%) (5). A point which deserves further discussion is the determination of the sol–gel transition. At first sight, the G′–G″ crossover could be taken at the criterion of this transition. However, it is well known that such a criterion would yield relatively different results depending upon the frequency measurement. A better determination of the gel point in such systems can be taken as the time at which the viscoelastic spectrum, that is G′(ω) and G(ω) traces, deviates from that of a macromolecular solution (5). Therefore, the results of Figures 1 and 2 are not enough to allow us to determine the gel point with good accuracy.

A rapid and simpler way of investigating those lightly structured systems may

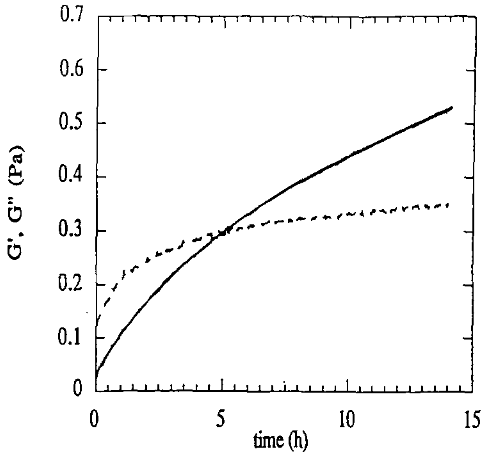

Fig. 1. Kinetics of gel formation of the 54/46 *kappa-carrageenan*/LBG at the 0.4% total polymer concentration. Temperature, 15°C; frequency, 1 rad/s. (——) G′ and (---) G″.

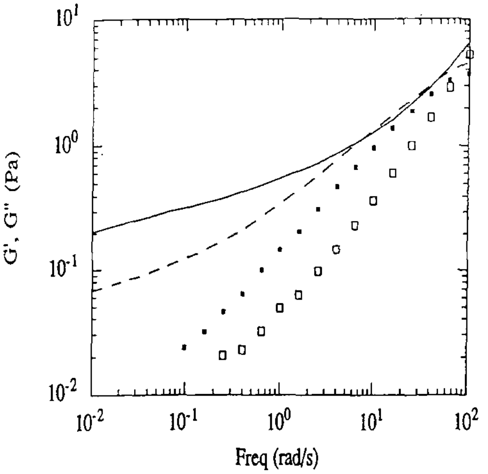

Fig. 2. Frequency dependence of the storage. G′, and the loss, G″, moduli of the 54/46 *kappa-carrageenan*/LBG at the 0.4% total polymer concentration. Temperature, 15°C, t = 0 h;–(□) G′ and (■) G″; t = 14 h;–(——) G′ and (---) G″.

be the performance of viscosity measurements at low shear rate as illustrated in Figures 3 and 4. The curve obtained at the end of the gelling process (14 h) is shown in Figure 3. Dramatic thixotropic properties were exhibited reflecting the properties of a highly structured system. This may be paralleled with the existence of the network as evidenced by the dynamic spectrum. The curves obtained at intermediate stages (30 min and 3 h) are shown in Figure 4. Here also, a highly thixotropic behaviour was seen which became more and more pronounced as the system aged. We suggest that since the measurements are not

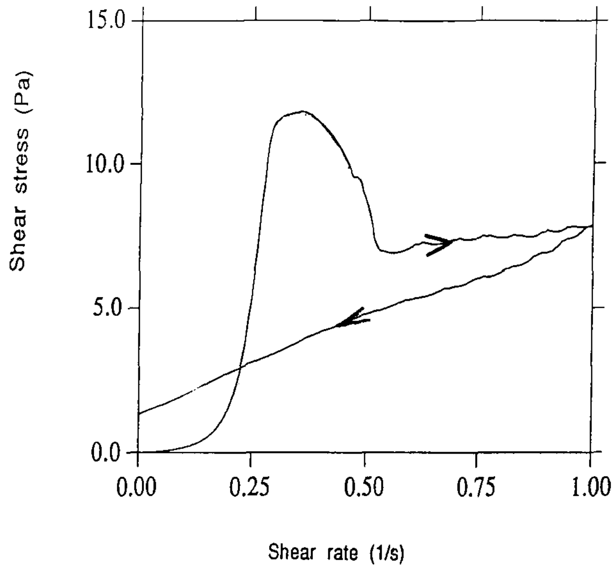

Fig. 3. Flow curve of the 54/46 *kappa-carrageenan*/LBG at 0.4% total polymer concentration at the end of ageing period (14 h). Temperature, 15°C.

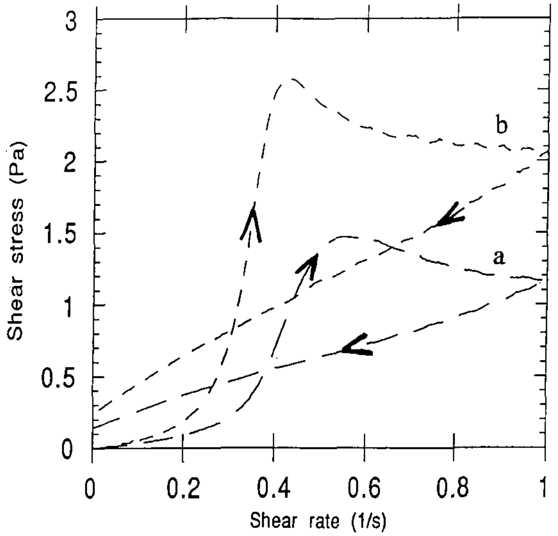

Fig. 4. Flow curve of the 54/46 *kappa-carrageenan*/LBG at 0.4% total polymer concentration at the end of (a) 30 min and (b) 3 h. Temperature, 15°C.

taken under equilibrium conditions, the thixotropic loop is none other than a manifestation of 'stress overshoot'. Hence, the maxima merely reflect the elastic limit of the system. The more developed the network, the lower is its threshold for failure under strain; hence the progressive shift in the maxima on the shear rate axis (Figure 4) with time. In Figures 3 and 4, after the testing procedure a residual stress in the material is observed. This is typical of gelified systems and, like solids, they present a residual stress for a long time even after repose. It must be emphasized that these two last curves (Figure 4) were obtained at times shorter than for the G′–G″ crossover. This means that gelation does begin at times much shorter than the time of the crossover and is evidence that further viscoelastic measurements should be required at intermediate times.

Conclusion

The present data are consistent with our previous reports (4,5). Gelation in *k-car*/LBG mixed systems takes place at concentrations far below that required with *k-car* alone. The sol–gel transition in such systems can be monitored by viscosity as well as by dynamic experiments. Thixotropic loops in the first category of methods provide an overall observation of the phenomena. However, the second type of method is more powerful by allowing a complete characterization of the viscoelastic properties of the systems. In general both rheological methods used have been shown to be complementary. The fact that the dynamic spectra of the mixtures are comparable to those of *k-car* in the vicinity of the sol–gel transition may indicate that the same network is obtained in both cases. It is thus likely that gelation in *k-car*/LBG mixtures would arise from the formation of a primary network that would originate from gelation of *k-car*. The peculiar characteristics of these mixed systems should find them applications in liquid food systems for their suspending or stabilizing abilities.

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