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Short Communication

Rheological measurement of κ-carrageenan during gelation

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Recent studies of the rheological properties of κ-carrageenan during gelation have revealed unusual and interesting effects. Under certain conditions of concentration and ionic strength, a pronounced initial peak in G' has been reported, although the magnitude is highly susceptible to changes in experimental conditions, particularly strain and rate of cooling. An investigation of the gelation properties of κ-carrageenan in the pure potassium salt form (Hermansson, 1989), using combined rheology and microscopy, suggested the possibility that the peak could be attributed directly to changes in microstructure as an initial fine network was superseded by a coarser, more rod-like structure due to some form of aggregation. A similar peak in G' has been reported by Roesen (1992), although here a higher imposed strain value was used ($\gamma = 0{\cdot}0103$).

The shape of the gelation traces obtained in these studies is reminiscent of those produced when there is slippage between sample and measuring geometry. However, in studies of κ-carrageenan and mixed κ-carrageenan–locust bean gum systems (Hermansson, 1989; Stading & Hermansson, 1993), great care was exercised to detect and prevent slippage, including the use of serrated concentric cylinder geometries of different sizes and the adoption of a very low strain ($\gamma = 4 \times 10^{-4}$) during cooling. The rigorous experimental procedure even extended to the incorporation of a cup-holder constructed from low-expansion alloy to minimise effects due to dimensional changes in the rheometer.

Our own investigation of the κ-carrageenan–locust beam gum system, using a sensitive rheometer constructed by one of us (R.K.R.) with a truncated cone-and-plate geometry, gave similar results for the κ-carrageenan component with added KCl. It was found that under constant normal experimental conditions (frequency of 10 rad s^{-1}, 0·5% strain and a cooling rate of 1°C min^{-1}), a peak appeared but its size and shape was variable. Also, it was sometimes possible to eliminate the peak if a very low rate of cooling was applied through the gelation stage (0·3°C min^{-1}). Changing the rate of cooling might be expected to bring about differences in the microstructure but the rather random nature of the effect suggested that, to some extent at least, the source could be other than a direct influence of the internal structure. It was further surmised that any serious problem with dimensional changes was unlikely to originate from the rheometer, but rather from the very rapid gelation process inducing equally fast shrinkage effects in the sample, together possibly, with some syneresis (Therkelson, 1993).

So that meaningful interpretations could be derived from interactions in the mixed system, it was essential that consistent and reproducible results should be obtained for the individual components. To this end, a different geometry, intended to eliminate the possibility of tangential slippage, was adopted. This had been constructed and successfully employed some years previously in an examination of the gelling properties of gellan gums under varying salt conditions where slippage had proved to be problematical. It consists of a tubular, perforated concentric cylinder system whose measuring regions are completely surrounded, and penetrated by, the sample, thus effectively locking sample and geometry together so that catastrophic slippage is rendered impossible (Fig. 1). Although syneresis may still have a minor influence, any non-linear strain distribution should have negligible effect provided that local deformation is large compared

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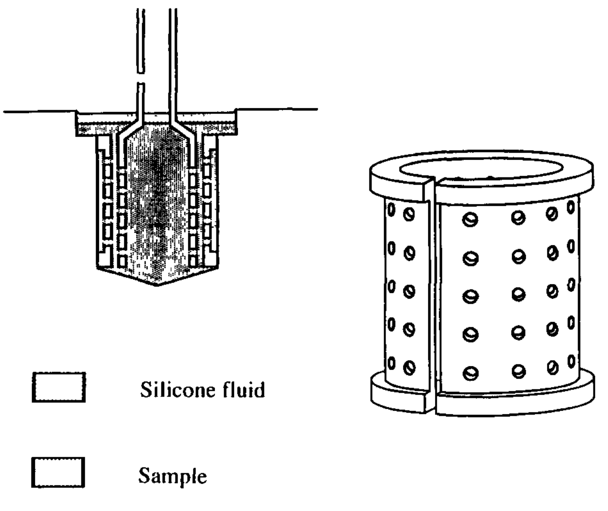

Fig. 1. Diagram of device used to study κ-carrageenan and other gels which may be subject to slippage using conventional geometries. A section through the perforated cylinder arrangement is shown (a) together with a view of the outer cylinder (b). The latter is machined to fit the standard cup of a rheometer and split on one side for easy removal and cleaning whilst maintaining a non-slip 'spring' grip.

with the thickness of the water layer between sample and geometry. This measuring system is not well defined, being perforated and of small dimensions to allow strong gels to be examined on the sensitive rheometer. For this reason, the simple expedient of calibration with a gelatin sample referred to the cone-and-plate measurement and checked using a commercial rheometer (Carri-Med CSL500) was adopted.

Figure 2(a) shows the setting traces after calibration for a 15% (w/w) sample of acid pig-skin gelatin (Sanofi Bio-Industrie) at pH 3·8 when monitored using the cone-and-plate geometry and concentric cylinder arrangement. The points recorded above the gelation temperature represent the baseline noise level due to the reduction in sensitivity (by a factor of approximately 250) when using the perforated cylinders. It was gratifying to find that it was necessary to increase the calculated factor between the two geometries (assuming no holes in the concentric cylinders) by only 22% to account for a 27% reduction in the working surface area of the inner cylinder due to the holes.

A κ-carrageenan sample (X6960 from Hercules) was converted to the K^+ form by ion exchange at high temperature (Amberlite IR 20 column, BDH) and the recovered solution dialysed against 0·1 M KCl. Setting curves for a 1% (w/w) sample are shown in Fig. 2(b) where values of G' obtained using both geometries are plotted against temperature. Here, experimental conditions using the cone and plate were kept as close as possible to those detailed and illustrated in the previous work (Hermansson, 1989), i.e. cooling at 1·5°C min^{-1} with 0·3% strain at a frequency of 10 rad s^{-1} (1·6 Hz). In the case of the cone-and-plate measurement, a sharp, narrow peak is observed immediately after gelation falling to uncertain, but generally increasing values, as cooling continues. Using the perforated cylinder arrangement, quite different results are obtained. An equally sharp gelation process is indicated, but measured values of G' increase monotonically throughout the cooling regime. The slope of the trace subsequent to gelation suggests that network conversion is achieved over a narrow time/temperature range and, although substantial internal rearrangements may occur

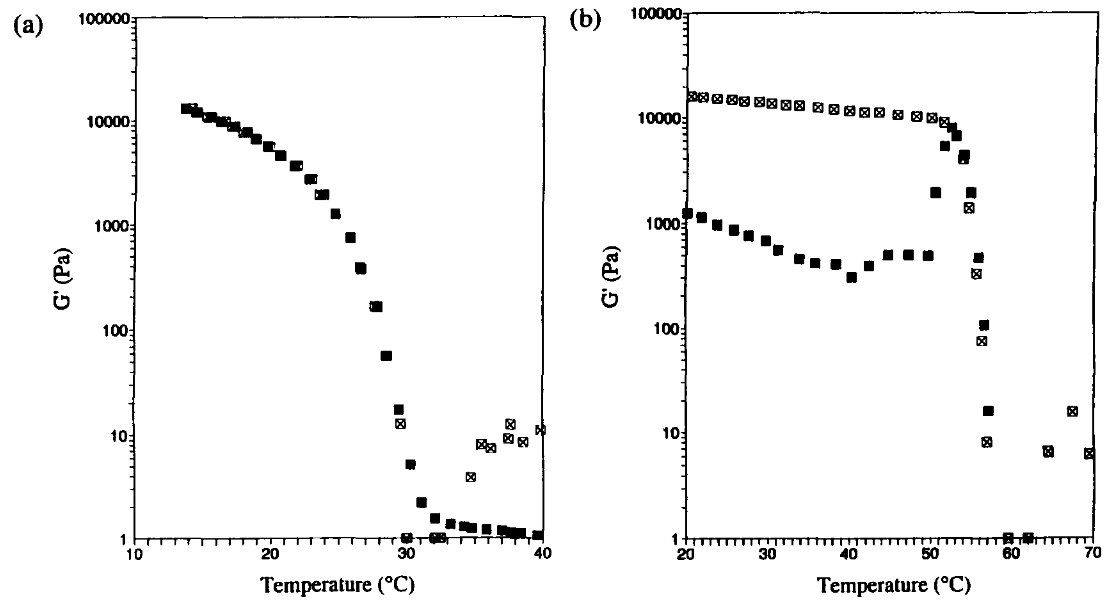

Fig. 2. Temperature-course of gelation as monitored by changes in storage modulus G' (10 rad s^{-1}) using a truncated cone-and-plate geometry (■) and the perforated concentric cylinder arrangement (⊠) for (a) 15% (w/w) gelatin at pH 3·8, 2% strain and a cooling rate of 1°C min^{-1} and (b) 1% (w/w) K^+ κ-carrageenan in 100 mM KCl, 0·3% strain (cone and plate) and 1% strain (perforated cylinder) with a 1·5°C min^{-1} cooling rate in both cases.

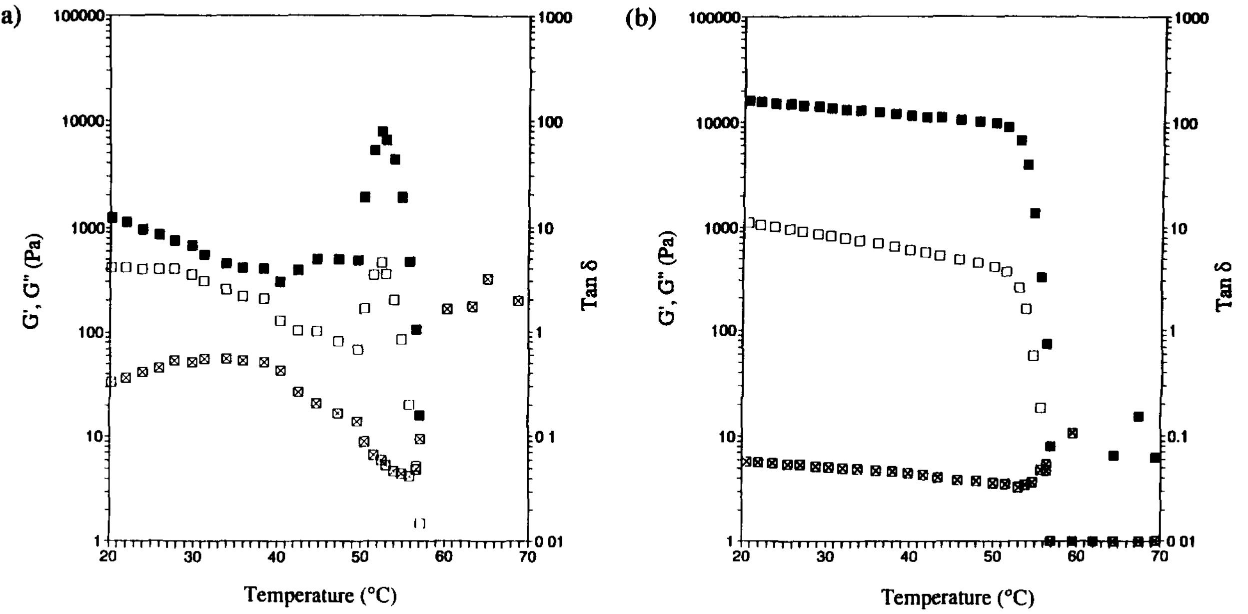

Fig. 3. Gelation of 1% (w/w) K^+ κ-carrageenan in 100 mM KCl as monitored by changes in G' (■), G'' (□) and tan δ (⊠) using cone-and-plate geometry (a) and perforated cylinders (b). Data are from the experiments illustrated in Fig. 1(b).

later, these are not made manifest by large changes in the measured modulus. In Fig. (3), the values of G', G'' and tan δ recorded during gelation are shown for the two geometries separately. The rather uncertain trace obtained using the cone and plate, Fig. 3(a), seems to be dramatically improved when the new geometry is substituted (Fig. 3(b)).

With the aid of this geometry, lack of reproducibility and extreme dependency upon cooling rate and imposed strain have been eliminated, the latter being illustrated by the use of 1% strain whilst maintaining a cooling rate of 1·5°C min^{-1} in the experiment of Fig. 3(b). Similar improvements in consistency have been reported (Moldenaers *et al.*, 1989) using a porous platen-measuring system, slippage observed with more standard geometries being attributed to the same gelation characteristics of syneresis and contraction. We do not assert that this method gives ideal shear conditions and it might be argued that such a complex geometry could influence gelation behaviour, but other methods intended to reduce slippage, e.g. serrations, could have similar effects.

These results do not contradict the evidence that structural change takes place during the cooling of the κ-carrageenan system below the gelation temperature, nor that, under some conditions, this may be observed by rheological measurement. They do, however, indicate that the measured mechanical properties of this and similar gel types may be strongly influenced by sample contraction/surface effects. To quantify the importance of these, a more detailed comparison of the relative reproducibility of the two methods under different gelling conditions, (cooling rate, strain, etc.), is necessary. We venture to suggest, however, that such a measuring system, being simple to construct and use in combination with a commercial concentric cylinder rheometer, would be useful in the rheological investigation of any single or mixed-component gelling system where the occurrence of contraction or syneresis is known or suspected.

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