Viscoelastic behaviour of alginate gels
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Introduction
A number of polysaccharides are employed in food products partly because of their ability to gel under various conditions. In recent years considerable interest has been shown in these materials and a certain amount of progress has been made in elucidating the chemical nature of the inter-chain linkages which form on gelation (1).

The rheological properties of these gels have been investigated mainly by empirical methods which often involve the subjectation of the material to very high stresses. Although work of this sort has proved useful in predicting the performance of the gel for a particular application, it is difficult to obtain detailed information about the gel structure from such methods. It is considered that a systematic study of the viscoelastic behaviour of polysaccharide gels in the small deformation region could provide valuable results which would complement the information on gel structure obtained from other techniques.

In this paper we report some preliminary data obtained from creep measurements on calcium alginate gels. The influence of the polysaccharide concentration, calcium ion concentration and pH on the rheological properties of gels formed from one alginate sample are considered. Recently Smidsrod and Hauge have reported the effect of other variables, in particular the polysaccharide composition and the molecular weight on the stiffness of calcium alginate gels (2).

Experimental
1. Formation of gels
A sample of sodium alginate containing a relatively high proportion of D-mannuronate residues was generously supplied by Alginate Industries 1). Calcium alginate gels were formed from this sample by two different methods both of which involved the slow release of calcium ions from a calcium salt dispersed in a solution of sodium alginate (3).

Method 1
Gels with a pH of approximately 3.5 were obtained when a solution of glucono delta lactone was added to a dispersion of calcium hydrogen orthophosphate (CaHPO₄) in a sodium alginate solution. The glucono delta lactone hydrolyses to give gluconic acid and the resultant lowering of the pH increases the solubility of the CaHPO₄. A gel is formed as the calcium ions released with the soluble alginate. In this work the concentration of sodium alginate and CaHPO₄ was varied but that of glucono delta lactone was maintained at 2% w/v in the final mixture.

Method 2
Gels with a pH of approximately 6.0 were prepared by mixing an aqueous slurry of calcium citrate with a sodium alginate solution. In certain cases the pH of gels of this type was varied either by the addition of different amounts of glucono delta lactone to the calcium citrate slurry or by adding sodium hydroxide to the alginate solution.

The gelling mixtures were allowed to set in rectangular moulds.

2. Measurement of creep compliance
Creep measurements were made using the parallel plate viscoelastometer described by Shama and Sherman (4). The movement of the centre plate after the application of the shear stress was followed continuously by recording the signal from a displacement transducer. The humidity of the air surrounding the gels was kept high by enclosing the viscoelastometer in a perspex box, the walls of which were coated with moist filter paper. The temperature of the gels was maintained at 24 ± 1 °C by pumping water through tanks in contact with the two samples. The measurement of the creep compliance at long times was complicated by the fact that some of the gels prepared exhibited considerable syneresis. Although the rate of loss of water from an unstressed gel which had been aged for several hours was very small, a significant quantity of water was exuded when the aged gel was compressed.

To minimise errors caused by changes in the volume of the material during the course of an experiment the following procedure was adopted. The gels were aged for 24 h after formation at room temperature in a high humidity atmosphere. The samples were then placed in the viscoelastometer, compressed by approximately 5% and aged for a further hour before the stress was applied. During this time the temperature of the gel equilibrated, the stress exerted by the gel on the plates relaxed and the samples prone to syneresis exuded some
water. The shear stress was then applied and measurements were taken for a period of 1 h. The creep recovery was generally followed for a few minutes after the stress was removed. It was found that the largest decrease in weight during the course of the creep experiment amounted to 2–3%.

The magnitude of the stress applied depended on the strength of the gel under investigation and was in the range 1000–3000 dyne cm\(^{-2}\). Preliminary measurements showed that for strains up to at least 0.1 the viscoelastic response was linear within experimental error. The stress was normally chosen so that the maximum strain observed was less than this value. It was not possible to obtain satisfactory measurements of the creep compliance at the longer times for the weak gels formed at neutral pH. In such cases the only result reported is the compliance measured ten seconds after the application of the stress.

Results

Gels formed at pH 6.0 by method 2 exhibited little syneresis and were relatively weak in comparison with gels formed at lower pH's. Fig. 1 illustrates the compliance measured ten seconds after the application of stress for a gel at pH 6.0 which contained 2% sodium alginate and varying quantities of calcium citrate. As with all the data presented here the results were obtained after the gel had been aged for 25 h following formation. The properties of the gel changed only very slowly after this period. It was clear from the results shown in fig. 1 that the strength of the gel was independent of the calcium citrate concentration provided this was sufficiently high. Fig. 2 shows that an approximately linear relationship was observed between the reciprocal of the ten second compliance and the alginate concentration for the gels at pH 6.0. The calcium citrate level was maintained at 0.035 M.

Gels with a final pH of approximately 3.5 formed by method 1 exhibited considerable syneresis. Because gels of this type were appreciably stronger than those formed at higher pH's it proved easier to make satisfactory creep measurements for long times.

Fig. 3 illustrates the influence of CaHPO\(_4\) concentration on the resultant creep compliance curve obtained from a gel which on formation contained 1% sodium alginate. The quoted concentrations of CaHPO\(_4\) refer to the amount of the salt in the gel on formation. Table 1 displays the quantity of water lost from the system during the 25 h ageing period before the creep measurements were made. The extent of syneresis increased with the calcium ion concentration.

The influence of polysaccharide concentration on the resultant creep curve is shown in fig. 4. The concentration of CaHPO\(_4\) in these systems on formation of the gel was 0.15 M. In