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How brittle are gels?

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Gels of different polysaccharide concentrations were cracked quasi-statically by driving a 40° included angle wedge into intact specimens in order to determine their fracture toughness. This could not be determined for some of the gels tested, gellan gum and xanthan gum blend. The work to fracture of alginate and agar gels, calculated without respect to energy loss due to visco-elastic or frictional effects between gel and wedge, varied from 4–32 J m^{-2}. The magnitude of fracture toughness values were found to be agar > high guluronic acid alginate > high mannuronic acid alginate. Agar gels were found to behave in a manner typical of starch gels; as gels became firmer their toughness increased, whereas the reverse appeared to hold for alginate gels.

INTRODUCTION

Alginates are polysaccharides obtained from brown seaweed. They are linear copolymers of D-mannuronic acid and L-guluronic acid, each molecule containing regions where the constituent sugars are continuous and others where they alternate. In contrast agar, which is extracted from red seaweed, can be fractionated into two components: agaropectin and the main gelling component, agarose. An idealized structure of agarose is an alternating copolymer of 3-linked-β-D-galactose and 4-linked-3,6-anhydro-α-L-galactose. These two polysaccharides have found widespread use in the food and allied industries by virtue of their gelling properties.

The mechanisms of gelation for the two polysaccharides are very different. Agar is a thermosetting polysaccharide which gels readily when a previously boiled solution of this polysaccharide is cooled to below 37°C. In contrast, a cold solution of alginate will gel in the presence of divalent cations, especially calcium. The properties of agar gels result primarily from the concentration of the polysaccharide in solution, whilst properties of alginate gels are more complex, being dependent not only upon polysaccharide concentration but also upon the concentration of divalent cations (Mitchell & Blanshard, 1976).

An important component of the perceived texture of a food is its fracture behaviour (Vincent, 1990). A recent paper by Vincent *et al.* (1991) describes a new test for food scientists that measures the work to fracture. Strain energy is fed into a specimen with a sharp wedge which is displaced in a controlled manner. The work done in this part of the test also includes permanent or plastic deformation in a small region on either side of the blade. However, if the wedge is removed from a gel specimen just before a crack is formed, only a small region, 1 mm or so on either side of the point of wedge penetration, is permanently deformed (Lucas *et al.*, 1992). Initially, this wedge is pressed onto an intact (unnotched) food sample. A crack is initiated only after a period of indentation. After rapid crack growth, paid for by the strain energy in the specimen, the rate at which the wedge travels through the sample then controls the rate of crack growth. After a crack has initiated, the penetration of the wedge into the specimen can be stopped at any point. This prevents the crack propagating any further and the strain energy remaining in the material can then be taken back into the testing machine by reversing the motion of the wedge. If the unloading curve returns to the origin, the fracture toughness of the material can be estimated from the area under the loading curve (total work done) divided by the nominal surface area of the crack formed. This is the 'work-area' method described by Gurney and Hunt (1967) and Atkins and Mai (1985). However, visco-elastic materials always display some energy loss when they are unloaded. Lucas *et al.* (1992), using gels of mung bean starch, determined that energy losses remote from the crack due to hysteresis and the work of friction between the gel and wedge could often be neglected (being <10% of the work done) provided that the displacement rate of the wedge was low (e.g. 5 mm in). In this paper the aim was to survey a range of gels to ascertain whether a wedge test would be suitable for obtaining their fracture properties. The test was employed in its simplest form without energy loss corrections. In these circumstances the work done can be termed the 'work to fracture' (Dobraszczyk *et al.*, 1987), a term that includes the specific work of fracture as well as various energy losses due to the material and the test conditions.

MATERIALS AND METHODS

Materials

Samples of Manucol DMF, a high mannuronic acid alginate (high M alginate); Manugel DMB, a high guluronic acid alginate (high G alginate); Kelcogel, (gellan gum) and GFS, which is a blend of xanthan gum, locust bean gum and guar gum, were all kindly donated by Kelco International, Tadworth, UK.

Method of gel preparation

Alginate
A mixture of calcium hydrogen orthophosphate (0·185 g) and alginate was added to 87·5 ml distilled water which was stirred using a IKA Ultra-Turrax T25 Disperser (Staufen, Germany), fitted with a S25N-18G generating shaft, for 5 min. Then, 15 ml of a freshly prepared glucono delta lactone (0·575 g) solution was added to the alginate dispersion with vigorous stirring, for 30 s. The solution was poured into cube-shaped 20 mm plastic moulds and left to set. The gels were aged (24 h) in a humid atmosphere prior to testing. Some gels were made using double the quantity of calcium hydrogen orthophosphate.

Agar
Agar (1–20 g) was dispersed in 200 ml of water and heated with stirring. All solutions were boiled for 1 min, poured into cube-shaped 20-mm plastic moulds and aged for 3 h prior to testing.

Gellan gum
Gellan gum was mixed into water preheated to 75°C. This solution was then further heated to 84°C. An equal quantity of 20 mM calcium chloride equilibrated to 84°C, was added to the hot gellan solution with mixing. Gels were set by cooling in 20-mm plastic moulds.

Xanthan gum blend
Xanthan gum was added to water preheated to 77°C with vigorous stirring. Solutions were further heated to 82°C and the gels set in 20-mm plastic cubes by cooling.

Measurement of fracture toughness

Testing was performed on a Shimadzu (Kyoto, Japan) DCS-5000 Universal Testing Machine at crosshead speeds of 5–100 mm min^{-1} using a sharp 40° (included angle) steel wedge attached to a 500 N load cell. The cube of gel to be tested was placed on a steel block such that when the crosshead was lowered, the wedge would contact the cube across the entire upper surface and act to divide the gel into two equal parts (Fig. 1). The crosshead was lowered until a steady force was obtained (Vincent *et al.*, 1991). After the crack had propagated a variable length, the crosshead was reversed. The area under the force-displacement curves, which gives the work done, was obtained by digitizing with a Janel Sigmascan (New York, USA) system. The new crack surface formed during the tests was rectangular and therefore calculated as the product of the width of the cube and the depth of the crack, these being measured with engineering calipers. The work to fracture was given by the work done divided by the area of the crack. This estimate was compared to a simpler method, that calculates the work to fracture as the final force divided by the cube width (Atkins & Vincent, 1984).

For the concentrations of the two types of alginate, the energy referable to viscoelastic energy losses was

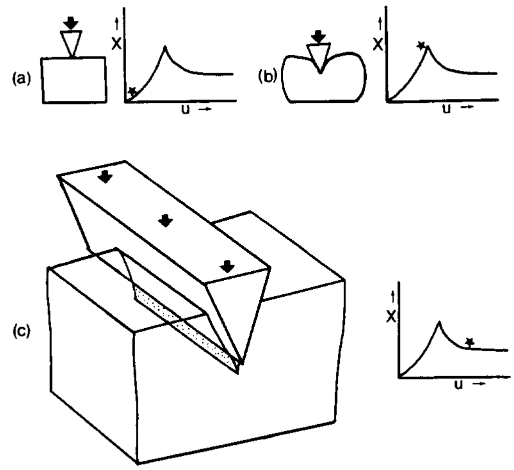

Fig. 1. Diagram showing the strain in the gel with progressive displacements of the wedge (direction indicated by the arrows). Position on the force displacement graph (X–u) is indicated by a star. (a) Initial position of the wedge. (b) Distorted shape of the gel just before crack formation. Reversal of the crosshead at this point revealed a small region extending 1 mm either side of the wedge of plastic deformation. (c) Cracked gel returned almost to its original shape. Further displacement of the wedge required a constant force with the only observable result being a further extension of the crack, just ahead of the wedge.

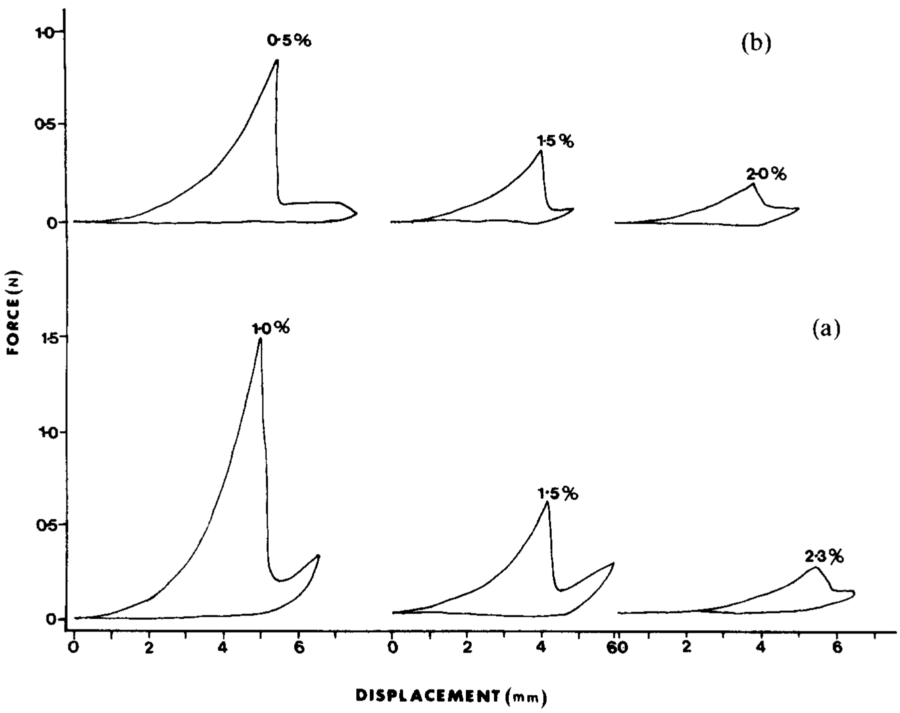

Fig. 2I. Force–deformation curves for (a) high M and (b) high G alginate gels at different concentrations.

measured. Specimens were loaded with the wedge to about 90% of the load at which they would start to crack. The gels were then unloaded by reversing the crosshead. The areas enclosed by the loading-unloading curves were again digitized and the results expressed as a proportion of the total energy imparted to the specimen at the peak load (Lucas *et al.*, 1992).

RESULTS

Alginate and agar gels did not synerese during penetration by the wedge, as was very clear. The very distorted shape of the gel specimen prior to crack initiation quickly returned to its original shape after cracking, the elastic strain energy stored in the specimen paying for the crack growth. There was little variation of fracture toughness with the length of crack.

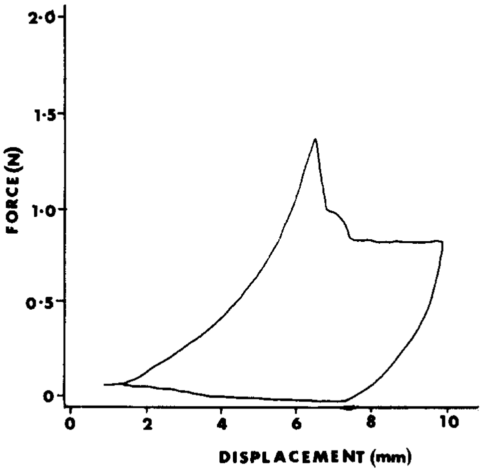

Fig. 2II. Force–deformation curve for 5% agar gel.

Examples of force–deformation curves from wedging differing concentrations of alginate gels are shown in Fig. 2I and for agar gels in Fig. 2II. The steepness of the loading curve, the force at which stable cracking took place and the total area under the curve were dependent upon the concentration of the gel. Work to fracture of the alginate gels decreased as polysaccharide concentration increased, this effect being more apparent for high G alginate gels (Fig. 3). The effect of doubling the calculated calcium ion concentration was negligible in gels of high M alginate but increased the work to fracture of high G alginate gels (Table 1).

An estimate of fracture toughness, derived directly from the final force divided by cube width, could be obtained for most gels. Comparison with work-area methods demonstrated that values were not significantly different ($p < 0{\cdot}01$, Student's t-test) to the total work done.

The energy losses due to hysteresis are shown in Fig. 4. For both types of alginate gel, this energy increased with concentration, the effect being more significant with the high M alginate gels.

For three concentrations of both alginate gels, the effect of crosshead speed on the work to fracture was investigated (Fig. 5). The behaviour of the two gels was very different. Work to fracture determined at low concentration for the high M alginate gels decreased at faster crosshead speeds whilst, with high concentra-

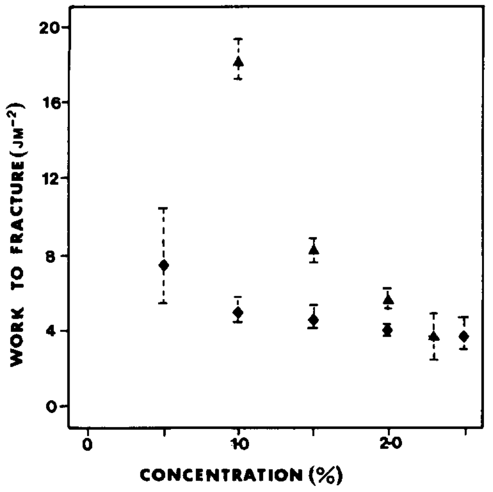

Fig. 3. Work to fracture values of alginate gels as a function of polysaccharide concentration. (♦) High M alginate; (▲) high G alginate.

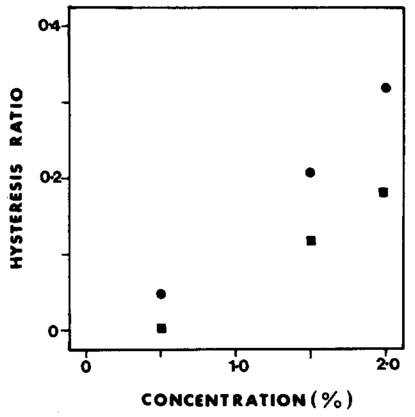

Fig. 4. Energy losses due to hysteresis for alginate gels. (●) High M; (■) high G.

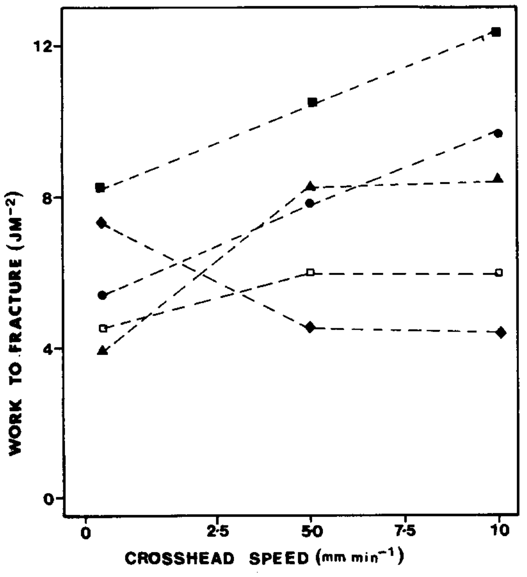

Fig. 5. Influence of crosshead speed on the work to fracture of alginate gels; (♦) high M, 0·5%; (□) high M, 1·5%; (▲) high M, 2·0%; (■) high G, 1·5%; and (●) high G, 2·0%.

Table 1. Work to fracture values for high M and high G alginate gels at two calcium ion concentrations; mean ± standard deviation

Relative calcium concentration	Work to fracture ($J\ m^{-2}$)	
	High M—2·5%	High G—2·3%
Standard	3·80 ± 0·52	3·83 ± 0·97
2X	3·72 ± 0·76	5·73 ± 1·10

tions of this polysaccharide, the work to fracture increased. Over the range of crosshead speeds investigated, the work to fracture of high G alginate gels increased linearly as crosshead speed increased.

In contrast to the fracture properties of alginate gels, which would seem to decrease at higher gel strength, agar gels behave in a manner more typical of mung bean starch gels (Fig. 6). Higher polysaccharide concentrations are associated with increased work to fracture values, this increase being linear at concentrations below 5%.

Fracture toughness values could not be obtained for gels of gellan gum and the xanthan gum blends. Gellan gum gels exhibited extremely marked syneresis as the wedge penetrated the gel, which apparently toughened the gels in the region surrounding the wedge. Cracks appeared late in the test and distant from this region, and work to fracture could not be calculated. Xanthan gum gels flowed as the wedge penetrated, no crack forming even when the wedge had virtually travelled the entire depth of the cube. Greater crosshead speeds were investigated in an attempt to initiate a crack, but in all cases the gel was found to flow.

DISCUSSION

The advantage of a wedge test over a simple compressive strength test, in which a cube of material is compressed

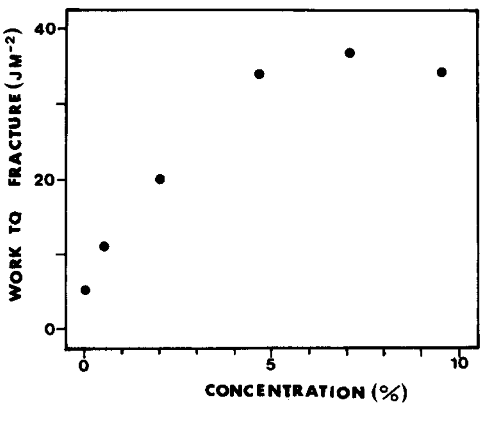

Fig. 6. Work to fracture values of agar gels as a function of polysaccharide concentration.

between flat plates (Oakenfull, 1987), is that the various mechanical processes operating (friction, flow and fracture) can, in principle, be partitioned. The test is also to some extent imitative of incisal biting (Vincent *et al.,* 1991). The work of fracture, which is also commonly referred to as the fracture toughness of a material (Atkins & Mai, 1985), can be directly estimated and is much more likely to be a material property (independent of specimen size) than the average stress at which the cube fails in simple compression. Both the results given here and those of mung bean starch gels (Lucas *et al.,* 1992) support the view that, at low displacement rates of the wedge, energy losses due to flow and friction are often low enough for the test to be suitable for estimating the specific work of fracture. It should be emphasized that, at higher crosshead speeds, friction is an important factor. The test failed with xanthan gum gels because the entire structure flowed, which quickly dissipated the energy imparted to the gel by the wedge. The problem with gellan gum gels was not that the structure flowed but the 'open' nature of its network, which allowed water to be squeezed out like a sponge. The test probably only works for gels with a relatively close network that do not synerese easily.

In alginate gels it would appear that hysteresis is greater at high concentrations. This requires further study as it is the opposite in mung bean starch gels (Lucas *et al.,* 1992). Our results also support the view of Luyten and van Vliet (1989), Lucas *et al.* (1992) and Luyten *et al.* (1992) that the fracture toughnesses of gels are extremely low (in the range ascribed to ceramics; Atkins & Mai, 1985). Nevertheless, these values are also somewhat higher in most gels than the minimum energy required, that to overcome the surface tension of water (Luyten *et al.,* 1992).

We have followed a more conservative procedure in this study than Lucas *et al.* (1992) and refer to the total work done on the specimen, divided by the crack surface area, as the work to fracture. This simplifies the test; nevertheless, it is clear that agar gels behave in a manner similar to starch gels, in that gel concentration is approximately linearly related to the work to fracture up to a critical value. However, this was clearly not true for alginate gels. The work to fracture of these gels was considerably lower at higher polysaccharide concentrations. This is difficult to explain. The only theoretical predictions that can be employed follow from the suggestion of Ashby (1989) that gels be treated as isotropic cellular solids with a cell size of molecular dimensions. The fracture toughness of cellular solids depends on their density. With gel concentration being equivalent to gel density, the work to fracture (roughly equivalent to the critical strain energy release rate) would increase as the square of the concentration if this characteristic is correct (Gibson & Ashby, 1988). The fact that this prediction is not met suggests that the buckling and bending of the fibrillar structural parts of these gels when they are loaded is not important. The best candidate for 'cellular modelling', the 'egg box' arrangement suggested for alginate gels, behaves contrary to Gibson and Ashby's (1988) predictions. We have found that the fracture toughness of mung bean gels is approximately linearly related to concentration. This reflects the importance of spherical granules in its structure, for which bending/buckling models are inappropriate (Lucas *et al.,* 1992).

A considerable difference in the fracture properties between the two alginate types was evident at low concentrations, whilst at higher concentrations these differences were not as apparent. This could be interpreted as suggesting that, initially, the two alginates form gels by different mechanisms but at higher calcium concentrations the gels possess similar molecular interactions.

In contrast to gels prepared by thermal treatment, alginate gels are formed by the coupling of segments of poly-guluronic acid (junction zones) by divalent cations, especially calcium. Rheological properties of these gels are therefore dependent not only upon the concentration of polysaccharide but also on the amount of available calcium (Smidsrod, 1974). Unfortunately, as the proportion of calcium is raised above 7·2% of that of alginate (based on alginate containing a high proportion of guluronic acid residues), the gels synerese as the non-junction zone regions of the polysaccharide chains associate. We wished to study fracture properties of alginate gels as affected by the comparative number of junction zones. In an endeavour to avoid complications arising from interaction of non-junction zone regions and the limited understanding of the amount of poly G regions in each of the alginates, the calcium concentration was maintained at a constant level, which was below that which causes syneresis but above that required for gelation. It is conceivable that, at the higher alginate concentrations, calcium may well have become limiting. Investigating the effect of doubling the calcium concentration (Table 1), it was interesting to note that there was no significant difference in the work to fracture for 2·5% high M gels, whilst the work to fracture of gels of high G was increased, though not to the extent that might be expected. This is suggestive of the fact that, at concentrations above 2% for the high G alginate, there remained a number of free reaction sites, while for the high M alginate, these sites were fully satisfied. Unfortunately, information on the relative proportions of poly G, poly M and alternating regions was not available. Therefore it is difficult to establish if these effects could be attributed to poly G region association or to the association of poly M regions which would take place in excess calcium (Oakenfull, 1987).

Polymer chains within a gel will be present both in highly associated regions (crystalline state) and regions of little interaction. Fracture lines may well take a path of least resistance, namely through non-crystalline regions. Fracture properties of a gel may therefore reflect the nature of the non-junction zone material as opposed to the physical properties of the junction zones *per se*. Gels made with the two types of alginates and different polymer concentrations will represent systems containing variable proportions of junction zonal material. Different fracture properties between these systems may well reflect the density of intercrystalline polymer chains.

In contrast, the initial increase in work to fracture values for agar with increasing concentration may reflect greater chain strength of this secondary structure. It is also of interest to note that the fracture properties of starch gels were found to decrease at a lower 'threshold' value for starches which had previously been retrograded (Lucas *et al.*, 1992). The retrograded material will contain a far greater number of interacted chains and therefore possess much weaker intercrystalline regions.

High concentrations of alginates are difficult to disperse completely. Incomplete dispersion of the polysaccharide may, in part, contribute to the observed effect. Inhomogeneity of the hydrated material could result in regions of high concentration 'microgels' within the main gel network. This may well account for only a small proportion of the decreasing work to fracture, since the dependence of the work to fracture upon concentration is greatest at low alginate concentrations; at such low levels, complete dispersion would not normally be expected to be a problem.

Textural observations on these gels have suggested that unlike gel strength, the perception of brittleness cannot be manipulated by increasing the calcium concentration above that necessary for gelation (Kelco, pers. comm.). In contrast, compressive strength is dependent upon the number of interacting junction zones. Crosslink density, a function of calcium interaction, if reduced, will result in an increased average length of reorienting segments at the point just before crack formation. Mitchell and Blanshard (1976) have suggested that long reorienting segments at the point of gel failure will ultimately result in elastic gel properties. Fracture properties would therefore seem not to be related to elastic properties in these gels. The elastic and fracture properties of gels should therefore be considered separately.

CONCLUSION

We suggest that the fracture properties of gels are dependent not only upon the properties of the junction zones but also the integrity and extent of interaction of the non-junction zone material. Measurement of fracture properties provides additional information on the rheological properties of gels not picked up by deformational studies. However, further work is required before mechanisms responsible for fracture properties can be elucidated.

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