Fracture toughness of mung bean gels

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Mung bean starch gels, of 4.5–14 wt% solid content, were stored at room temperature and at 4 °C in a refrigerator and then cracked quasi-statically by driving a 40° included-angle wedge into intact specimens in order to determine their fracture toughness. The work to fracture of the gels, calculated without respect to energy loss due to viscoelasticity or to frictional effects between wedge and gel, varied from 0.5 to 22 J m^{-2} and were higher for those gels stored at low temperature. For gels stored at room temperature, the effect of viscoelasticity and wedge–gel friction was examined. Hysteresis (viscoelastic energy losses) was concentration-dependent. In 8 wt % gels, it accounted for about 10% of the total work done in the wedge tests and did not depend significantly on crosshead speed. Frictional work, largely due to adhesion between the gel and the wedge, was negligible at low speeds but increased rapidly with crosshead speed. However, whether correction factors are introduced or not, the results substantiate the very low fracture toughness of gels. Between 5 and 11 wt % concentrations, the work of fracture varied linearly with gel concentration. Variation in crosshead speed from 2 to 200 mm min^{-1} increased the work to fracture by a factor of two.

1. Introduction

Gelling agents are generally high molecular weight proteins or polysaccharides which, in small amounts and under certain conditions, bind large quantities of water into fracturable solids. Polysaccharides are used extensively as gelling agents in foodstuffs [1]. However, differences in the mode of gelation, quality and stability of the resulting gels are wide enough that the various gel-forming polymers cannot be used interchangeably [2]. In order to determine specific textural applications for a gelling agent, the physical properties of the gels must be determined.

Starch, a natural polysaccharide obtained from plants in the form of granules, is used extensively by the food and allied industries as a gelling agent. The size range (2–100 μm) and stability of these granules varies between botanical sources. Some, like potato starch, are easily broken up by the shear forces experienced as a paste is mixed, while others, like mung bean starch, are very stable. Unlike other commercially viable polymers, starch is composed of two primary components, amylopectin and amylose. Both are homopolysaccharides of glucose but they differ in the extent of their molecular branching. Amylopectin is a highly-branched molecule (4–5% of the inter-unit linkages constitute branch points) with a molecular weight of about 10^8. Amylose is essentially linear, branching at the rate of one per several thousand glucose units. Associated also with the granules in variably small amounts are lipids, proteins and ash.

Starch granules are unaffected by water until heated above a certain temperature (the "gelatinization" temperature) at which crystalline regions in the granule "melt" with subsequent solvation of the macromolecules. The process is progressive, usually starting at about 60 °C and completed above 110 °C. Concomitant with loss of crystallinity, granules swell irreversibly. The amylose, which is insoluble below 150 °C, leaches from the granules and disperses in the intergranular spaces. This heated suspension behaves as a viscoelastic paste but, on cooling, amylose precipitates out and the paste transforms into an elastic gel. This gel can be described as a composite with the swollen amylopectin as a filler in an amylose gel network [3]. Gelation of amylose involves microcrystalline regions where parts of the amylose chains associate to form "junction zones", thereby producing a continuous three-dimensional framework [4].

We were interested in two issues. Firstly, the only prior report of the fracture toughness of pure gels is that of Luyten and van Vliet [5] who report potato starch gels as having a work of fracture of 1–2 J m^{-2}, utilizing a cutting wire of various diameters. We investigated the range of values associated with gel concentration and strain rate. Secondly, we were concerned as to whether such measurements could help to define the transition concentration at which a sol is capable of gelling. We used mung bean starch because granules of this starch are unusually resistant to shear forces experienced during gel preparation [6]. Pilot

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studies indicated that the wedge test [7–9] which we employed worked well with such gels. Mung bean starch is used in the food industry in noodles due to its good gelling properties. It forms gels at relatively high concentrations without the addition of sequestrants or the manipulation of pH.

2. Experimental procedure

Dispersions of mung bean starch (4.5–14 wt %) in distilled water were heated in a round-bottomed flask, rotating at 120 r.p.m., at 90 °C for 15 min. This method was selected to minimize disruption of individual starch granules. Gels were set in cube-shaped 20 mm plastic moulds and left either at 22–24 °C (room temperature) or 4 °C for 24 h in a saturated atmosphere. Most tests were done with gels of 6–12 wt % concentrations.

Testing was performed on a Shimadzu DC-5000 Universal Testing Machine at crosshead speeds of 2–100 mm min^{-1} using a sharp 40° included-angle steel wedge pressed on to the gel and splitting it gradually into two equal parts [7–9]. This wedge was attached to the undersurface of the crosshead in line with 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 (Fig. 1).

In such tests, to a degree depending on the material being tested, the load increases with displacement as at first elastic and then plastic deformation takes place. Once a critical amount of strain energy has been imparted to the material, a crack forms ahead of the tip of the wedge. At any chosen moment, the crosshead can be stopped which prevents the crack from propagating further. Any strain energy remaining in the material can be taken back into the testing machine by reversing the crosshead. If the unloading curve returns to the origin, the fracture toughness of the material can be estimated from the area under the loading curve (the total work done) and this be divided by the nominal surface area of the crack formed. This is the "work-area" method described by Gurney and Hunt [10] and Atkins and Mai [11].

The method is straightforward only for elastic materials. Viscoelastic materials always display some energy loss (hysteresis) when they are unloaded. Thus, even without cracking, there is an area formed on force–deformation plots. In these circumstances, the work done can be termed the "work to fracture" [7]. Further analysis is necessary to establish the specific work of fracture by subtracting energy losses remote from the crack from the total work done. In the wedging test, in addition to the intrinsic energy loss due to viscoelasticity, energy is also dissipated due to friction between the wedge and the gel. The wedges can be lubricated to try to avert this [8] but we found that this made no difference with the gels tested. The angle of the wedge is liable to affect this frictional force with a large included angle, such as that used, being likely to reduce it [12]. Neither of these sources of energy loss is necessarily large, but they need to be estimated. We attempted this only for gels stored at room temperature.

Schematic diagrams of force–displacement graphs that we obtained with wedges are shown in Fig. 2. As the wedge contacted the gel, loading followed the uppermost curve in Fig. 2a from O to A, at which point the cube of gel was very distorted. Beyond A there was a decrease in the gradient, followed by a sharp decrease in force to B as the gel cracked. The specimen had regained its original shape by point B except for a slight enlargement due to the shape of the wedge. From A to B, the gel was cracking at a much higher velocity than the crosshead displacement rate. From B to C, with further displacement of the crosshead, the gel continued to crack, but much more stably and at a rate consistent with the crosshead speed. At C, the crosshead was reversed at the same speed. The gel unloaded rapidly to zero load at D. Further retraction of the crosshead either resulted in a zero load back to the origin O (i.e. following the line
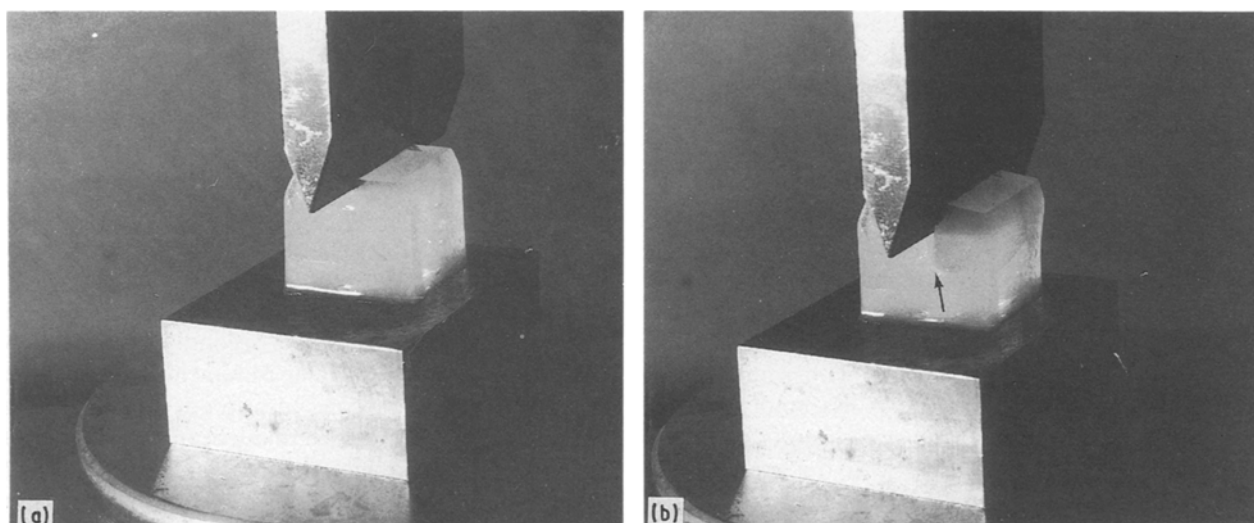

Figure 1 (a) Wedge indenting a cube of mung bean starch gel positioned on a steel block sitting on a compression platen in the early part of a test. (b) A crack (arrowed) has formed in front of the wedge. This can be seen propagating through the entire thickness of the gel.
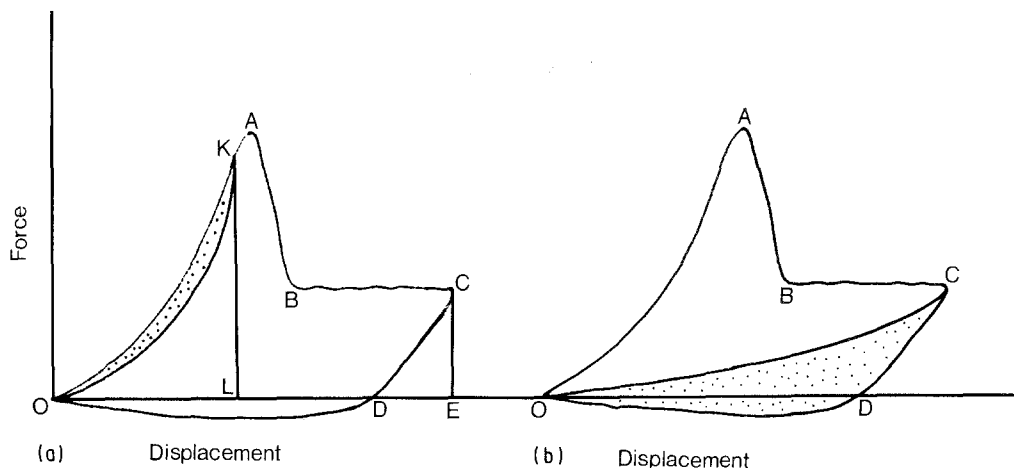
Figure 2 Schematic diagrams of force–displacement curves for mung bean starch gels (see text).

DO) or a return to the origin via the curve with a tensile force. The latter indicated that adhesional friction was important.

It is clear that the total area contained by this curve (OABCD in Fig. 2b) cannot be assumed to be that necessary for crack formation. Hysteresis was estimated by the method of Holt and Schoorl [13]. The load A at which cracking started with the wedge was noted and, in a second test with an identical cube, the gel was loaded to between 70 and 90% of that cracking force (indicated by K in Fig. 2a). The crosshead was then reversed producing a hysteresis loop (shown as the stippled area in Fig. 2a). This stippled area divided by the strain energy imparted to the specimen at this maximum load (area given by OKL with OK following the uppermost, loading, curve) gives the hysteresis ratio β [14]. Assuming the same ratio to apply at point A in Fig. 2a, the total work done in cracking can then be multiplied by $(1 - \beta)$ to give a "work to fracture" corrected for hysteresis.

The other method attempted to compensate for both viscoelastic and fractional effects combined. Reversal of the crosshead during unloading of a cracked specimen was stopped just before (< 1 mm) the tip of the wedge cleared the gel. At this point, the force was usually zero. The crosshead was then advanced once more into the gel until the displacement at C in Fig. 2b was reached. The loading curve passed through O to C but not through D. The crosshead was then again reversed. The unloading curve passed from C to O through D as before. The stippled area in Fig. 2b formed an estimate of frictional work plus hysteresis. This was expressed as a proportion of the total work done in cracking.

The constant force for stable cracking (the height CE in Fig. 2a) could be used to derive fracture toughness directly by dividing this final force by the width of the cube, as with microtoming [15]. However, we were not sure that all the strain energy imparted by the wedge in this phase of the test was going into fracture. Therefore, we compared this direct estimate with those derived by the work-area method.

The areas under the curves were obtained by digitizing with a Janel Sigmascan 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, measurements being made with engineering calipers.

3. Results

Examples of force–deformation curves obtained from wedging are shown in Fig. 3 with differing concentrations of gel. At the crosshead speed of 5 mm min^{-1} shown, at which most tests were done, the tensile force during crosshead reversal was negligible. The steepness of the loading curve, the force at which stable cracking took place (between B and C in Fig. 2) and the total area under the curve increased in general with concentration up to 11 wt %, more steeply with refrigerated than with room-temperature specimens. When the crosshead was reversed just before the loading at which cracking generally ensued, an indented region of up to 1 mm width could generally be seen. Provided that cracking had started, there was little variation of fracture toughness with the length of crack. The upper few millimetres of the fractured surfaces of all gels showed parallel striations but were otherwise smooth. The remainder of the surface was rough.

Refrigerated gels had higher works to fracture than those stored at room temperature (Table I). However, cracking in refrigerated gels was rarely stable, even between points B and C (Fig. 2), showing a distinct "stick–slip" form (Fig. 3).

The hysteresis ratio β decreased sharply with concentration (Fig. 4), no apparent difference being seen between refrigerated or room-temperature stored specimens. The relationship $\beta = -0.0203$ (wt %) $+ 0.343$ was derived from a least-squares regression ($r^2 = 0.64$). This relationship was used to correct the work to fracture by multiplying uncorrected values given in Table I by $(1 - \beta)$. Whether the work of fracture is corrected for hysteresis losses or not, this work increased approximately linearly with concentration up to 11 wt % (Fig. 5). The effect of correction for hysteresis (Fig. 5b) was to decrease the slope of this relationship. Least-squares regressions gave the x intercept as 5.1–5.3 wt % for room-temperature storage and 4.7–4.9 wt % for refrigerated specimens. Tests on

TABLE I Comparison of the works to fracture of mung bean starch gels depending on storage condition; values are means ± standard deviation

Concentration (wt %)	Room temperature		Refrigerator	
	n	Work to fracture $(J\,m^{-2})$	n	Work to fracture $(J\,m^{-2})$
6	11	2.04 (0.92)	11	3.91 (1.07)[a]
7	10	4.27 (0.62)	8	8.29 (0.57)[a]
8	11	7.85 (1.51)	10	14.27 (3.53)[a]
9	9	10.73 (1.6)	10	19.38 (3.85)[a]
10	12	12.88 (2.71)	10	22.7 (3.24)[a]
11	10	14.3 (2.17)	10	22.04 (3.28)[a]
12	8	13.8 (2.45)	11	22.34 (6.2)[a]

[a] Indicates a significant difference between conditions (Kolmogorov–Smirnov two-sample test) at $p < 0.01$.
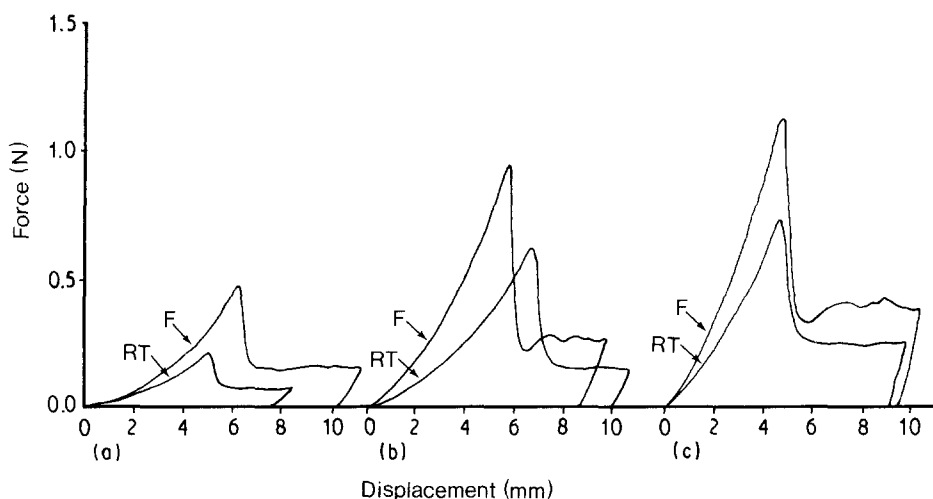

Figure 3 Actual force–deformation curves obtained for mung bean starch gels of (a) 7, (b) 9 and (c) 11 wt % concentrations stored at room temperature (RT) and in a refrigerator (F) at 4 °C. The refrigerated gels are all "tougher" (higher work to fracture) than those stored at room temperature (Table I).
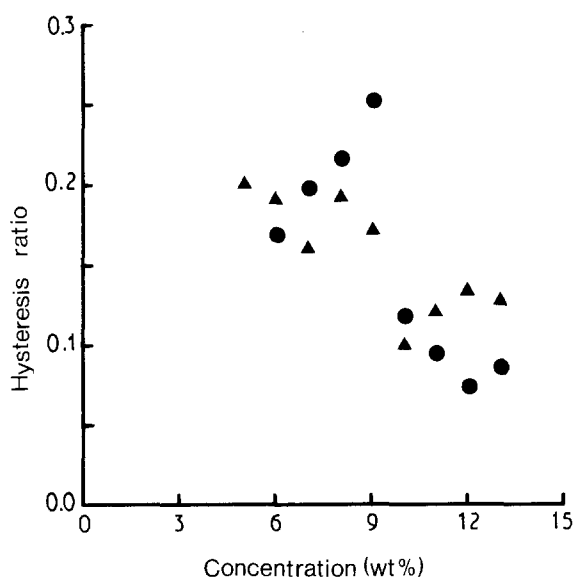

Figure 4 Hysteresis ratio plotted against gel concentration for (●) room-temperature stored and (▲) refrigerated gels. A common slope was calculated and used to correct for energy dissipated within the gel during the test.

4.5 wt % gels, however, showed that both were fracturable solids, though the work areas for those stored at room temperature were too small to measure.

The estimate of fracture toughness, derived directly from the final force divided by cube width, could only be obtained easily for gels stored at room temperature. A comparison with work-area methods demonstrated that values were equivalent to the total work done. Correction of the work done for friction and hysteresis produced lower estimates (Fig. 6).

For 8 wt % gel concentrations, the effect of cross-head speed on the work to fracture was investigated. The hysteresis ratio was not affected by the displacement rate of the wedge, while friction and hysteresis combined increased markedly with speed (Fig. 7).

At higher crosshead speeds, the tensile force became much greater upon crosshead reversal and the cube could be seen to be lifted a short distance above the platen on which it rested before detaching from it. Whether the work of fracture is corrected for friction plus hysteresis or not, the work to fracture increases over two orders of magnitude of crosshead speed by a factor of 2 to 3 (Fig. 8).

4. Discussion

Whether correction for energy losses or work done against friction was made or not, the works to fracture for these gels were very low, confirming a previous
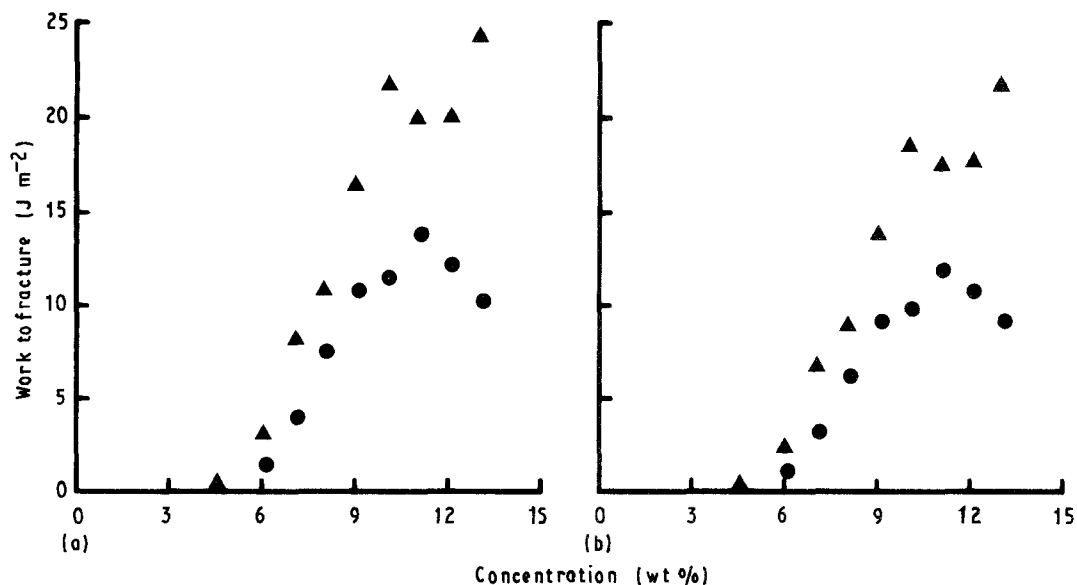
Figure 5 Work to fracture of gels, (a) uncorrected and (b) corrected for hysteresis, plotted against gel concentration for (●) room-temperature stored and (▲) refrigerated gels. Whether corrected for hysteresis or not, the work to fracture is approximately linearly related to concentration up to about 11 wt %.
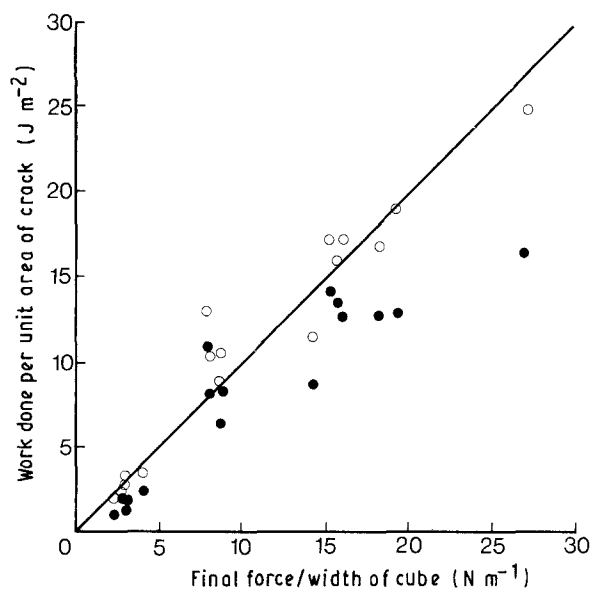

Figure 6 Work to fracture, (●) corrected for friction and hysteresis or (○) left uncorrected, plotted against the final cracking force divided by the width of the gel cube (room-temperature stored gels only). Corrected work areas give the smallest values.
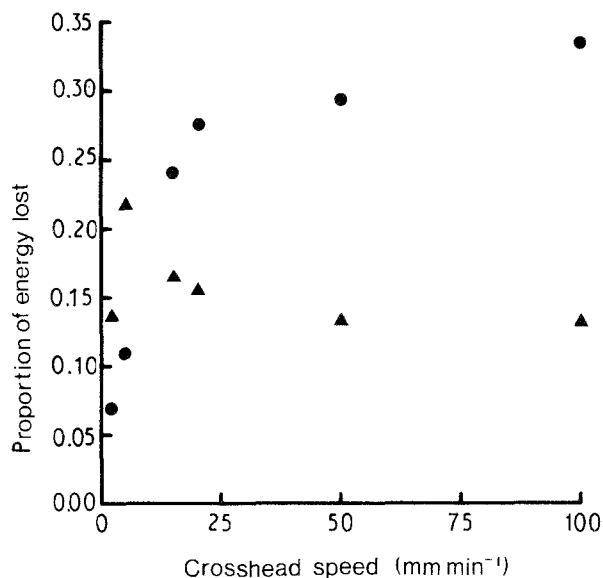

Figure 7 Proportion of energy lost (i.e. unrelated to cracking) in wedging tests attributable to (●) friction plus hysteresis and (▲) hysteresis alone, plotted against crosshead speed. At low speeds, both are of similar magnitude. Friction plus hysteresis increases markedly with speed, implying that it is the frictional component that causes this.

study [5]. The similar estimates for toughness obtained either from the total work done or from the final cracking forces suggests that energy is not dissipated at crack initiation in excess of that required to propagate the crack. However, in circumstances where accurate estimates of toughness are required, the smaller values derived from corrected work areas would seem better than those derived from the cracking-force method.

The study suggests that gel concentration may be linearly related to the work to fracture over the range of concentrations that would normally be used in applications.

For most of the duration of the fracture tests, the crack velocity was more or less that of the crosshead

speed. At low crack velocities, such as the 5 mm min^{-1} crosshead speed at which most tests were done, friction was apparently negligible and hysteresis can probably be neglected because a 10% error is probably less than other errors in the test method. As such, wedging forms a convenient and simple test [9]. It also offers the further possibility of examining the yield stress of gels since this could be derived from the load at cracking and the indented area, providing something akin to a hardness value. If extreme accuracy were needed, then it might be important to estimate gravitational effects. Even with a thickness of 10 mm of gel on either side of the wedge, the low-concentration gels are so compliant in bending that gravitational forces could aid crack propagation and also be
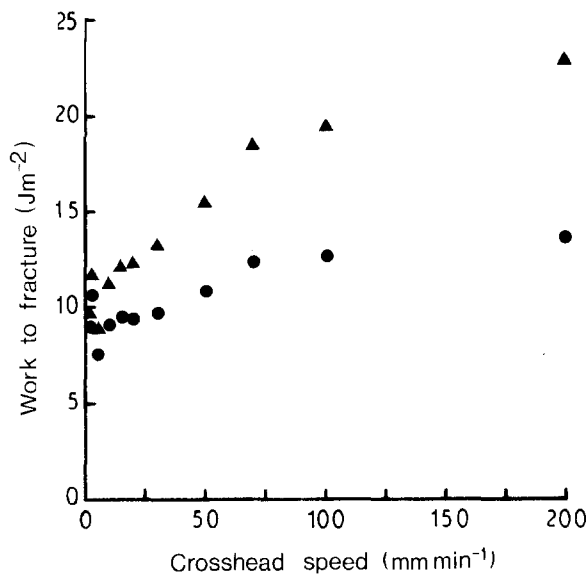
Figure 8 Work to fracture, (●) corrected for friction plus hysteresis or (▲) left uncorrected, plotted against crosshead speed.

partly responsible for the rapid unloading of the gel with crosshead reversal.

Initial cracking (between points A and B in Fig. 2a) was much more rapid than crosshead speed. Since the work of fracture increases with crack velocity (Fig. 8), the overall toughness will be slightly overestimated at any given crosshead speed due to this. However, this effect is probably small.

The effect of lowering the temperature at which the gels were stored was probably to increase their crystallinity. The fact that the force in the cracking phase of the test did not stabilize for refrigerated gels suggests that this crystallization was uneven, possibly indicating that it involved the granules and not the matrix.

The fracture toughnesses reported here are among the lowest ever reported for solids, this extreme brittleness being the major reason for their use in foodstuffs. Other polysaccharide gels, such as those made from agar and alginates, are also very brittle [16] and it must be doubted whether any gels have substantial toughness. In consequence, they are the least engineerable of materials in isolation. They are widespread in nature, no doubt partly as a cheap packing material to obstruct bacterial invasion. The alginate gel in *Laminaria digitata*, a common seaweed, may function like this. The fracture toughness of *L. digitata* between the fronds is extremely low, being less than $1 \, J \, m^{-2}$ [17] and is probably attributable to the gel. However, when incorporated into a composite like skin, gels may provide considerable resistance to fracture because their shear modulus is so low that strain energy cannot be transferred between the fibres.

A J-shaped stress–strain curve in tension is typical of animal soft tissues, with the initial part of the curve having a very low slope [18]. Interestingly, mammalian tooth enamel, the stiffest of all vertebrate tissues, has a stress–strain curve whose slope increases at higher strains [19]. The structure of its hydrated proteinaceous matrix is unclear but, unlike the matrix

of bone and other mesodermally derived vertebrate hard tissues, it is not generally described as fibrous [20]. Fox [19] has shown that mature enamel is significantly viscoelastic (as are gels in general). The fracture toughness of enamel between the highly mineralized prisms is very low, some $10–15 \, J \, m^{-2}$ [21, 22]. Though this has been compared to ceramics [21], the fracture path is entirely within the matrix. This might offer indirect support for considering tooth enamel as being a highly-filled gel.

Acknowledgements

References

1. G. J. BROWNSEY and V. J. MORRIS in "Food Structure – Its Creation and Evaluation", edited by J. M. Blanshard and J. R. Mitchell (Butterworths, London, 1987) p.7.
2. G. GLICKSMAN, in "Polysaccharides in Foods", edited by J. M. V. Blanshard and J. R. Mitchell (Butterworths, London, 1987) p. 185.
3. S. G. RING and G. STAINSBY, *Prog. Food Nutr. Sci.* **6** (1982) 323.
4. M. J. MILES, V. J. MORRIS and S. G. RING, *Carbohyd. Res.* **135** (1985) 257.
5. H. LUYTEN and T. van VLIET, in "Gums and Stabilisers for the Food Industry 5", edited by G. O. Phillips, D. J. Wedlock and P. A. Williams (Oxford University Press, Oxford, 1989) p. 117.
6. C. G. OATES and W. P. LEE, Unpublished Results.
7. B. J. DOBRASZCZYK, A. G. ATKINS, G. JERONIMIDIS and P. P. PURSLOW, *Meat Sci.* **21** (1987) 25.
8. J. F. V. VINCENT, *Adv. Bot. Res.* **17** (1990) 235.
9. J. F. V. VINCENT, G. JERONIMIDIS, A. A. KHAN and H. LUYTEN, *J. Texture Stud.* **22** (1991) 45.
10. C. GURNEY and J. HUNT, *Proc. R. Soc. Lond.* **A299** (1967) 508.
11. A. G. ATKINS and Y. W. MAI, in "Elastic and Plastic Fracture" (Ellis Horwood, Chichester, 1985) p. 80.
12. G. A. HANKINS, *Proc. Instn. Mech. Engrs.* **1** (1925) 611.
13. J. E. HOLT and D. SCHOORL, *J. Mater. Sci.* **18** (1983) 2017.
14. E. H. ANDREWS, in "Mechanical Properties of Biological Materials", edited by J. F. V. Vincent and J. D. Currey (Cambridge University Press, Cambridge, 1980) p. 22.
15. A. G. ATKINS and J. F. V. VINCENT *J. Mater. Sci. Lett.* **14** (1984) 2747.
16. C. G. OATES, P. W. LUCAS and W. P. LEE, *Carb. Poly.*, in press.
17. J. F. V. VINCENT and K. GRAVELL, *J. Mater. Sci. Lett.* **5** (1986) 353.
18. J. E. GORDON, "Structures" (Penguin, London, 1978) p. 156.
19. P. G. FOX, *J. Mater. Sci.* **15** (1980) 3113.
20. W. G. ARMSTRONG and R. L. SPEIRS in "Dental Anatomy and Embryology", edited by J. W. Osborn (Blackwell, Oxford, 1981) p. 206.
21. R. T. RASMUSSEN, R. E. PATCHIN, D. B. SCOTT and A. H. HEUER, *J. Dent. Res.* **55** (1976) 154.
22. R. HASSAN, A. A. CAPUTO and R. F. BUNSHAH, *ibid.* **60** (1981) 820.