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Deformation and Fracture of Wheat, Corn and Rice Starch Gels in Lubricated and Bonded Uniaxial Compression

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SUMMARY

Wheat, corn and rice starch gels were prepared by heating 10% dispersions at 80°C, 94°C and 121°C for 30 min. The response of these gels in uniaxial compression was determined under both bonded and lubricated conditions up to the point of fracture. For corn and wheat starch gels the stress–strain curves in lubricated compression were relatively insensitive to gel preparation temperature. For rice starch, the modulus in lubricated compression was lower than for corn and wheat. Further, the modulus of rice starch gels decreased with increasing temperature of gel preparation. Stress at fracture for all starches was strongly dependent on preparation temperature, being highest for samples prepared at 94°C and lowest for the 80°C gels. In bonded compression, samples become barrel shaped but the elastic modulus can be corrected for this geometric effect. When this is done, the stress–strain curves for both bonded and lubricated compression agree, but stress and strain at fracture are much lower in bonded compression. Uniaxial compression measurements such as these can provide deeper insight into the ultimate properties of gels and offer a viable alternative to purely empirical methods, such as the embedded disc, for evaluating fracture behavior of gels and other soft foods.

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INTRODUCTION

The concept that texture is not a simple property of foods but is extremely complex is generally recognized (Kruger & Murray, 1976; Larmond, 1976). In food systems starch occupies a central position and hence the instrumental determination of texture profiles in starch gels is of exceptional interest. Further, an ultimate goal of research in this area is to relate textural and functional properties to molecular structures and interactions. Zobel (1984) suggests that the extent to which amylose and amylopectin are separated or associated, in the granule as well as in the disperse state, could govern the physical properties of fresh and aged gels. New technologies in thermal processing of starch products in both unlimited and limited amounts of water demand a new look at the gelatinization and gelation of starch under various conditions of mechanical work input and temperature.

Textural profiles obtained by uniaxial compression experiments yield a number of characteristics such as hardness, cohesiveness, adhesiveness, etc., as enumerated by Larmond (1976). It has been shown that these uniaxial compression experiments as normally carried out yield stress–strain data that depend not only on a bulk material property (modulus of elasticity) but also on frictional effects at the sample/platen interfaces (Bagley *et al.*, 1985*a*,*b*). The problem has long been recognized, for example by Ward & Saunders (1958) and Forster (1955), and has been addressed in recent years in food systems by Culioli & Sherman (1976). To characterize separately and accurately in fundamental terms the bulk material property of elastic modulus and the surface behavior, it is thus essential to control the frictional effects, by lubricating the interface, as is routinely done by Montejano *et al.* (1983), or by bonding the sample to the platen.

Fracture properties of food systems can be of both practical and theoretical significance in evaluating effects of molecular structure and interactions on food properties. Interesting fracture effects of hydrocolloid–starch interaction have been reported (Christianson, 1982), but often fracture or strength properties are measured by empirical or semi-empirical methods which are difficult to interpret. This is because of the stress patterns, e.g. in the embedded disc or penetrometer methods, which are too complex to analyze. Analysis of stress and strain patterns in lubricated and bonded uniaxial deformation does appear possible, however (Gent & Lindley, 1959).

This present work was undertaken to examine the effect of sample preparation temperature on the properties of gels from three different starches. Corn, wheat and rice starch gels were prepared at 80°C, 94°C and 121°C. Gel rigidity and gel strength were evaluated in both lubricated and bonded uniaxial compression. It will be shown that, while both modes of measurement yield the same initial modulus values, failure in bonded compression occurs at much lower apparent stress and strain levels than in lubricated compression.

MATERIALS AND METHODS*

Materials

Starches used in these experiments were obtained from commercial sources. Wheat starch (Aytex P) was obtained from the Henkel Corp., Minneapolis, Minnesota, corn starch (Globe 3005) from CPC Inc., Chicago, Illinois, and rice starch (No. S-7260) from Sigma Chemical Co., St Louis, Missouri.

Gel preparation

Starch (10% dry weight) was dispersed in distilled water and stirred for 15 min to wet the starch thoroughly before heating. Dispersions were then stirred in a Corn Industries Viscometer (CIV) at 80°C or 94°C for 30 min after the samples had reached a final temperature (24–27 min). For the samples processed at 121°C, starch dispersions were precooked in the CIV at a bath temperature of 70°C for 30 min. This step was necessary to swell the granules and reduce their density (as well as increase dispersion viscosity) so that the granules remained suspended during subsequent autoclaving under static conditions. Approximately 5 min were required to transfer the hot dispersion to the autoclave. After cooking or autoclaving for 30 min, the processed dispersions were poured immediately into molds (77 mm diameter and 20 mm height) and held at room temperature for 24 h. Gels so

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the US Department of Agriculture over other firms or similar products not mentioned.

formed are referred to in the text as 80/30, 94/30 and 121/30 gels. Corn starch gels were also tested after autoclaving in a zipperclave (Autoclave Engineers, Inc., Erie, Pennsylvania) with turbine-type agitation. The turbine operates at 70 rpm. Wheat and rice starch gels prepared at 10% solids in the stirred autoclave were not rigid enough to permit compressional testing.

Mechanical testing

Compressional tests were carried out on an Instron Universal Testing Machine (Model TT-CM) with a 50 kg load cell, at a cross-head speed of 0·5 cm min^{-1}. Gels were lubricated with paraffin oil on both upper and lower surfaces and then were compressed between Instron platens covered with adhesive-backed Teflon. In bonded compression, cyanoacrylate adhesive was used to bond the gel to aluminum foil which interfaced with the Instron platens. Compressional tests were carried out in a controlled temperature (22°C) and relative humidity (50% RH) room. Three batches were prepared separately at each temperature and four gels from each batch were examined in compression to verify data reproducibility.

Starch solubility

Starch dispersions were prepared under the same temperature/time conditions that were used for the preparation of gels except that the concentrations were reduced to 4% for the 80/30 and 94/30 preparations and to 2% for the unstirred 121/30 gels. It would have been preferable to measure starch solubility on 10% dispersions but experimental difficulties made this impractical. Previous experience with starch heated in the gelatinization range showed good correlation between viscous behavior over a wide concentration range and swelling behavior measured at 2–4% (Christianson & Bagley, 1983). The procedure was thus followed in this work too but it is recognized that, while the results at 2–4% may provide a comparative index for relative changes in starch solubility during processing at 10%, the results do need to be regarded with caution. For the stirred 121/30 gels a 10% dispersion was prepared, then diluted to 5% with 70°C water prior to filtering. Aliquots of the hot dispersions were filtered im-

mediately according to a method established earlier (Christianson & Bagley, 1983). Filtrates were lyophilized to obtain weights of filtered material. The 80/30 and 94/30 filtrates were clear but the 121/30 filtrates were cloudy both in the stirred and unstirred preparations.

Calculations

In lubricated uniaxial compression the cylindrical sample of initial height h_0 and initial radius R_0 deforms to a cylinder of shorter height h but larger radius R. Assuming constant volume, R is calculated from $\pi R_0^2 h_0 = \pi R^2 h$ and if F_{TL} is the total compressive force applied to the lubricated sample the true stress, σ_L, is given by

$$\sigma_L = F_{TL}/\pi R^2 \tag{1}$$

$$= \frac{F_{TL} h}{\pi R_0^2 h_0} \tag{2}$$

The calculation of stress in bonded compression is complicated by the change in sample shape when the original cylinder is deformed to a barrel-shaped sample. The area of contact remains constant (πR_0^2) during this deformation. The extent of the bulge (Christianson *et al.*, 1985) depends directly on the strain, ε_m, in terms of $\Delta h = (h_0 - h)$, given by

$$\varepsilon_m = \frac{\Delta h}{h} \tag{3}$$

The apparent modulus, E_a, is related to the true modulus, E, by

$$E_a = E\left(1 + \frac{R_0^2}{2h^2}\right) \tag{4}$$

The stress, σ_B, in bonded compression is given by

$$\sigma_B = F_{TB}/\pi R_0^2 \tag{5}$$

where F_{TB} is the applied force. This gives the stress–strain relation as (Christianson *et al.*, 1985)

$$\sigma_B = E_a \frac{\Delta h}{h} \tag{6}$$

$$= E\left(1 + \frac{R_0^2}{2h^2}\right)\left(\frac{\Delta h}{h}\right) \tag{7}$$

Thus a plot of a corrected stress, σ_{BC}, calculated as

$$\sigma_{BC} = \sigma_B \Big/ \left(1 + \frac{R_0^2}{2h^2}\right) = E\left(\frac{\Delta h}{h}\right) \tag{8}$$

should give the same modulus, E, from the slope of a plot of σ_L against $\Delta h/h$.

RESULTS

Lubricated compression

Figure 1 shows true stress, σ_L, versus strain, $\Delta h/h$, for corn starch gels prepared at 80, 94 and 121°C (static and stirred). The response is non-linear for all samples and the responses up to a strain of approximately 0·30 for the 80/30 and 94/30 gels are nearly identical. The reproducibility of the data is good, as indicated by the variation of the stress at the midpoint of these stress–strain plots, which is better than ± 7% from batch to batch and sample to sample. The response at low strains for the 121/30 samples is appreciably lower. When corn starch is stirred during autoclaving at 121°C the resultant gel is very weak indeed. All samples were deformed beyond the point of fracture which occurs at the maximum of the stress–strain curves. The 80/30 gel is considerably weaker than the 94/30 gel but the 121/30 gel autoclaved without stirring is only marginally weaker than the 94/30 gel and breaks at about the same strain level.

Compressional response of the wheat starch gels is shown in Fig. 2. Here the stress–strain curves essentially superimpose but the 121/30

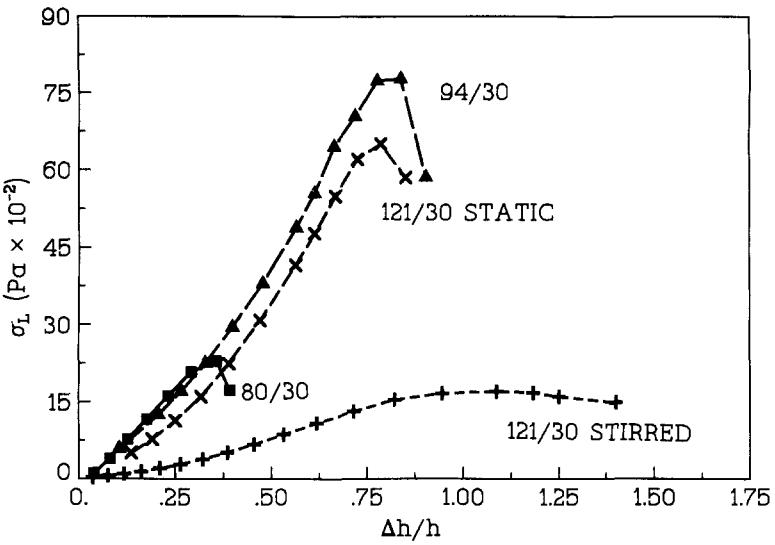

Fig. 1. Stress, σ_L, versus strain, $\Delta h/h$, for lubricated compression corn starch gels prepared by heating for 30 min at 80, 94 and 121°C (static and stirred).

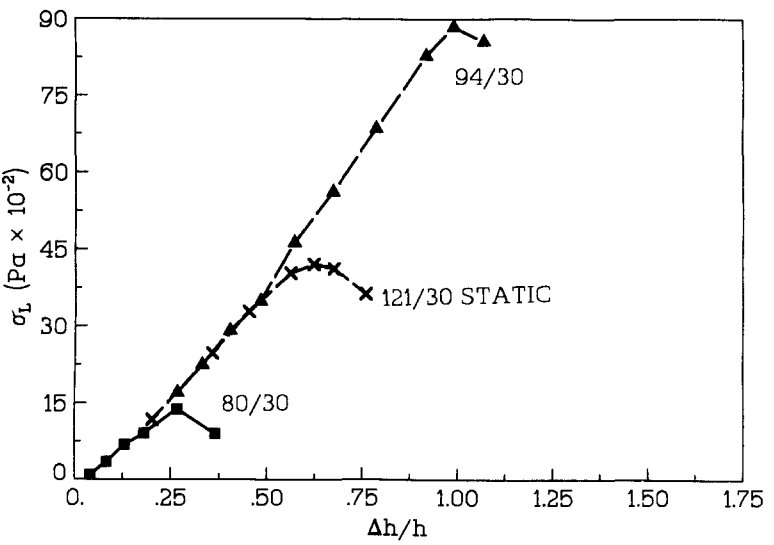

Fig. 2. Stress, σ_L, versus strain, $\Delta h/h$, for lubricated compression of wheat starch gels processed for 30 min at 80, 94 and 121°C.

sample breaks at less than half the stress of the 94/30 gel. When mechanical stress is placed on the granules by stirring during autoclaving (121°C) a viscous fluid results; a gel is not formed.

The most outstanding difference observed with the processed rice starch gels is that the moduli of all these gels (Fig. 3) are lower than those seen in wheat and corn starch. The strain at fracture is over 1·25 when rice is processed at 94/30 or 121/30. In contrast, wheat and corn starch gels fracture at strains below 1·00. The slopes of the plots for the rice gels decrease in the order 80°C to 94°C to 121°C, so that the apparent modulus is decreasing with increasing preparation temperature. The fracture stress for the 94/30 rice gel is more than six times that of the 80/30 gel. The gel autoclaved at 121°C under static conditions has only half the strength of the 94/30 gel but the strain at fracture is the same.

Bonded compression

Figure 4 shows the stress–strain curve of a 94/30 wheat starch gel, obtained under bonded conditions (curve B). The reproducibility of

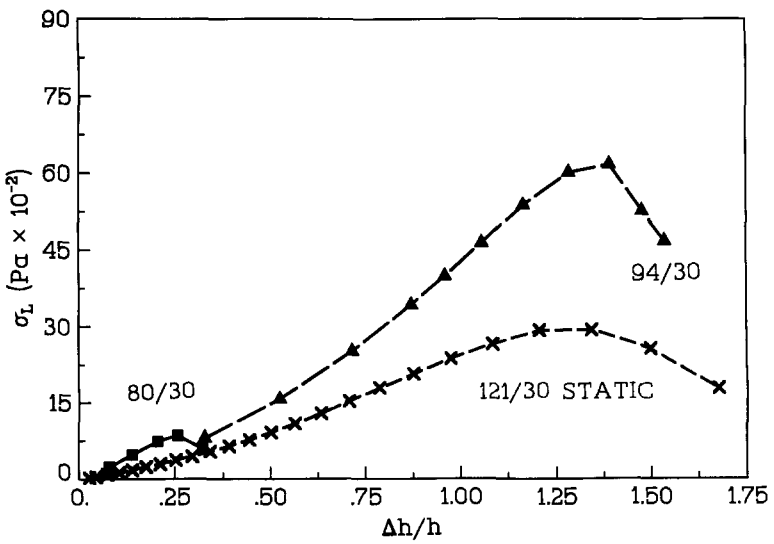

Fig. 3. Stress, σ_L, versus strain, $\Delta h/h$, for lubricated compression of rice starch gels prepared by heating for 30 min at 80, 94 and 121°C.

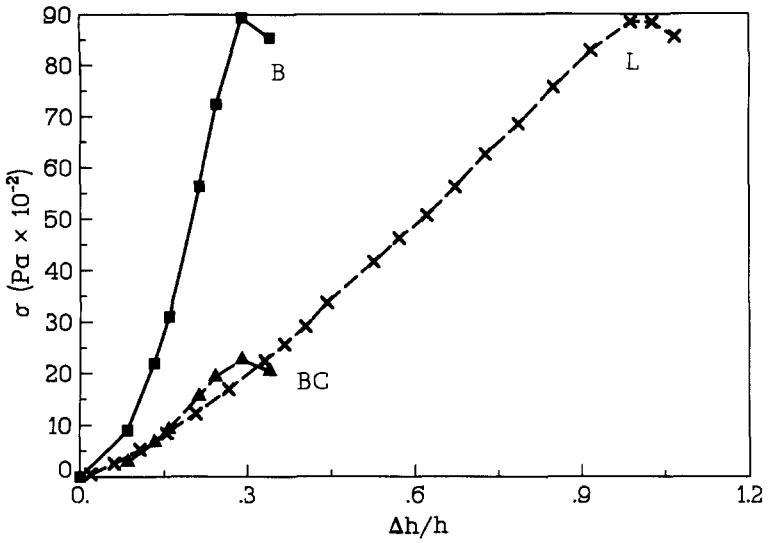

Fig. 4. Comparison of stress–strain curves of a wheat starch gel, prepared by heating for 30 min at 94°C, for samples bonded (B), lubricated (L), and bonded after correction (BC) according to eqn (8).

the stress–strain data at fracture is excellent, as exemplified by the data in Table 1.

The effect of the correction factor is also illustrated in Fig. 4, where the stress–strain curve is given for a 94/30 wheat starch gel for lubricated (L), bonded (B), and bonded corrected compression (BC). Essentially the same stress–strain response is obtained for both L and BC compression, at least to strains of about 0·3, but fracture occurs at a much lower stress and strain in the BC curve. The fracture mechanism in bonded compression is related to the shear strain imposed on the gel material in the parabolic region formed during the compression process. Samples in bonded compression fracture in shear, a different mechanism than fracture in lubricated compression (Christianson *et al.*, 1985). Note that the weaker the gel the less satisfactory the agreement between the lubricated and the corrected bonded curve (Christianson *et al.*, 1985).

Table 1 summarizes all the results obtained on fracture stress in lubricated and bonded compression, with the calculated bonded corrected result for comparison. Replication is well within 10%

TABLE 1
Reproducibility of Fracture Stress

Preparation (temperature/time)	*Corn fracture stress (Pa)*	*Wheat fracture stress (Pa)*	*Rice fracture stress (Pa)*
Lubricated compression			
80/30	2216 ± 98	1290 ± 83	871 ± 31
94/30	7930 ± 700	8466 ± 541	6185 ± 392
121/30 (static)	6510 ± 384	4225 ± 385	3089 ± 216
121/30 (stirred)	1757 ± 75	—	—
Bonded compression			
80/30	2633 ± 77	1863 ± 113	1280 ± 10
94/30	8314 ± 497	8799 ± 213	6175 ± 258
121/30 (static)	5663 ± 95	6354 ± 394	3425 ± 200
Corrected bonded compression			
80/30	818 ± 25	541 ± 22	376 ± 11
94/30	2107 ± 181	2272 ± 66	1306 ± 97
121/30 (static)	1367 ± 125	1732 ± 83	737 ± 37

and suggests that these compression experiments are a reasonable approach to evaluating gel strength.

Starch solubility and dispersibility

Table 2 shows the solubility and dispersibility of the three starches under the heating conditions investigated. At 80°C, the hot filtrate is clear with 5–7% of the starch extracted. The filtrate solids from the 94/30 preparations give 30·3, 28·5 and 18·0%, respectively, for corn, wheat and rice as the percentage of total starch released. Again the filtrates were clear, suggesting that the starch in the filtrate is truly in solution. At 121°C the hot filtrates are cloudy, suggesting that the starch is well dispersed but not necessarily all in solution. It is also evident in comparing the static and stirred results at 121°C (Table 2) that stirring essentially results in all the starch being dispersed or solubilized. The shearing action of the turbine may also degrade or otherwise affect the solubilized and/or dispersed starch molecules.

TABLE 2
Solubility and Dispersibility of Starch

Processing conditions	*Filtrate weight (% of original starch)*		
	Corn	*Wheat*	*Rice*
80/30	7·0	5·6	6·0
94/30	30·3	28·5	18·0
121/30 (static)	86·5[a]	73·3[a]	95·0[a]
121/30 (stirred)	99·0[b]	—	—

[a] 2% starch precooked for 30 min at 70°C prior to autoclaving (121°C).
[b] 10% starch precooked for 30 min at 70°C and autoclaved with stirring. Processed dispersions were diluted and filtered hot.

DISCUSSION

In considering the results summarized in Table 1 it is evident that uniaxial compression tests under either bonded or lubricated conditions give reproducible data (in absolute units) on gel fracture. This approach, then, to the strength properties of gels is to be preferred to purely empirical gel strength measurements, such as those obtained with an embedded disc. Further, the lubricated or bonded uniaxial compression measurements also give reproducible stress–strain curves uncomplicated by frictional behavior at the gel/platen interface.

The actual stress–strain behavior of the corn and wheat starch, as shown in Figs 1 and 2, was surprising to us. First of all, the stress–strain curves had been expected to reflect, in a more startling way, the temperature of gel preparation, yet the initial modulus for wheat is identical for the 80/30, 94/30 and 121/30 (static) gels and for corn there was only a small change in initial modulus for corn starch in going from 80 to 121°C gel preparation temperature (Fig. 1). The response of rice starch gels to gel preparation temperature (Fig. 3) was more in line with our expectation.

A detailed interpretation of the results of Figs 1, 2 and 3 is difficult. The gels prepared in this study are complex in composition. They

consist of solubilized and dispersed starch leached from the granules, swollen and disrupted granules and granule fragments. (See also, for example, Doublier's study of wheat starch pastes (Doublier, 1983).) The solubilized and dispersed starch, consisting of both amylose and amylopectin (with molecular weights depending on starch source (Young, 1984)), will form a gel structure in which the swollen granules and granule fragments are suspended as reinforcing filler (see Ring & Stainsby (1982)). The effectiveness of these granules and fragments as filler should depend on the extent of swelling (the volume fraction of filler) and on the rigidity of these filler particles, which will depend, in part, on the amount of amylose and amylopectin leached from the granules. All of these factors can be affected by stirring (see Doublier (1983)), as is evident in comparing the gels prepared under static and stirred conditions at 121°C. Further, as Ott & Hester (1965) show, and as noted also by Zobel (1984) and others, amylose and amylopectin may interact in ways which affect the final gel properties.

Thus the data reported here (Table 2) are inadequate to provide a realistic interpretation of the results obtained on these wheat, corn and rice starch gels.

While a detailed interpretation of these results at the molecular level would require greater elaboration of such factors as starch solubility, solubilized amylose and amylopectin ratios (Kobayashi *et al.*, 1985) and extent of granule swelling and disruption, the use of bonded and lubricated uniaxial compression data alone yields information on material properties of value for food characterization. Hamann (1983), in a recent review, has emphasized that 'if we are to truly engineer foods we should be able to discuss the deformation, fracture and flow of food materials in terms of the fundamental units of physics'. Properly carried out, fundamental measurements yield data not tied to specific test geometry, as Montejano *et al.* (1984) have demonstrated in comparing results on various materials using torsional and compressional deformation modes. The equivalence of these various methods, also demonstrated with gelatin and starch gels in simple shear, torsion and dynamic measurements (Christianson *et al.*, 1984), thus, in principle, permits concentration on experimentally simple methods, of which uniaxial compression is particularly interesting because it is widely used in texture profile analysis. Under bonded and lubricated conditions the compression experiment yields basic information on bulk properties. The frictional properties of food

materials offer additional research challenges which also need to be explored to fully characterize the textural properties of foods.

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