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Measurement of the Rheology of Polysaccharide Gels by Penetration

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Abstract

The influence of penetration depth, probe radius and gel depth on the shear modulus calculated from penetration by the method of Oakenfull et al., 1988 was determined for alginate, carrageenan and gelatin gels. For all three gels it was found the calculated modulus was independent of penetration distance at low distances (< 5 mm) and independent of gel depth provided this was not small. For the polysaccharide gels, however, the calculated modulus depended on probe radius whereas for gelatin gels it was radius independent. This suggested that, in contrast to gelatin, the use of this approach to obtain fundamental moduli for alginate and carrageenan gels from penetration experiments at forces measurable with commercially available Texture Analysers is invalid.

Keywords: Gelatin gel; Alginate gel; Carrageenan gel; Polysaccharide gels; Penetration depth; Shear modulus

1. Introduction

There is currently a trend in the food industry towards improving quality control and therefore many simple tests have been developed in order to measure the physical/textural attributes of food materials. Amongst these, the measurement of 'gel strength' is of great importance. This is frequently accomplished by penetrating gels formed in containers using a force-deformation instrument. Methods of measuring the quality of food gels using penetration date back over a century, for example, the industry standard method for gelatin gels (the Bloom test) is a penetration method (British Standard BS757).

Simple instrumentation and methodology make the penetration type of test very suitable for the Quality Control area and improvements in data handling over the past decade through computer interfacing has further increased its potential. The results of such methods are generally considered to be empirical, however, there is currently a desire to move toward more fundamental measurements. Such measurements allow a deeper understanding through the application of theory and allow comparisons to be made between results gained from this and alternative test methods.

Oakenfull et al., (1988) reported a method of converting penetration Forces into an absolute shear modulus value using a factor found through finite element analysis. This factor depended only on the geometry of the measuring system. It was shown that the method was valid for weak (2% and 5%) gelatin gels at small penetrations. The forces employed, however, were much lower than could be measured using conventional texture measurement equipment.

Smewing (1996) extended this approach and showed that the shear modulus values obtained from the penetration method are comparable to those obtained using a rotational rheometer for various gelatin gel concentrations. For these experiments a TA.XT2*i* Texture Analyser was used to measure the gels at greater forces and penetration depths. It was found that results were only valid when the depth of the gel in the container was above a critical value. Below this, the gels appeared to be stiffer due to 'base effects'.

This paper is concerned with some of the limitations of this approach and its suitability for measuring the properties of polysaccharide gels. Gelatin gels were compared with gels prepared from the polysaccharides; alginate and carrageenan. The effect on the calculated modulus on varying gel depth, penetration depth and probe radius were investigated to determine the limits within which absolute values may be obtained.

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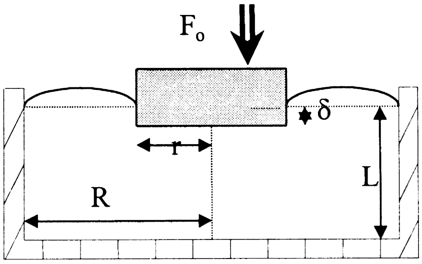

Fig. 1. Geometry of the measuring device. R is the radius of the container (m), r is the radius of the probe (m), δ is the depth of penetration (m), L is the gel depth (m) and F_o is the force applied (N).

2. Materials and Methods

2.1. Gel Preparation

2.1.1. Gelatin

Gelatin with a Bloom strength of 200, supplied by Rousselet, France, was used. The gels were made by following the standard Bloom method (British Standard BS757), but using a concentration of 5% w/w. The incubation temperature was 10°C.

2.1.2. Carrageenan

An Irish Moss Type 1 carrageenan powder, supplied by the Sigma Chemical Company, was used. The gels were made by slowly adding the requisite quantity of carrageenan powder for a 0.5% concentration gel to pH 7.0, 0.2 M phosphate buffer (plus 0.1 M KCl) heated to 80°C whilst continuously stirring. The gels were boiled under reflux for 10 minutes and then poured into the moulds.

2.1.3. Alginate

Sodium alginate powder (10 g), as supplied by Fisons, was dissolved in cold distilled water (800 ml) using a Silverson mixer. A 0.25 M glucono-delta-lactone, 0.125 M calcium hydrogen phosphate dihydrate solution (200 ml) was added to the alginate solution and rapidly poured into moulds. The resulting gel had an alginate concentration of 1%.

2.2. Gel Measurement

2.2.1. Penetration Method

For the penetration measurements, a cylindrical probe is forced into a gel formed in a cylindrical container. The parameters used to describe the geometry of the measuring system are described in Fig. 1. For these experiments, 50mm radius Perspex containers were used. These were filled to various levels, thereby changing the L/R value (as described later). The gels were allowed to reach approximately room temperature before being covered, placed into an incubator at 10°C and left for 18 hours.

Cylindrical probes were used to penetrate the gels at a constant velocity of 0.5 mms^{-1}. The measured force, F_o (N), and the force due to buoyancy, F_b (N), were used to calculate the force corrected for buoyancy, F_{cb} (N), using the equations (1) and (2). The density of the gel is given as σ (kgm^{-3}) and g is the acceleration due to gravity ($9.81\mathrm{ms}^{-2}$).

Table 1
Factors (f) for converting apparent Young's modulus into absolute shear modulus for different sizes of container and probe (taken from Oakenfull et al., 1988).

r/R	L/R = 0.1	L/R = 0.2	L/R = 0.5	L/R = 1.0
0.05	0.157	0.0752	0.0381	0.0186
0.10	0.208	0.104	0.0634	0.0331
0.20	0.185	0.102	0.0912	0.0522
0.40	0.0549	0.0632	0.0930	0.0574
0.50	0.0264	0.0490	0.0803	0.0485
0.60	0.0138	0.0384	0.0622	0.0359

$$F_{cb} = F_o - F_b \tag{1}$$

$$F_b = \frac{\pi\sigma\delta g r^2 R^2}{R^2 - r^2} \tag{2}$$

The penetration distance and corrected force were used to calculate an apparent Young's modulus, Ye (Pa), using equation (3).

$$\mathrm{Ye} = \frac{F_{cb} L}{\delta\pi r^2} \tag{3}$$

The absolute shear modulus, G (Pa), can be found using equation (4).

$$G = f\cdot Ye \tag{4}$$

The ratios r/R and L/R were used to obtain f by extrapolation from the data published by Oakenfull et al., (1988) (see Table 1).

Experiments were conducted for each gel designed to determine the dependence of the shear modulus on the gel height and penetration depth (using a constant probe radius of 6.35 mm) and probe radius (using a constant penetration depth of 1 mm).

2.3. Rotational Rheometry

The shear moduli obtained from the penetration method were compared with the storage moduli measured for the polysaccharide gels using a Bohlin CS-10 rotational rheometer in oscillation at 19°C. Results were taken within the linear region of each gel at a frequency of 1Hz.

Disks of gel were made in moulds which comprised of 3 pieces of 5.8 mm thick Perspex sheeting clamped together. The central sheet was cut with 31.3 mm diameter holes which could be filled whilst the top sheet was removed. Once the top sheet had been replaced, the moulds were put into a 19°C incubator and left for 18 hours. Medium viscosity 'release oil' was used to coat the moulds in order to prevent leakage whilst the gel was liquid and to

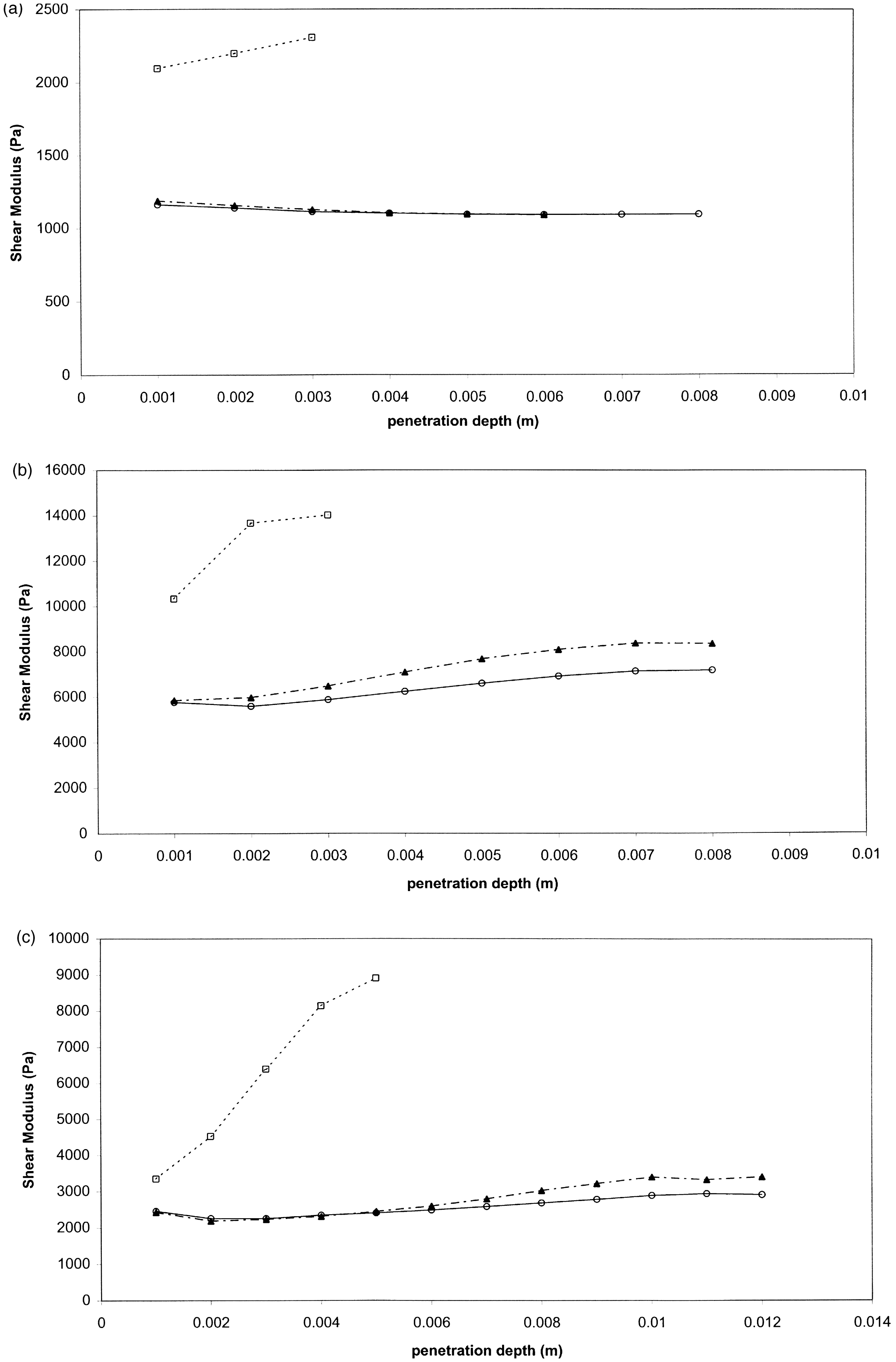

Fig. 2. Calculated shear modulus as a function of penetration depth for (a) 5% gelatin, (b) 0.5% carrageenan and (c) 1.0% alginate gels. L/R values: □ = 0.2, ▲ = 0.6 and ○ = 1.0. Probe radius 6.35 mm.

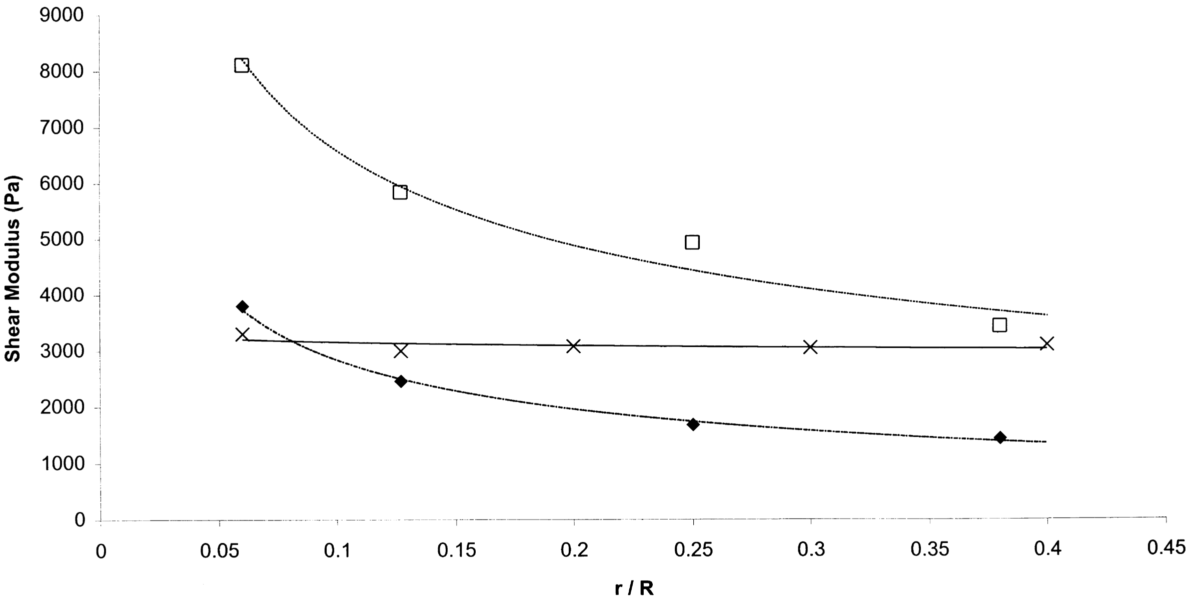

Fig. 3. The effect of probe radius on the calculated shear modulus. ◆ = 1% alginate (L = 30 mm), □ = 0.5% carrageenan (L = 50 mm) and × = 5.0% gelatin (L = 50mm). Penetration depth = 1 mm.

prevent damage to the solid disks when removing them from the moulds.

3. Results

3.1. Dependence on penetration depth and height

For gelatin gels, the shear modulus is independent of penetration depth, at least up to 8 mm, above an L/R value of 0.2 (see Fig. 2a). At low gel heights it appears that the theory does not adequately take into account the perceived gel stiffening, probably due to a squeeze flow action, when the gel depth is small. It is not yet known whether the critical factor is an absolute value of L, below which the base effect become important, or the ratio L/R. These results suggest that the Bloom test, which uses a similar geometry to that used in these tests and a penetration of 4 mm, will be within the penetration depth independent region.

Shear modulus is initially independent of penetration depth using the polysaccharide gels so long as the L/R value is above 0.2 (see Figs. 2b and 2c). The modulus then rises with increasing penetration depth after this initial linear period. The results also suggest that the rise in modulus is greater when the L/R value is lower.

3.2. Dependence on Probe Radius

The results show that within the limitations of this study the modulus calculated for gelatin gels is independent of probe radius (see Fig. 3). For polysaccharide gels, the modulus decreases with increasing probe radius.

3.3. Comparison of Moduli from Penetration and Rotational Methods

For gelatin gels (Smewing, 1996) the penetration technique produces values for the modulus close to those obtained using a rotational rheometer. The validity of the penetration test for use with gelatin is strengthened by the independence of the results on gel height, penetration depth and probe radius within the constraints mentioned above. The alginate and carrageenan results using the penetration test were dependant on probe radius making a comparison with a modulus gained from rotational rheometry (see Table 2) more difficult. The results from rotational tests, however, lie within the range of values shown in Fig. 2.

4. Discussion

Although this is not an exhaustive study of the possible variables, the results show that when using gelatin gels a good estimate of the shear modulus can be achieved so long as the gel depth is sufficient. The f-factor therefore takes into account the differences in the apparent Young's modulus which arise from changes in both the gel depth and the probe width. The independence of the modulus on penetration depth shows that the gradient of the force-deformation curve is constant at all depths measured.

The method does not work so successfully with alginate and carrageenan for which there is a strong dependence on the radius of the probe as well as a slight dependence on the gel height and penetration depth. In contrast with gelatin gel, both alginate and carrageenan produce gels at much lower concentrations and are comprised of polysaccharides

Table 2
Shear storage modulus (G') values from a rotational rheometer for two polysaccharide gels, 1% alginate and 0.5% carrageenan. (Results obtained at a frequency of 1Hz and at a temperature of 25.0°C)

Gel Type and Concentration (%)	Storage Modulus from Rotational Rheometer G' at 1Hz
1% Alginate	2318 Pa[a]
0.5% Carrageenan	4527 Pa[b]

[a] 2320 ± 200 pa.
[b] 4540 ± 400 pa.

rather than proteins. Rheologically, they are relatively viscoelastic, have shorter linear elastic regions, fracture more easily, show syneresis and do not adhere to the walls of the Perspex containers. One or a combination of these differences may be the reason for the limitations of this method for polysaccharide gels.

5. Conclusions

For gelatin, fundamental moduli can be obtained from penetration data using forces which are possible to measure using common texture measuring instruments. This approach is less satisfactory for polysaccharide gels as the results depend on the radius of the probe.

Further work could be done to determine whether the critical factor at low gel depths is L or L/R and whether other parameters, such as probe velocity, probe shape, probe / gel surface slip, would significantly influence the resulting modulus. An investigation into the reasons for the geometry and penetration depth dependencies of the modulus for polysaccharide gels may also be beneficial.

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References

British Standard BS757, Methods for Sampling and Testing Gelatine (Physical and Chemical Methods), 1975 British Standards Institution, 2 Park Street, W1A 2BS.

Oakenfull, D.G., Parker, N.S., Tanner, R.I, A Method for Determining the Absolute Shear Modulus of a Gel from a Compression Test, pp. 231–239, in Gums and Stabilisers for the Food Industry 4, eds G.O. Phillips, P.A. Williams, D.J. Wedlock, IRL Press, Oxford, pp. 231–239, 1988.

Smewing, J., Determination of a Shear Modulus from Penetration Tests on Gelatin Gels, MPhil Thesis, University of Nottingham, 1996.