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Correlation between sagging and shear elasticity in pectin, gelatin and polyacrylamide gels

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Abstract

The relationship between the height of gels determined by a sag test and their elastic shear modulus (G') has been both investigated experimentally and simulated using a finite element analysis for the inhomogeneous deformation of gels due to gravity. It was assumed in the simulations that gels can be modeled as incompressible linear elastic materials. General relationships between the sag of gels and their elastic modulus were obtained from the simulations for slip and no-slip conditions. The relationships were tested experimentally on pectin, gelatin and polyacrylamide gels with a range of concentrations and rigidities. The good agreement between the predictions and the results shows that these gels can be modeled accurately as incompressible elastic materials. A standard 150° SAG pectin gel, which sags 23.5% in the SAG test, has G' moduli of 429 and 379 Pa under slip and no-slip conditions, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Elastic modulus; Pectin; Gelatin; Polyacrylamide; Gel; Sag; Rheology

1. Introduction

Pectin is a polysaccharide, which is widely used in the food industry as a gelling agent (Thakur, Singh & Handa, 1997). Pectin is the dominant agent used in the industry to provide texture in jams and other sweet gels, e.g. confectionery gels (Rolin, Nielsen & Glahn, 1998). The consumer's acceptance of a jelly is largely dependent on its gel strength which is due to the pectin network in the gel (Crandall & Wicker, 1986). It is therefore important to be able to determine the gel strength of pectin gels. In 1959 the American Pectin Committee finished several years of research resulting in the development of the widely used "SAG test" for determining the grade strength of pectins (Baker et al., 1959). This test is based on measuring the sag, which is the height decrease due to gravity of a pectin gel made in glasses of very precise dimensions. A ridgelimeter is used to determine the percent sag (Baker et al., 1959; Cox & Higby, 1944). The conventional SAG test fails to give information about gel strength for many pectin applications, since it only describes the pectin grade at well-defined pH and soluble solid content conditions. The measured sag is slightly dependent on time, and it is determined 2 min after inversion of the gel in the recommended SAG test (Baker et al., 1959). A typical standardized jelly strength for a commercial pectin sample is 150° grade SAG and this grade corresponds to 23.5% sag. In the standard SAG test the pectin and sugar contents are varied until the gel has the desired grade, e.g. 150° (Cox & Higby 1944; Ehrlich, 1968).

A correlation between the pectin SAG grade, intrinsic viscosity and breaking strength has been proposed (Christensen, 1954; Swenson, Schultz & Owens, 1953). They showed that the intrinsic viscosity allows a quick estimate of the SAG grade. Dunstan, Mahon, and Boger (1997) proposed a linear relationship between sag or normalized slump and G'. It has also been shown that high methoxyl (HM) pectin SAG gels exhibit viscoelastic properties, and that an increase in the pectin concentration results in a decrease in percent sag (Watson, 1966).

In the same way in which the SAG test is a common test for pectin gels, gelatin is often graded by the Bloom test (Bloom, 1925), which has been evaluated by Borker, Stefanucci and Lewis (1966). A 6.67% gelatin gel in an aqueous solution is prepared, and the gel strength is determined with a plunger-weight system, where the load for penetrating 4 mm into the gel is determined. Gelatin gels are cast in special glasses and test results are only of comparative value (Borker et al., 1966; Stevens, Wijaya & Paterson, 1997). Another simple laboratory test was proposed by Lockwood and Hayes (1931), but this test

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has not replaced the widely used Bloom test. Cobbett and Ward (1968) showed that the elastic modulus of gelatin gels at small deformations could be related to results from the Bloom test.

Rheological techniques have been used to obtain detailed information about biomolecular structures in several biopolymer gels (see, e.g. reviews by Clark & Ross-Murphy, 1987; te Nijenhuis, 1997). The SAG value only serves as a standardization parameter for pectins, and it is desirable to link the SAG value to more fundamental rheological properties of the gels. The deformation in a SAG test, which is due to gravity, is inhomogeneous and complex. The top part of the gel is expected to be deformed less than the interior and lower parts of the gel. In order to determine the deformation in various parts of the gel a finite element analysis has been used. These calculations result in knowledge about the shape and the sag of a gel, which has the geometry used in the standard SAG test. We report here results of such simulations, which correlate the sag with fundamental properties of the gel. The results of the simulations are, furthermore, compared with experimental sag and rheological results on pectin, gelatin and polyacrylamide gels.

2. Materials and methods

2.1. Materials

Pectin GENU types B rapid set (150° SAG) and D slow set (150° SAG) from Hercules Copenhagen were used. The gelatin SG 720N, 250 Bloom, type A was from Extraco. Polyacrylamide gels were prepared using acrylamide, N,N,N',N'-tetramethyl-ethylenediamine (TEMED), ammoniumpersulfate and N,N'-methylene-bis-acrylamide from Sigma. Other chemicals were of analytical grades from Merck.

A ridgelimeter (Sunkist Growers, Inc.) and SAG glasses (Hercules Copenhagen) were used for the SAG tests. A CS 100 rheometer (Haake) equipped with a Z20 couette was used for the rheological experiments.

2.2. Gel preparations

Pectin GENU types B and D stock solutions were prepared by dissolving 9–27 g pectin in hot deionized water to a total of 300 g solution, which was then mixed for 5 min at high speed in a laboratory blender. A 1 l buffer solution containing 3.933 g potassium citrate, 18 ml 50% w/v citric acid and 1.0 g sodium benzoate was prepared in deionized water, and the pH was adjusted to 3.4–3.5. Solutions were prepared by mixing 270 ml of the buffer solution with 770 g glucose. This solution was allowed to boil for 2 min until the sugar was dissolved completely. Pectin stock solution (240 g) was added and boiled until a final weight of 1200 g. Finally, 4 ml 50% w/v citric acid was added just before the solutions were poured into SAG glasses and the preheated (90°C) rheometer cell.

Gelatin gels were prepared by mixing gelatin with hot deionized water (70°C) for approximately 10 min until the gelatin was completely dissolved. The solutions were then poured into SAG glasses and the preheated (70°C) rheometer cell.

Polyacrylamide gels were prepared by mixing 45–75 ml acrylamide of a stock solution containing 30% acrylamide and 0.8% bis-acrylamide with 0.45 g ammoniumpersulfate and water to a total of 450 ml. TEMED (240 μl) was added to initiate the polymerization just before the solutions were poured into SAG glasses and the rheometer cell at 25°C.

2.3. Sag measurement

Twenty-eight SAG glasses were used with measured bottom and top diameters of 39.7 ± 0.5 and 63.5 ± 0.3 mm, respectively, and a height, H_0, of 79.4 ± 0.2 mm. A ridgelimeter was used to measure the height of the deformed pectin gels after a specified time. The maximum bottom diameter of the gels on the ridgelimeter plate was measured with a slide caliper as an average of three measurements. The gels on the glass plate were in most cases observed as sticking to the plate in the ridgelimeter and thus follow no-slip conditions. In order to observe slip conditions the glass plates were in some cases covered with a thin layer of paraffin oil prior to inverting the gels.

2.4. Rheometer measurement

Experiments were performed on a Haake CS-100 controlled stress (CS) rheometer using couette geometry (Z20). The top of the gel surface in the couette was covered with paraffin oil to prevent dehydration. The rheometer was used to measure the elastic storage modulus, G', and the loss modulus, G'', as a function of frequency, time, temperature and strain amplitude. Small amplitude oscillatory stresses are applied to the sample and the oscillatory strain monitored. The instrument was also used to measure compliance, J, which is the strain divided by applied stress in a creep experiment.

The formation of a gel with time was measured on the CS-100 instrument. Hot pectin solutions were cooled from 90 to 25°C and hot gelatin solutions from 70 to 25, 10 or 5°C. The cooling rates were 0.5–1°C/min, frequency 1 Hz and the stress amplitude 0.5 Pa. Hardening of the gel vs. time was subsequently monitored for a minimum of 2 h at the final temperature (1 Hz, 1–100 Pa depending on the hardness of the gel). After at least 3 h, to ensure that gels have fully developed, the frequency dependencies of G' and G'' were measured between 10 and 0.01 Hz, with stress amplitudes ranging from 2 to 200 Pa. It was ensured that measurements were done in the linear viscoelastic region, where G' and G'' are independent of stress amplitudes.

The gelling profile for polyacrylamide was measured as a time curve (2 h) at 25°C, frequency 1 Hz and stress amplitude in the range 0.5–20 Pa. The oscillatory properties from 10 to 0.01 Hz were then measured using a stress amplitude from 10 to 50 Pa. The frequency properties were measured simultaneously with the determination of the sagging of the gel. The gels were also investigated by a creep and creep-recovery test. The time dependence of the strain was monitored when a constant stress was applied for 300 s and followed by a recovery part for 300 s. The stresses applied were between 10 and 200 Pa depending on the hardness of the gels, but always within the linear range, where strain is proportional to stress.

The densities of the gels were measured gravimetrically, by weighing each gel in the SAG glass and comparing it with the weight of water in the same SAG glass.

2.5. Simulations

The computer simulations of the deformation were performed by finite element analysis using a method and program described elsewhere (Rasmussen & Hassager, 1993, 1995). An initially undeformed gel with dimensions of the SAG glass was used with the height, H_0 (79.6 mm) and top and bottom radii, R_1 and R_2 (20.8 and 32.0 mm, respectively). Advantage is taken in the simulations of the axial symmetry of the gel from the SAG glass. A mesh was therefore constructed by first dividing the height of the gel into N_1 slices, and each slice was then further divided into N_2 concentric rings. The values of N_1 and N_2 were increased in preliminary simulations until the mesh deformation was independent of their values. These simulations showed that a mesh with 70 × 30 elements for the slip simulations and a no-slip mesh containing 100 × 30 elements were sufficient. The mesh used for slip conditions is shown in Fig. 1.

The sag was defined as a dimensionless variable, $\Delta H/H_0$, where ΔH is the decrease in height at the center axis after the gel has sagged. A dimension analysis shows that $\Delta H/H_0$ is a function of the dimensionless variable $\rho g H_0/G$, where G is the elastic modulus at zero frequency, ρ the density of the gel and g the acceleration of gravity. It was assumed that the material is an incompressible ideal elastic material, obeying the law for a neo-Hookean solid with proportionality between stress (σ) and Finger strain (B), $\sigma = GB$ (Bird, Curtiss, Armstrong, & Hassager, 1987). Simulations, which involve solving the force deformation equations for all rings in the mesh, were performed using either slip or no-slip boundary conditions, allowing the surfaces of the lowest mesh elements to either slide or stick to the bottom surface, respectively. The results of the simulations are the deformed mesh for different values of $\rho g H_0/G$ between 0 and 2. Higher values than 2, corresponding to very soft gels, could not be simulated under no-slip conditions, since such values led to predictions that parts of the deformed gel would be below the bottom surface.

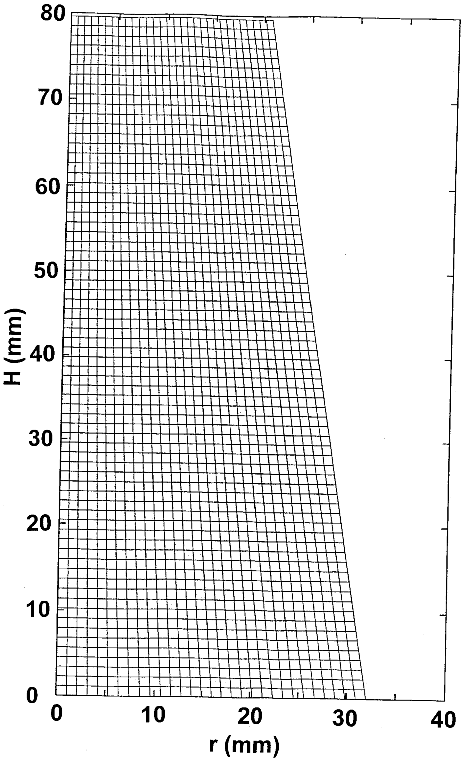

Fig. 1. The initial undeformed mesh used for the finite element simulations of an inverted gel under slip conditions. The figure shows the mesh in a vertical half-plane through the central axis of the gel. Mesh consists of 30 × 70 elements, which are concentric rings.

3. Results

3.1. Simulations

The contours of the sagged gels vary depending on the model used in the simulations. The contours of one illustrative gel under both slip and no-slip conditions are shown in Fig. 2 for the same value of ($\rho g H_0/G$). The figure shows, as expected, that the relative height decrease is greater for the slip condition. Simulations were carried out for a range of relevant $\rho g H_0/G$ values. The sag results are summarized in Fig. 3 for both slip and no-slip conditions. The figure illustrates that small sags should be expected when either the density is low or the elastic modulus is large. A slightly curved relationship between sag and the dimensionless factor is observed in the figure. The data sets can be accurately represented by second-order polynomial fits as shown in the figure. The equations for the fits are:

$$\Delta H/H_0 = 0.1327[(\rho g H_0)/G] - 0.0147[(\rho g H_0)/G]^2 \text{ (no-slip)} \quad (1)$$

and

$$\Delta H/H_0 = 0.1149[(\rho g H_0)/G] - 0.0106[(\rho g H_0)/G]^2 \text{ (slip)} \quad (2)$$

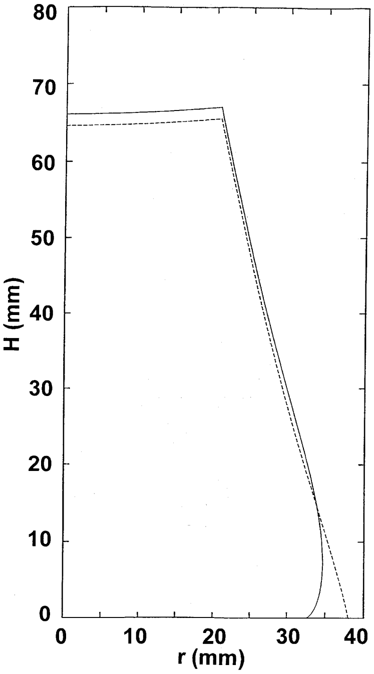

Fig. 2. Contours of a sagged gel at $(\rho g H_0)/G = 1.759$ for slip (broken curve) and no-slip conditions (solid curve). The undeformed gel has a height, H_0, of 79.4 mm, as shown in Fig. 1. The sag, ΔH, is defined as H_0 minus the height of the deformed gel at the axis.

These equations enable a conversion between relative sag and the more fundamental properties density and elastic shear modulus.

3.2. Rheological measurements

Typical frequency dependencies of the storage and loss moduli for the three investigated systems are shown in Fig. 4. The figure shows that all systems exhibit nearly frequency-independent G' values which exceed G'' values at all measured frequencies. Such characteristics are typical for gels (Almdal, Dyre, Hvidt & Kramer, 1992). The equilibrium elastic modulus of a gel network is literally given by the G' value at zero frequency. In practice, however, measuring at very low frequencies is time consuming. The equilibrium elastic storage moduli used in the comparison with simulation results were estimated from measured G' values at 0.0147 Hz, since the storage moduli are only slightly dependent on frequency, as seen in Fig. 4.

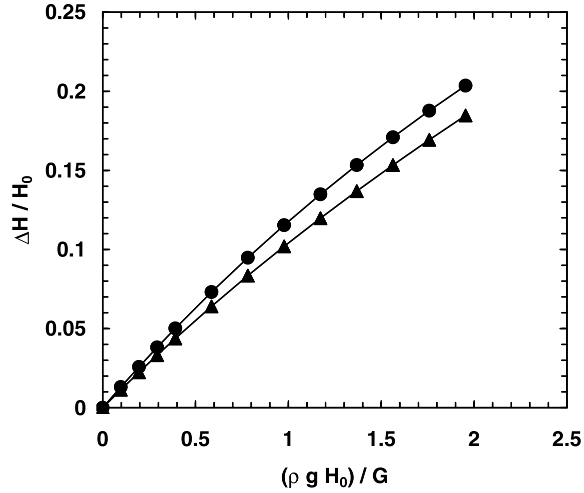

Fig. 3. Simulated relative sag, $\Delta H/H_0$, plotted against $(\rho g H_0)/G$ for slip (●) and no-slip (▲) conditions. The curves are second-order polynomial fits to the simulated data.

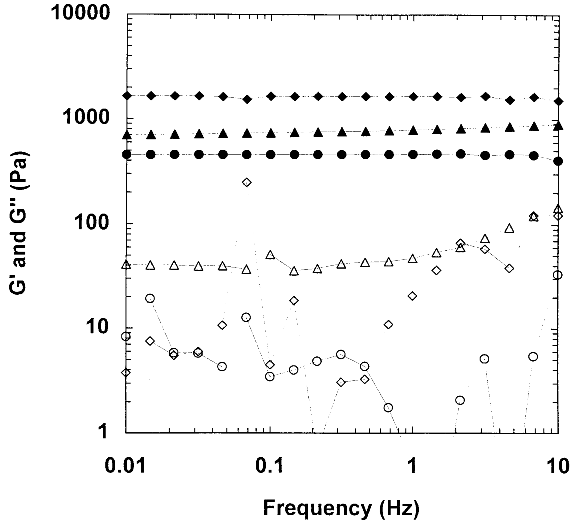

Fig. 4. Plots of the frequency dependencies of G' (filled symbols) and G'' (open symbols) for 2% pectin type D (▲), 3% gelatin (●) and 4.5% polyacrylamide (◆) gels on logarithmic scales.

The SAG test is actually a creep test where the gel, after inversion on the plate, is subjected to a gravity force acting on the gel. Fig. 5 shows typical creep and creep-recovery curves for 2.0% pectin (D slow set), 3% gelatin and 4.5%

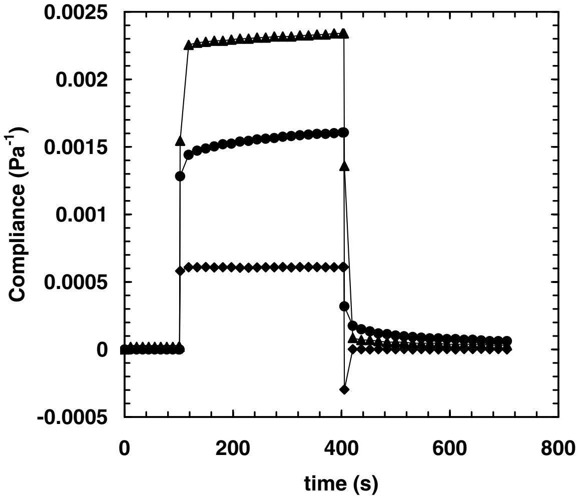

Fig. 5. Creep and creep-recovery responses for 2% pectin type D (▲), 3% gelatin (●) and 4.5% polyacrylamide (◆) gels. The compliance is plotted against time. The stresses applied in the creep region between 100 and 400 s were 15, 10 and 50 Pa, respectively.

polyacrylamide gels. The compliance is plotted against time. It is seen that especially the polyacrylamide gel has the characteristic response expected for an ideal elastic material: a rapid elastic response to the stress applied, no further creep, and a complete recovery when the stress is removed. The pectin and gelatin gels show less ideal elastic behavior, but the elastic properties dominate. The time dependence of the creep curves as well as the frequency dependencies of G' indicate that the gels are primarily elastic. The assumption in the simulations that the gels can be modeled as elastic materials seems, therefore, justified. The low measured shear moduli and the low stresses applied to the gels also make the assumption about constant volume or incompressibility reasonable.

The density of the gels depended slightly on concentration of the polymer and the amount of sugar added. Pectin gels varied from 1.31 to 1.36 g/cm^3, whereas the density for gelatin and polyacrylamide gels were close to the density of water, e.g. gelatin gels varied from 1.03 to 1.06 g/cm^3 and polyacrylamide gels varied from 1.02 to 1.04 g/cm^3.

In general covering the glass plate with paraffin oil resulted in a larger maximum diameter, but no clear evidence of whether the pectin gels follow the slip or no-slip model could be deduced. Fig. 6 shows the average maximum diameter (±SD) of gels on plates either without or covered with paraffin oil. The results suggest that there is a shift from slip to no-slip conditions when the pectin gels get softer. Assuming a slip model, the softest gels having a $(\rho g H_0)/G$ of 2–2.7 were predicted to deform to a maximum diameter of 77–80 mm, whereas the no-slip model predicted a diameter ranging from 70 to 75 mm at the same $(\rho g H_0)/G$. However, the diameters of the inverted gels were found experimentally to reach a maximum of approximately 74 mm, which indicates that the softer gels follow the no-slip model. Pectin gels are quite sticky gels, due to the sugar added, whereas gelatin and especially polyacrylamide gels are less sticky. These gels are therefore expected to follow the slip model, and as seen in Fig. 7, the polyacrylamide gel data fits perfectly with the slip model predictions. The results for the gelatin gels follow the slip model predictions quite well, as seen in Fig. 8, but with more scatter around the predicted curve than seen for the polyacrylamide results in Fig. 7.

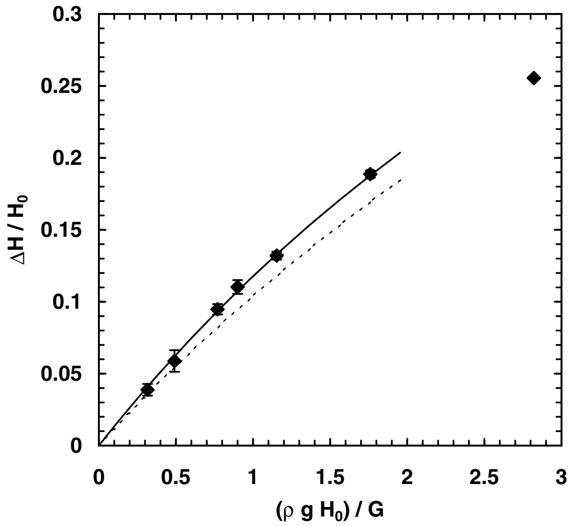

Fig. 7. The relative sag, $\Delta H/H_0$, plotted against $(\rho g H_0)/G$ for polyacrylamide gels with concentrations between 3 and 5% acrylamide. Full curve is simulated prediction for slip conditions and broken curve for no-slip conditions.

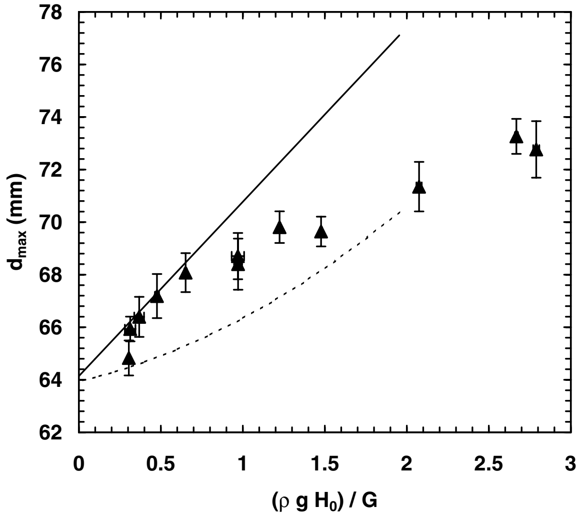

Fig. 6. The measured maximum diameter of the gel ($d_{\max}$) against $(\rho g H_0)/G$ for different concentrations of pectin D slow set gels. Full and broken curves show predicted maximum diameters from simulations with slip and no-slip conditions, respectively.

The pectin gel results are plotted together with the no-slip model predictions in Fig. 9. In general there is good agreement between the simulated predictions and the

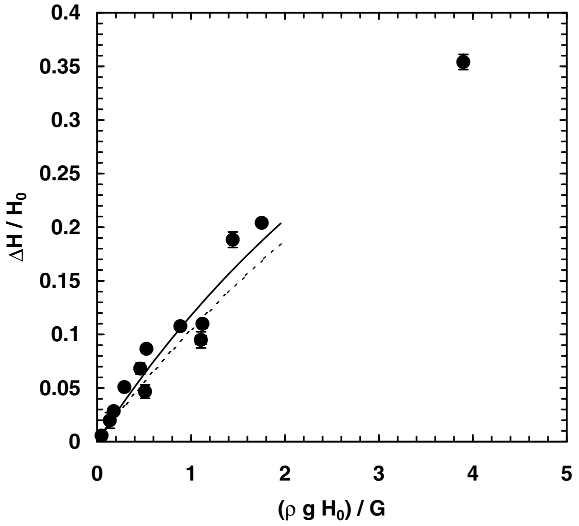

Fig. 8. The relative sag, $\Delta H/H_0$, plotted against $(\rho g H_0)/G$ for gelatin gels with concentrations between 2 and 10%. Full curve is simulated prediction for slip conditions and broken curve for no-slip conditions.

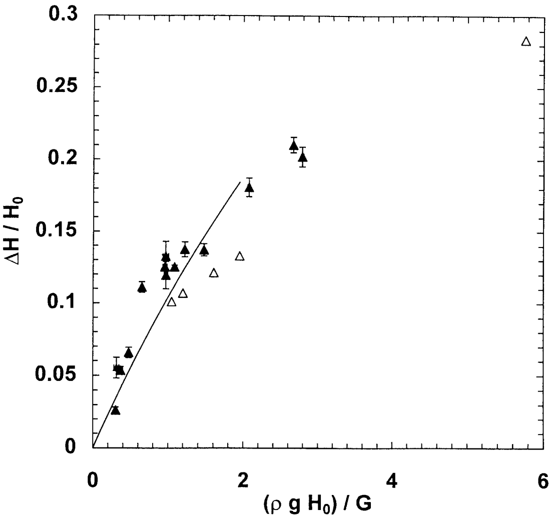

Fig. 9. The relative sag, $\Delta H/H_0$, plotted against $(\rho g H_0)/G$ for pectin B rapid set (△) and D slow set (▲) gels with concentrations between 0.6 and 2.0%. Full curve is simulated prediction for no-slip conditions.

experimental data, when the experimental scatter is considered. Reproducibility tests show that the sag is highly reproducible for all concentrations investigated. The measured G'-values, however, are less reproducible. The variation in the rheological data is probably due to reproducibility problems when hot solutions are loaded into the rheometer cell and small variations in the cooling history. A more direct approach would be to measure G' of the same gels used for the sag test. However, we have shown in a previous study that measurements on slices cut from such gels also exhibit G' variations (Nielsen, Kolte, Nielsen & Hvidt, 1998). These variations were assigned to difficulties in slicing gel samples and to loading slices into the rheometer in a reproducible manner.

Despite the scatter in the data, good agreement has been confirmed between the simulated and measured sag. The simulations are able to predict the right order of sag, and it has been demonstrated that the sagging of the different gels can be modeled quite accurately using the simple incompressible elastic model. Furthermore, the results in Figs. 6 and 9 show that the experimental data are closest to the no-slip simulation predictions for the pectin gels. Eqs. (1) and (2) show that 23.5% sag corresponds to G' values of 379 and 429 Pa for no-slip and slip conditions, respectively, for a gel with a density of 1.33 g/cm^3.

4. Conclusions

The SAG test is very attractive and practical, since it gives highly reproducible results and is fairly simple to use without the need for expensive instruments. Our simulations have demonstrated that the sag numbers can be predicted theoretically from measured values of the elastic shear modulus and the density of the gels. The difference between the slip and no-slip model is small at low $(\rho g H_0/G)$ values (hard gels). The measured diameters of the inverted gels indicate that the softer gels stick to the glass plate, therefore a no-slip simulation model gives the most accurate predictions of the sag numbers for pectin gels. The simulations presented here are not restricted to the gels investigated here, but they can be used to predict sag values for any incompressible elastic system if its shear modulus and density are known.

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References

Almdal, K., Dyre, J., Hvidt, S., & Kramer, O. (1992). Towards a phenomenological definition of the term gel. *Polymer Gels and Networks*, *1*, 5–17.

Baker, G. L., Barron, E. R., Boyles, P. R., Bristow, J. J. R., Buck, R. E., Campbell, H. A., Gilbert, P., Harper, L. K., Joseph, G. H., Kaufman, C. W., Kertesz, Z. I., Lataillade, L., Leo, H. T., Maclay, W. D., Meschter, E. E., Mottern, H. H., Nelson, J., Olliver, M., Owens, H. S., Reeves, R., Rooker, W. A., Scardino, W., Shockey, H., Walde, W. L., Webb, R., Willaman, J. J., Williams, P., & Woodmansee, C. W. (1959). Pectin standardization — final report of the IFT committee. *Food Technology*, *13*, 496–500.

Bird, R. B., Curtiss, C. F., Armstrong, R. C., & Hassager, O. (1987). *Dynamics of polymeric liquids*, *Kinetic theory*, vol. II. New York: Wiley.

Bloom, O. T. (1925). *Machine for testing jelly strength of glues, gelatins, and the like*. US Patent Office 1540979.

Borker, E., Stefanucci, A., & Lewis, A. A. (1966). Gelatin and gelatin products, dessert gel strength testing. *Journal of the Association of the Office of Analytical Chemistry (A.O.A.C.)*, *49*, 528–533.

Christensen, P. E. (1954). Methods of grading pectin in relation to the molecular weight (intrinsic viscosity) of pectin. *Food Research*, *19*, 163–172.

Clark, A. H., & Ross-Murphy (1987). Structural and mechanical properties of biopolymer gels. *Advances in Polymer Science*, *83*, 57–192.

Cobbett, W. G., & Ward, A. G. (1968). A simple extension apparatus for dilute gelatin gels. *Rheologica Acta*, *7*, 217–222.

Cox, R. E., & Higby, R. H. (1944). A better way to determine the jelling power of pectins. *Food Industries*, *441* (pp. 72–73 and 136–138).

Crandall, P. G., & Wicker, L. (1986). Pectin internal gel strength: theory, measurement, and methodology. *ACS Symposium Series*, *310*, 88–102.

Dunstan, D. E., Mahon, J. L., & Boger, D. V. (1997). Measurement of the visco-elastic properties of pectin gels with temperature. *Australasian Biotechnology*, *7*, 87–92.

Ehrlich, R. M. (1968). Controlling gel quality by choice and proper use of pectin. *Food Product and Development*, *2*, 36–42.

Lockwood, H. C., & Hayes, R. S. (1931). A method for testing agar and gelatin jellies. *Journal of the Society of Chemical Industry*, *50*, 145T–151T.

te Nijenhuis, K. (1997). Thermoreversible networks. Viscoelastic properties and structures of gels. *Advances in Polymer Science*, *130*, 1–267.

Nielsen, H., Kolte, M., Nielsen, B. U., & Hvidt, S. (1998). Modelling of the

SAG test for pectin gels. *Annual Transactions of the Nordic Rheological Society*, *6*, 59–62.

Rasmussen, H. K., & Hassager, O. (1993). Simulation of transient viscoelastic flow. *Journal of Non-Newtonian Fluid Mechanics*, *46*, 289–305.

Rasmussen, H. K., & Hassager, O. (1995). Simulation of transient viscoelastic flow with second order time integration. *Journal of Non-Newtonian Fluid Mechanics*, *56*, 65–84.

Rolin, C., Nielsen, B. U., & Glahn, P.-E. (1998). Pectin. In S. Dumitriu, *Polysaccharides: structural diversity and functional versatility* (pp 377–431). New York: Marcel Dekker.

Stevens, P. V., Wijaya, I. M. A. S., & Paterson, J. L. (1995). Modeling of physical properties of gelatin: gel strength. *Food Australia*, *47*, 167–172.

Swenson, H. A., Schultz, T. H., & Owens, H. S. (1953). Pectin grading-application of intrinsic viscosity. *Agricultural and Food Chemistry*, *1*, 616–620.

Thakur, B. R., Singh, R. K., & Handa, A. K. (1997). Chemistry and uses of pectin — a review. *Critical Reviews in Food Science and Nutrition*, *37*, 47–73.

Watson, E. L. (1966). Stress–strain and creep relationships of pectin gels. *Journal of Food Science*, *31*, 373–380.