

Shear Modulus in Closely Packed Gel Suspensions

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Synopsis

Rheological properties and swelling were examined in a series of concentrations of particles of crosslinked polyacrylate gels in water or salt solutions. The modulus during steady shear $G_s = 2\tau^2/P_{11}-P_{22}$ was determined from shear stress τ and primary normal force difference $P_{11}-P_{22}$ in a cone-and-plate rheometer. G_s was nearly constant with shear rate for the gel particles in the closely packed condition. The dynamic storage modulus G' determined by eccentric rotating disc rheometry increased with increasing frequency for all concentrations. The apparent equilibrium shear modulus G_e determined by stress relaxation agreed closely at all concentrations and ionic strengths with the corresponding values of G_s , and hence G_s is considered a good estimate of equilibrium shear modulus for this gel material.

INTRODUCTION

For elastic gel systems, one of the important experimental properties that can be determined by rheological procedures is a shear modulus of elasticity G .^{1,2} In an idealized gel with a rubbery network

$$G = g\nu kT(1 - 2M_c/M_n) \quad (1)$$

where ν is the number of crosslinks per cm^3 , k is the molecular gas constant, T the absolute temperature, and g is a "front factor" usually considered to be unity or nearly so, but which may be significantly lower for systems polymerized in the presence of diluent.³⁻⁵ The expression $(1 - 2M_c/M_n)$ is a correction factor for free chain ends in the network where M_c/M_n is the ratio of effective molecular weight between crosslinks to the molecular weight of the polymer before crosslinking. There may also be trapped entanglements that contribute to G . Experimentally, G is measured in the linear stress-strain region at small strain amplitude by either a static or dynamic procedure.

In solvent swollen gel systems, G varies with solvent composition by a factor $v_2^{1/3}$, when v_2 is volume fraction of gel material.¹ Conversion to units of weight concentration, c (g gel/g swollen system), results in the close approximation

$$G/c^{1/3} = \rho^{-1/3}g\nu kT(1 - 2M_c/M_n) \quad (2)$$

where ρ is density of the polymer and the solvent density is 1. This equation permits a direct determination of an effective crosslink density in a water-swollen gel system, at least in principle. Both g and $(1 - 2M_c/M_n)$ may offer significant contributions in eq. (2), so $G/c^{1/3}$ can more appropriately be considered as an experimental estimate of a somewhat indeterminate network structure through which insight into rheological properties can be had.

In measurements at finite frequencies or times, values of G depend not only

on the variables of eq. (2) but also on chain entanglements and other interactions.² Consequently, estimates of the permanently crosslinked network require extrapolation of stress-strain relationships during stress-relaxation to infinite time to obtain an equilibrium modulus G_e . This argument applies to a single block of gel in a rheometer and should apply as well to a suspension of closely packed gel particles, provided that no slippage occurs between particles during small strain measurements of G .

In the closely packed gel thickeners that we have examined, relatively small stresses are developed in the gel systems during small strains. Extrapolation to low frequency or shear rate is difficult. We have therefore used the modulus in shear G_s , determined during steady shear in a cone and plate rheometer:

$$G_s = 2\tau^2/(P_{11}-P_{22}) \quad (3)$$

in which τ is shear stress and $P_{11}-P_{22}$ is the primary normal force difference measured as the total thrust on the plate. In the gels we have examined, G_s is often constant or only slightly varying with shear rate and appears to be at least qualitatively correlated with crosslink density in the gels.⁶ The required stresses can be measured with reasonable precision even in relatively dilute gel systems, and G_s is a valuable experimental characterization.

The theoretical significance of G_s is not reliably established for gel systems. Equation (3) is valid in the limit of low shear rates for second-order fluids,^{7,8} but whether it is applicable to systems of closely packed swollen gel particles has not been reported. To clarify this uncertain situation, we have examined a model system, composed of the gel fraction of Carbopol® 940 (® = trademark of the BFGoodrich Chemical Co.) swollen in water or salt solution, and have compared G_s with the dynamic storage modulus G' as well as the apparent equilibrium modulus G_e . This material was experimentally desirable because it has relatively high modulus values and the values of G_s were nearly constant with shear rate.

MATERIALS AND METHODS

Carbopol® 940, a crosslinked polyacrylic acid, was a gift from B. F. Goodrich Chemical Co. The isolated gel fraction of Carbopol® 940 (C940) was prepared by our earlier method⁹ for Carbopols.® The dry powder (10 g) was stirred into 1 L water, neutralized to pH 7.6, and stirred 2.5 h. Then 60 mL of concentrated HCl was added, and the suspension became thin and turbid. It was stirred 2 h, and the gel fraction was separated by centrifugation (1800 g 's, 20 min in an International centrifuge). The gel was resuspended in water with HCl (pH \approx 1.5) and recentrifuged.

This water washing procedure was repeated a total of six times, and then the gel was resuspended in water and freeze-dried. The dried powder was resuspended in water and titrated to pH 7.6 with NaOH. This stock gel preparation contained 0.0484 g polymer in Na form per g suspension and had been titrated with 0.402 meq NaOH per g final suspension. The polymer then contained 8.31 meq Na/g polymer Na form. The polymer is not completely titrated at this pH.

Dilutions of the stock gel were made in water or salt solution and, after stirring gently, were aged at least 1 h before testing. Their properties were constant after

this time for at least a few days. The stock gel preparation was stable in the refrigerator for months.

Rheological properties were determined on a Rheometrics Mechanical Spectrometer (Union, N.J.) either in cone-and-plate mode or eccentric rotating discs (ERD) mode. The cone and plate were 3.6 cm radii, with a cone angle of 0.040 rad. It was used with a guard ring¹⁰ and with a cup on the plate. The guard ring, suspended near the edge of the plate (~ 0.01 in clearance), permitted use of a horizontal free boundary at the cone edge and stabilized the normal force baseline. The viscosities of the Newtonian fluids agreed within a few percent when measured with the guard ring using horizontal free boundary and without the guard ring using vertical free boundary. Also, viscosities and corrected normal forces of polymeric gels agreed in this comparison within a few percent.

For cone-and-plate measurements the conditioned torque signal was read with a digital volt meter. It was calibrated to within a few tenths of 1% of full scale (lowest range 200 g-cm). The vertical thrust F_Z was read on a strip chart recorder, as were also F_X and F_Y horizontal forces. They were calibrated to within about a half percent of full scale. P_{11} - P_{22} , calculated from F_Z , was corrected for the inertial term using values of the inertial coefficient $A = -40F_Z/3\pi\omega^2R^4\rho$ (where ω is the radian rotation velocity and R is the fixture radius) of 0.98 without guard ring and 1.05 with guard ring determined experimentally using water and glycerol solutions.¹⁰ A Moore (Spring House, Pa.) air pressure regulator was used in the air supply line to the machine. The rheometer was mounted on spring antivibration mounts to alleviate a vibration problem.¹⁰

Dynamic testing of samples was done in the ERD mode of the mechanical spectrometer.¹¹ The sample was held between parallel plates of 3.6 cm radius, and about 1.5–4 mm spacing. The free boundary was shaped to be vertical between the plate edges. The upper plate was rotated at a radian velocity ω , and the lower plate followed through forces transmitted by the sample. Speed was always adjusted gradually during start and stop operations.

The stage supporting the lower plate and its air bearing moves in the two orthogonal directions, X and Y , in which forces F_X and F_Y on the lower fixtures are also read out. Analysis of the system¹¹ discloses that during rotation the forces in the two directions which occur after an applied displacement, ΔY (departure distance of ERD shafts from concentricity), correspond to the storage and loss moduli:

$$G' = F_Y h / 2\pi R^2 \Delta Y \quad (4)$$

$$G'' = F_X h / 2\pi R^2 \Delta Y \quad (5)$$

where h is plate spacing. These moduli are equivalent to those obtained by small sinusoidal shear oscillations in the linear region of small strains.

There is usually some cycling of the forces in ERD, one period per revolution, during shaft motion. This cycling can often be reduced by applying a large displacement strain during rotation, e.g., 50% or 100%, and then gradually reducing the displacement to zero.

The ERD mode of testing is extremely sensitive to shaft alignment, especially with larger plates. With the 3.6 cm radius plates, the values of moduli were free from dependence on sample thickness (plate spacing) only if the shaft axes were aligned as precisely as possible. A micrometer gauge mounted on the upper shaft, reading vertical distance to the edge of the lower plate, deviated less than 0.00003

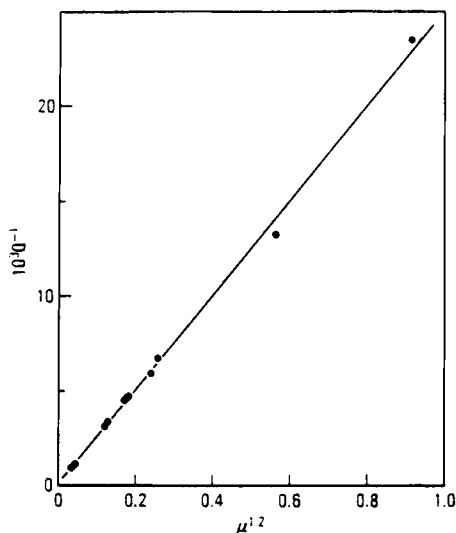


Fig. 1. Reciprocal of swelling weight, Q^{-1} , as a function of square root of ionic strength, $\mu^{1/2}$, for Carbopol® 940 gel in excess water or NaCl solution. The line represents $Q^{-1} = 0.0253 \mu^{1/2}$.

in. during a rotation. Even so, residual misalignment was indicated by the forces read in the X and Y directions changing with shaft velocity with no applied X or Y displacements.

A plexiglass chamber was made to enclose the region of the plates and sample to minimize evaporation from the free boundary.¹² It was a cylindrical housing made in two halves that could be placed around the fixtures leaving only small annular clearances around the shafts of the fixtures. It contained wet filter paper to keep humidity high and seemed adequate for keeping the free boundary constant for a few hours.

Stress-relaxation was performed with the sample between parallel plates, 3.6 cm radius, as for ERD, with the humidity chamber in place. Usually stress-relaxation was done after ERD measurements on the same sample. To relieve residual stresses that could be present initially, the sample was rotated at 4 rad/s and subjected to a strain of about 50%. The strain was slowly reduced to zero, and then rotation was stopped. After a rest period of 15 min or more during which the stress base lines were recorded, the experimental strain was applied and stress was recorded with time. Precision was poor because small stresses were observed at small strains, so a number of experiments were done to obtain average bias-free values.

RESULTS AND DISCUSSION

Swelling Curve

The equilibrium swelling capacity in excess solvent, Q (g swollen gel/g dry polymer), was determined in water and different concentrations of NaCl. Data (Fig. 1) demonstrated that the reciprocal of Q is proportional to the square root of ionic strength μ , as occurs for other polyelectrolyte gels at high swelling volumes. Ionic strength of the medium was calculated from:

$$\mu = \phi m + s \quad (6)$$

where ϕ is the osmotic coefficient, m is the molarity of carboxy coions in the polymer, and s is the molarity of added salt. ϕ was taken to be 0.15 from Katchalsky's review.¹³ The swelling capacity of C940 is about one-fourth that of Carbopol® 941 gel⁹ at any value of μ . Q in water was about 1060 for C940, and the swollen gel particles were about 2 mm in diameter.

Steady Shear Rheology

Apparent viscosities η and primary normal force $P_{11}-P_{22}$ were determined for the stock gel preparation and various series of dilutions. The viscosity flow curve is shown for the stock preparation (Fig. 2), as a function of shear rate of $\dot{\gamma}$. This preparation is a shear-rate thinning material typical of other closely packed gel suspensions. Modulus in shear G_s was calculated from eq. (3) at different shear rates, and these values are also given in Figure 2. The modulus is nearly independent of $\dot{\gamma}$ with only slightly increased values at the lowest and highest shear rates. Dilutions of the stock in water or salt solution also had G_s nearly independent of $\dot{\gamma}$, except at the highest dilutions, in which G_s increased with $\dot{\gamma}$.

C940 as a Closely Packed Thickener

In earlier analysis of dilution behavior, we compared values of η determined at $\dot{\gamma} = 100$ because these data could be obtained over a reasonably large concentration range. In Figure 3, η/cQ at $\dot{\gamma} = 100$ and at $\dot{\gamma} = 10$ are given as a function of cQ , in which c is the concentration of the polymer (g/g) and Q is the swelling weight ratio in excess solvent with ionic strength the same as that of the gel suspension. cQ is a reduced concentration, i.e., the ratio of concentration in the suspension to the concentration in the gel when excess solvent is present at constant μ .

Other closely packed thickeners have η/cQ nearly constant if cQ is sufficiently high, usually ≥ 2 . C940 reached a maximum in η/cQ at $cQ \approx 2$, and then decreased with increasing cQ to an apparent plateau value. In C940, as in other examples, the value of η was a function only of cQ during dilutions.

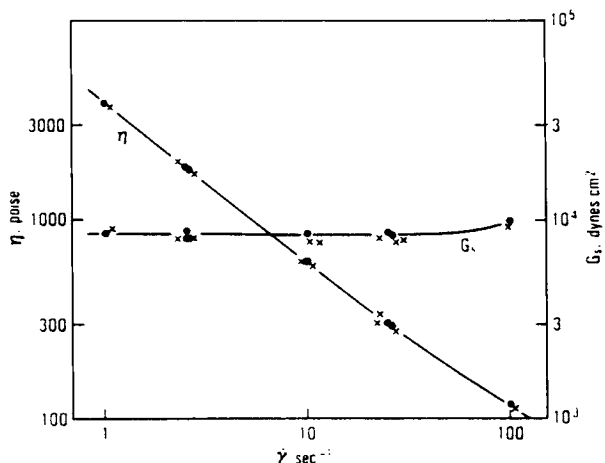


Fig. 2. Viscosity η and shear modulus G_s determined in set 3 cone and plate fixtures as functions of shear rate, $\dot{\gamma}$: (X) with guard ring; (●) without. In this figure and others, some of the points are slightly displaced parallel to the drawn lines, to avoid crowding.

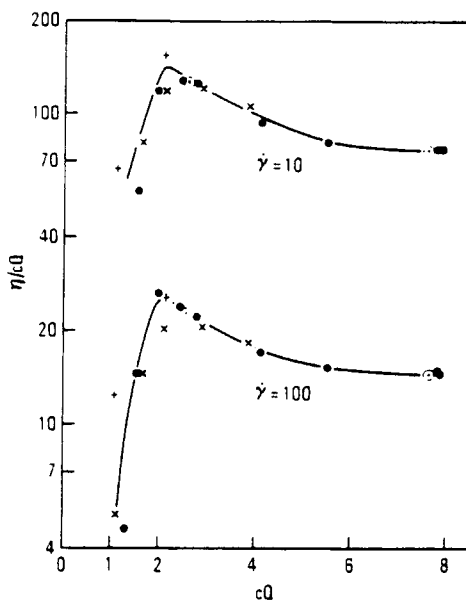


Fig. 3. Relationship of reduced viscosity η/cQ to reduced concentration cQ at two shear rates, $\dot{\gamma} = 10$ and $\dot{\gamma} = 100$. Data are: (●) stock and dilutions in H_2O ; (⊙) same partly filled fixture; (×) isoionic dilutions (in $0.0603M$ NaCl); (+) dilutions in $0.4M$ NaCl.

Steady-State Shear Modulus

For other closely packed gel systems, $G_{100}/c^{1/3}$ was nearly constant with dilution, except that $G_{100}/c^{1/3}$ tended to increase at higher dilutions in water. C940 had the expected behavior (Fig. 4), but the rise from the plateau value to the peak at high dilution was somewhat greater than for other gels.

The peaks in the water and isoionic salt dilution series both occurred at cQ

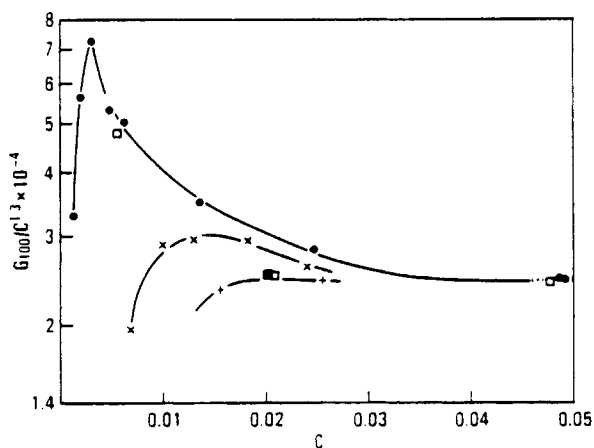


Fig. 4. Relationship of reduced shear modulus $G/c^{1/3}$ to reduced concentration c at $\dot{\gamma} = 100$. Data are: (●) stock and dilutions in H_2O measured with guard ring; (⊙) same, partly filled fixture; (×) isoionic dilutions (in $0.0603M$ NaCl); (+) dilutions in $0.4M$ NaCl. Apparent equilibrium moduli, $G_e/c^{1/3}$, from Figure 8, are given for comparison: (□) stock and dilution in H_2O ; (■) isoionic dilution.

$\cong 2$. A possible explanation of the increase in $G_{100}/c^{1/3}$ values above the plateau value is that the crosslinked chains are stretched by swelling to beyond a Gaussian distribution of lengths. If so, the increase in $G_{100}/c^{1/3}$ should depend on c and not cQ , a relationship which seems confirmed (Fig. 4) by the isoionic series (\times) following the water series (\cdot), where $cQ > 2$.

The several dilution series curves of Figure 4 would not superimpose if plotted vs. cQ . The maximum in $G_{100}/c^{1/3}$ appears not to have the same origin, i.e., overly stretched chains, as does the maximum in η_{100}/cQ (Fig. 3).

Dynamic Moduli

The storage moduli G' and the loss moduli G'' were determined for C940 by eccentric rotating discs rheometry. These moduli should be equivalent to dynamic moduli obtained by small sinusoidal oscillations in a cone-and-plate rheometer in the linear region of stress-strain behavior.

It is necessary that the moduli be measured in the linear region in order to interpret the moduli in structural terms. The moduli of C940 suspensions were linear over only small strain ranges, as is evident from Figures 5-7. The values of G' and G'' are the limiting slopes of the stress curves τ_Y and τ_X , respectively, vs. strain γ . The stock prep of C940 was linear up to about 10% γ for G' , at low γ . The linear region was very small, only a few percent γ .

The stress-strain behavior depended on sample conditions, though, and a high dilution in water (Fig. 6) behaved differently. Here, the linear region of storage stress covered only a few percent strain, and the loss stress was proportionately larger and more nearly linear. The changed behavior probably resulted from

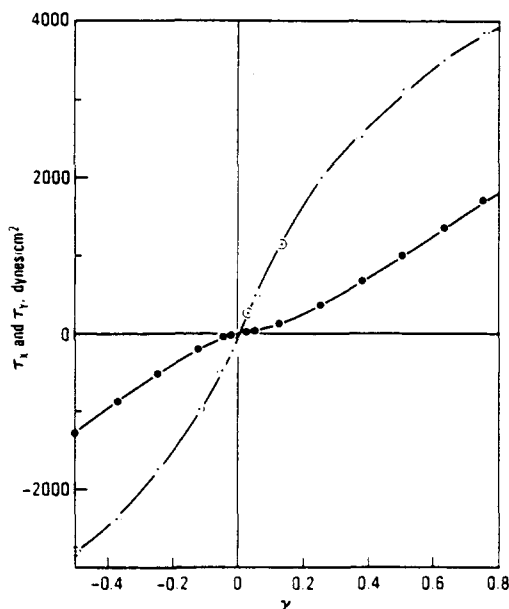


Fig. 5. Stresses in eccentric rotating disc (ERD) rheometry as functions of strain γ for the stock gel, $c = 0.0484$, $cQ = 7.8$. (\circ) Storage stress τ_y ; (\bullet) loss stress τ_x : 3.6 cm plates with spacing of about 2 mm were used; $\omega = 10$.

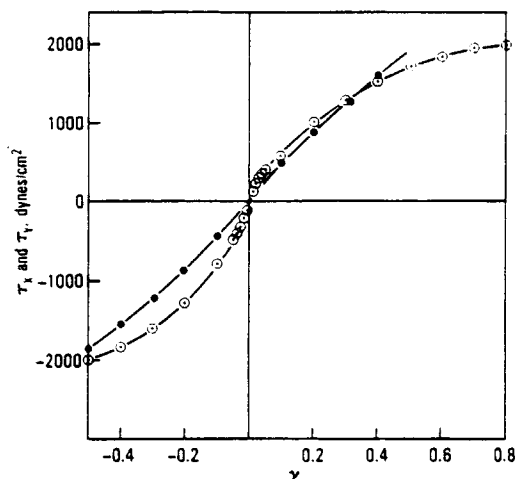


Fig. 6. Stresses in ERD rheometry as function of γ for a dilution of the stock gel dilution A, $c = 0.0056$, in water. $cQ = 2.64$; (○) storage stress; (●) loss stress. Conditions same as for Figure 5.

the high dilution, since isoionic dilution to about the same cQ but greater c (Fig. 7) resulted in behavior similar to the stock preparation.

The stress-strain diagrams show some asymmetry about the origin, especially Figure 6. This asymmetry demonstrates the need for critical alignment of the rheometer in ERD work. A very slight misalignment of the shafts causes some working of the sample during rotation. This working develops forces in X and Y directions that can be nulled by adjusting the signal conditioner of the instrument, but, if the working action maintains strains in the sample, the linear stress-strain region may be diminished for samples with small linear stress-strain ranges. The C940 and some other types of gels were very sensitive in this respect. Other materials have behaved more normally for us in ERD. To minimize this

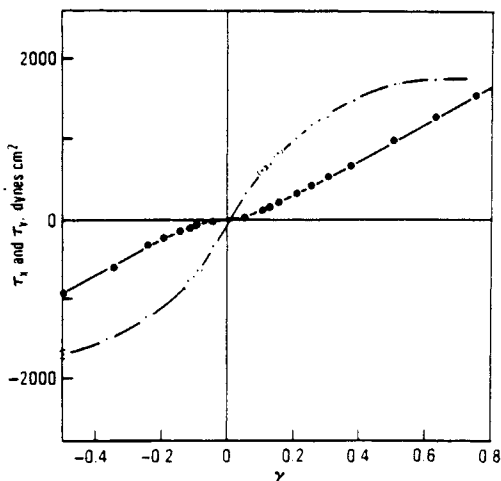


Fig. 7. Stresses in ERD rheometry as function of γ for an isoionic dilution of the stock preparation. $c = 0.0164$, $cQ = 2.65$. (○) Storage stress; (●) loss stress. Conditions same as for Figure 5.

problem, the machine was checked frequently for alignment. All moduli were measured over a stepwise series of strains in a range where linearity was adequate. Values of G'' are not reported owing to their low values and very small linear ranges.

Values of G' for C940 and three dilutions are given in Figure 8. The moduli depend on frequency of rotation ω , unlike the corresponding G_s values. Since G' values are not constant, it would be appropriate to extrapolate G' to zero frequency. G' values at low ω were difficult to obtain with precision, though, so stress relaxation moduli $G(t)$ were determined.

Stress-Relaxation Moduli

These moduli were determined in an experiment similar to ERD except without rotation. After a displacement in the Y direction, τ_Y was observed as a function of time. Figure 9 gives typical results. After a few minutes, values of τ_Y became nearly constant and extrapolation vs. reciprocal of time gave apparent equilibrium stresses [Fig. 9(A)]. G_e calculated from equilibrium τ_Y is plotted in Figure 9(B). These values are not constant with γ , i.e., stress-strain is not linear, but must be extrapolated to zero strain. Because these small strains had to be used, only small stresses were observed and, consequently, data are not precise. Stress base lines tended to drift with time, so that a number of tests with displacements in both directions of either the X or Y coordinate were required to eliminate bias owing to base line drift.

Values of G_e derived by the above procedure are given at $\omega = 0$ in Figure 8. These values are only slightly lower than the corresponding G' values at the lowest ω .

The four values of $G_e/c^{1/3}$ for C940 and its dilutions are entered in Figure 4 for comparison with corresponding G_s values at a given concentration. The

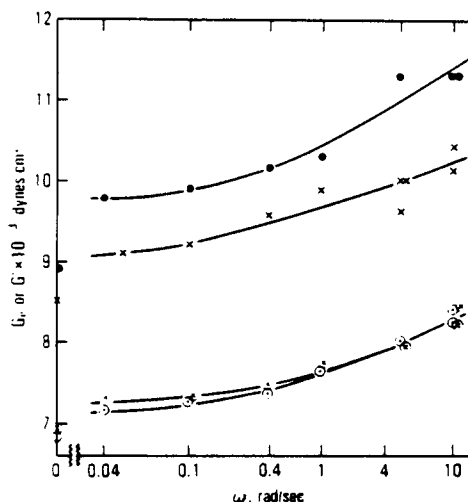


Fig. 8. Storage moduli G' determined by ERD for C940 samples plotted as functions of radian frequency ω . Samples are: (●) stock preparation; (×) dilution in H_2O , $c = 0.0056$, $cQ = 2.64$; (⊙) dilution in H_2O , $c = 0.0201$, $cQ = 5.04$; (○) dilution in isoionic $NaCl$, $c = 0.0201$, $cQ = 3.25$. The apparent equilibrium moduli G_e determined by stress relaxation are shown at $\omega = 0$.

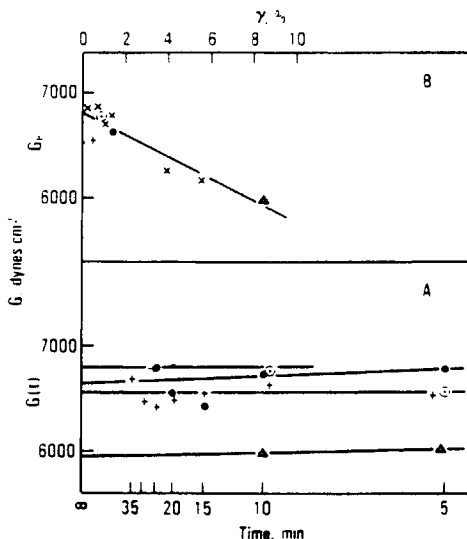


Fig. 9. Stress relaxation of C940 dilution in H_2O to $C = 0.0201$. (A) Four different strains (\odot , \bullet , $+$, Δ) observed with time t plotted vs. $1/t$; (B) extrapolated values plotted vs. strain γ . Other experiments (\times) not given in A are also plotted.

agreement with the corresponding G_s values is surprisingly good. It appears that either G_e or G_s can be used to infer structure properties of this gel. It remains to determine if other gels which have G_s constant with $\dot{\gamma}$ have as good agreement between G_s and G_e . Where G_s varies with $\dot{\gamma}$, G_e should be the better measure of structure, provided it can be measured with sufficient accuracy.

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

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Received April 2, 1982

Accepted June 3, 1982