JOURNAL OF APPLIED POLYMER SCIENCE VOL. 12, PP. 2415–2420 (1968)

A Recording, Air-Bearing Torsion Pendulum

F. RODRIGUEZ, R. A. VAN BREDERODE, and G. G. COCKS, *School of Chemical Engineering, Cornell University, Ithaca, New York 14850*

Synopsis

A recording torsion pendulum has been designed which allows the measurement of storage modulus and loss modulus for weak gels. The gel is held in a cone–plate geometry. The 5° cone, along with the inertial elements of the pendulum, is supported by an air-lubricated bearing. The decay of oscillations is sensed by a Proximeter which does not touch the moving apparatus and which converts the amplitude of oscillation into a dc signal of several volts. Storage moduli as low as 40 dyn/cm^2 and log decrements as low as 0.0054 have been measured.

The dynamic mechanical properties of weak, fragile gels are not easily measured in conventional instruments. With self-healing gels such as those formed by soaps in lubricating oil, many kinds of penetrometers and consistometers are available which measure gel strength, rigidity, and recovery. However, with gels of covalently crosslinked polymers in water, only small strains and stresses can be imposed without irreversibly disrupting the network structure. The torsion pendulum, properly designed and operated, can yield useful results within the limits of a shear strain less than 0.5 and with shear moduli down to 40 dyn/cm^2.

When a sample of a material is used as the restoring element in a torsion pendulum, the dynamic modulus and loss for the material can be estimated from the geometry of the sample together with the frequency and the decay rate of the oscillations. If the experiment can be confined to the region of linear viscoelasticity and if the damping of the oscillations is not excessive, the frequency of oscillation f (in radians per second) will be a function only of the moment of inertia of the system I (in g-cm^2) and the stiffness of the sample as torque k per unit of twist (in dyne-centimeters per radian):

$$f^2 = k/I \quad (1)$$

A useful measure of the damping properties of the material is the log decrement λ, which is the decay rate of maximum amplitude θ_m with cycle number n:

$$\lambda = -d(\ln \theta_m)/dn \quad (2)$$

The two observable parameters, f and λ, can be related to various properties of the material.[1] The dynamic storage modulus G' and loss modulus

G'' are connected in a later section to f and λ for the cone–plate geometry preferred in the present work.

The limiting condition of eqs. (1) and (2) is mainly that f and λ must be independent of amplitude. A pendulum which operates reproducibly at very small amplitudes has a real advantage for this reason. Equation (1) also presupposes that λ is small, on the order of 0.3 or less. The magnitude of λ is a function of the material and is not adjustable externally.

The geometry of the sample is directed by experimental convenience although mathematical tractability in analysis is desirable. For work with soft gels, cup-bob, parallel-plate, and cone-plate arrangements are useful. The cone–plate with an angle less than 5° is favored over the parallel–plate by mathematical considerations and over the cup-bob by experimental convenience under the present circumstances.

Many designs have been proposed for the pendulum itself. They offer various solutions to the problems of (*a*) maintaining alignment of moment arm or disk with sample and (*b*) reading the amplitude of successive oscillations. When the sample is stiff, alignment is not a great problem. By counterbalancing the inertia arm or disk so that the sample is not compressed or elongated, even rubbery samples can be measured. However, a lower limit of amplitude is established by the latitude of acentric movement permitted in the "free" end of the specimen. With very soft samples, a separate support bearing having small energy loss is desirable. The only bearing suitable for soft gels where the restoring force is very small is the gas-lubricated type. The advent of relatively inexpensive air-bearings with low run-out makes such a modification very practical.

Nonrecording pendulums are regulated by increasing the moment of inertia to give low frequencies so that the maximum amplitudes can be followed manually, often aided by optical levers. For higher frequencies, a popular design uses strain gages at the "fixed" end of the sample to measure the stored stress in successive oscillations.[2] The instrument being described now uses a Proximeter to measure successive amplitudes without contacting the oscillating system. The advantage of the present system for soft gels is that alignment and measurement are accomplished externally from the sample with a minimal contribution to the frequency and amplitude. Furthermore, the components are commercially available so that very little shop work is involved.

DESCRIPTION OF APPARATUS

A table-model drill press is used to support a Model IC-2036 air bearing (Lifetime Components, Sandusky, Ohio) which is supplied by dry air (Fig. 1). About 0.2 ft^3/min of air at 18 psig and 25°C is adequate. Attached to the lower shaft of the bearing is a moment arm and a collet-holder. The collet arrangement is preferable over other kinds of chucks since it permits exchange of sample systems with a minimum of disturbance to the sample holder. Various sample holders have been used for different types of materials. The cone-plate is especially useful with gels, while vulcanized rubber,

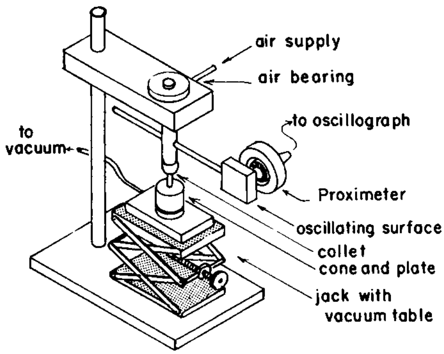

Fig. 1. Torsion pendulum. Proximeter mounting and sample-holder sleeve not shown.

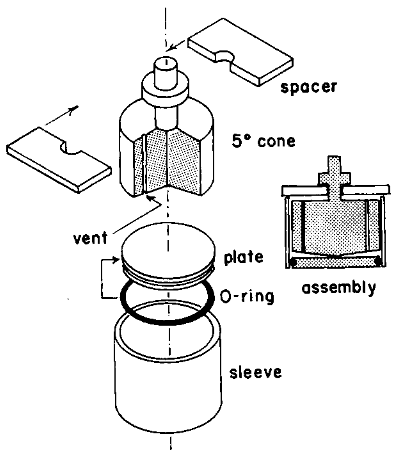

Fig. 2. Cone–plate sample holder for irradiation and testing. Sleeve removed during testing.

supplied in sheets, is most easily studied in parallel-plate geometry. In the former case, a shaft from the cone is connected through the collet to the air bearing. Once the viscometer is raised by the laboratory jack and the shaft locked in the collet, a vacuum is applied to hold the base plate in place.

At one end of the moment arm is an aluminum surface, about 1 in.^{2}, which is used in conjunction with the Proximeter to measure amplitude and frequency of oscillations. The Model 302 Proximeter (Bentley-Nevada, Minden, Nevada) is capable of measuring up to 4000 Hz at various distances from the detector. Signal linearity and recorder response establish 0.1 in. and about 20 Hz as upper limits for distance and frequency in the present mode of operation. Although higher frequencies could be accommodated by a recorder using light-sensitive paper, a Mark 250 rectilinear oscillograph (Brush Instrument, Cleveland, Ohio) has proven satisfactory and uses less expensive paper.

The cone–plate sample-holder used here is especially designed so that it can be charged with a deoxygenated liquid polymer solution and maintained under a nitrogen atmosphere. The liquid is gelled in place by exposure to γ-radiation from a ^{60}Co source. The holder acts therefore both as irradiation vessel and as part of the torsion pendulum. The cone and plate are enclosed in an acrylic plastic sleeve (Fig. 2). The cone is truncated as suggested by Markovitz[3] to insure, with minimum loss in accuracy, that there is no metal-to-metal contact which would severely distort damping measurements in the gel. A battery and light in series are used to check for separation when the cone and plate have been positioned in the pendulum.

While positioning the cone over the plate, excess polymer solution on the plate escapes via two vents. The transparent sleeve permits a visual check that there are no trapped bubbles between the cone and the plate. To assure accurate horizontal and vertical alignment, a spacer is set on top of the sleeve. The spacer and sleeve are removed only after the final positioning in the torsion pendulum. The sleeve is suspended by a separate clamp above the sample during measurements and touches no moving surface.

CALIBRATION AND OPERATION

Proximeter

The Proximeter is a transducer (a button with a wire-coil face, 0.3 in. in diameter) which converts distance between itself and a conducting surface into a voltage signal. It is driven by an 18-V dc input and produces a dc output of over 10 V/0.1 in. separation. The output is not linear with the distance except in the middle region (Fig. 3). Although an absolute calibration is not required, it is well to be aware when the linear region has been exceeded. Since the usual signal being generated does not decay so rapidly that amplitudes need be measured every half cycle, only one half of each

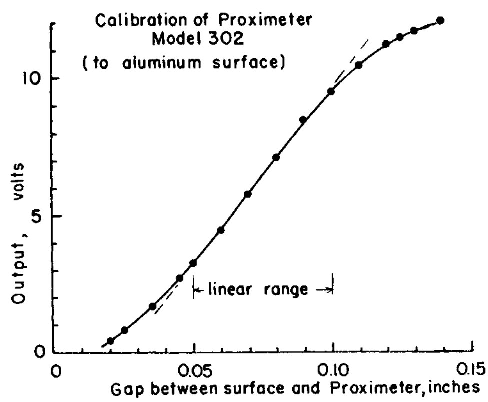

Fig. 3. Calibration of Proximeter for aluminum surface.

oscillation has to be in the linear region. This means that the maximum excursion for the moment arm at the Proximeter is about 0.1 in. from the rest point at the end of a 3-in. radius. The corresponding maximum shear strain in a 5° cone is 0.4 shear unit.

Pendulum-Bearing Friction

The practical lower limit of loss measurement depends somewhat on the geometry of the restoring element. The lowest loss measured so far by us on a gelled sample gave $\lambda = 0.0054$, that is, the amplitude decayed only about 5% in 10 oscillations. We regard this as the lower limit of accuracy in other gel measurements. The loss includes friction in the air-bearing and air-drag on the moment arm. The moment arm itself is surrounded by a plastic box to reduce adventitious air currents. Exponential decay of amplitude is shown both for weak gels and strong ones. Gel A (Fig. 4) received only enough radiation to achieve one-tenth of the maximum (plateau) modulus, whereas gel B was crosslinked to nearly half the plateau modulus. The loss for an uncrosslinked system can be estimated by adding an external spring as a restoring element and placing polymer solution in the cone-plate. The loss for such a system is substantially greater than for the lightly crosslinked gel A (Fig. 4). The spring was selected to give a frequency comparable to that of the gels, namely, from 0.2 to 4 cps and loss from the spring was subtracted from the measured loss of the solution.

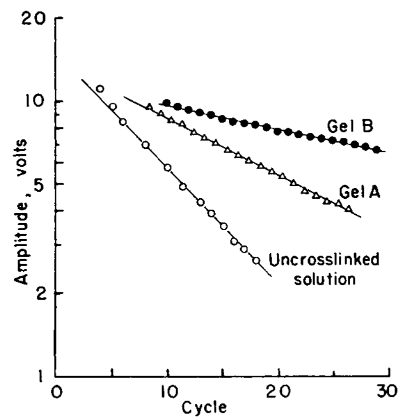

Fig. 4. Decay of oscillations for 1% Polyox solutions: (O) no irradiation; (Δ) 0.14 Mrad; (●) 0.70 Mrad. Frequencies were 0.465, 0.861, and 2.80 cps, respectively. An external spring was used with the unirradiated sample.

Calculation of Moduli

The mechanical properties of the gels are conveniently represented by the dynamic storage modulus G' and a loss modulus G'', both referring to shear experiments. It can be shown that

$$G' = 3\alpha I f^2 / 2\pi R^3 \tag{3}$$

and

$$G'' = \lambda G'/\pi \tag{4}$$

where α is the cone angle, R is the cone radius, I is the moment of inertia, and f and λ are the frequency and log decrement, as mentioned before. These equations apply when λ^2 is much less than $4\pi^2$, that is, when λ is less than about 0.5. For gel A of Figure 4, $\alpha = 5.00°$, $I = 7924$ g-cm^2, and $R = 2.20$ cm. Equations (3) and (4) with $f = 5.41$ radians/sec and $\lambda = 0.047$ give $G' = 905$ dyn/cm^2 and $G'' = 13.6$ dyn/cm^2. The storage modulus can be further interpreted as a measure of crosslink density by use of the well-known kinetic theory equation.[4]

The apparatus described here is currently being used to characterize gels obtained from the irradiation of polymer solutions by γ-rays. An interpretation of the moduli in terms of crosslinks produced gives a quantitative picture of the yield in the reaction taking place. Many past studies have been content to measure dose to gelation. This equipment makes it possible to study and propose mechanisms for processes that occur during crosslinking after initial gel formation and even for some after the storage modulus reaches a plateau because the loss modulus continues to change.

This work was conducted with the aid of Grant G.K.-1093 from the National Science Foundation. Poly(ethylene oxide) was furnished by the Union Carbide Corporation. The gamma radiation cell is part of the facilities subsidized by the AEC.

References

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, pp. 30–33 118, 455.

2. L. E. Nielsen, *Rev. Sci. Instr.*, **22**, 690 (1951).

3. H. Markovitz, L. J. Elyash, F. J. Padden, Jr., and T. W. DeWitt, *J. Colloid Sci.*, **10**, 65 (1955).

4. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Oxford Univ. Press, 1958, pp. 70–71, 88–89.

Received February 14, 1968
Revised March 11, 1968