Recoverable Shear Measurements in a Parallel Plate Rheometer

S. M. FRUH and FERDINAND RODRIGUEZ

Cornell University, Ithaca, New York

A parallel plate rheometer has been devised which permits measurements of shear stresses of 10^2 to 10^5 dynes/sq.cm. and shear rates of 10^{-5} to 1 sec.$^{-1}$. A linear, air lubricated bearing is used to align the apparatus, and a linear variable differential transformer is used to sense changes in position. With a sample of polyisobutylene and with several samples of poly(dimethyl siloxane), it has been established that a Hookean range exists for each sample at low stresses. Hooke's law in shear states that the modulus is independent of stress, where the modulus is defined as the ratio of the shear stress in steady, creeping flow to the strain which can be recovered after the stress is removed. Other conclusions supported by the present work are that the Hookean range does not extend to stresses which are high enough to cause non-Newtonian flow, that the modulus decreases with increasing molecular weight although not in direct proportion, and that a sample with a broad molecular weight distribution has a lower modulus than one with a narrow distribution.

The deformation of fluids in a parallel plate configuration is often used in defining viscosity and modulus in simple shear. However, viscometers using this geometry have never been very popular. There are inherent limitations. When a sample of finite area is deformed, strains cannot exceed several units before edge effects become important. Often the sample is used to support itself or part of the apparatus. Thus, the method is useful only for high viscosity materials at low shear rates. A commercial viscometer for asphalts is available (*1*), and several others have been described in recent years (*2*, *3*). One feature common to all three of these is that the sample itself is used to maintain the alignment between the sliding tongue and the stationary plates. In the present work, an apparatus has been developed in which alignment is assured apart from the sample by a linear, air lubricated bearing. Tongue displacement, which is proportional to shear, is measured by a linear variable differential transformer (LVDT) whose signal is recorded as a function of time.

The application of this new instrument still is limited to low shear rates and relatively high viscosities. However, it is within such limits that measurements are useful for testing linear viscoelastic models. Furthermore, it is likely that measurements in this region will be quite sensitive to small variations in polymer structure such as branching (*4*), microgel content (*5*), and molecular weight heterogeneity (*2*).

APPARATUS

The rheometer (Figure 1) consists of four basic parts: the plates, the linear air bearing, the linear variable differential transformer, and an air lubricated pulley. The sample, in two pieces on either side of the central plate, is sheared between the moving central plate and two outer stationary plates all mounted vertically. The central plate is attached to the shaft of a sliding air bearing such that the shear direction is along the shaft axis. The sliding bearing supports and aligns the

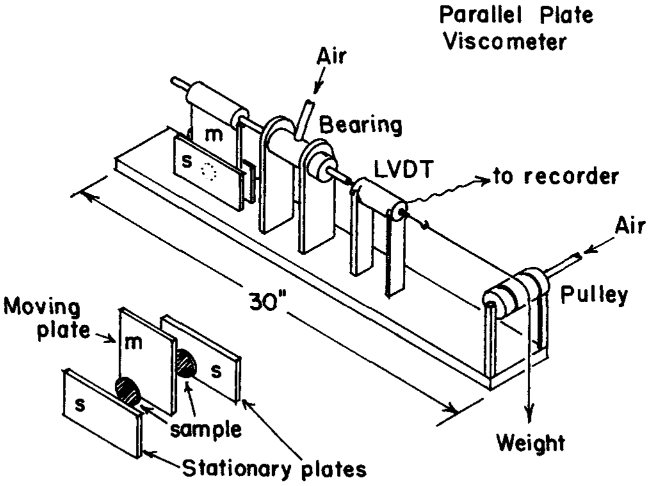

Fig. 1. Parallel plate viscometer.

S. M. Fruh is with Enjay Polymer Laboratories, Linden, New Jersey.

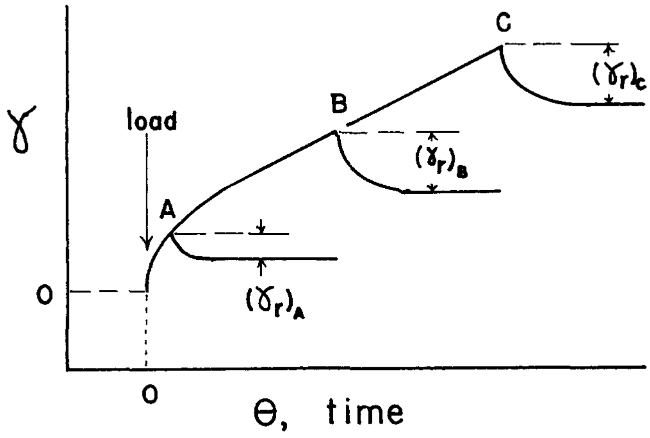

Fig. 2. Typical strain time curves.

moving system without itself exerting any significant force on it.

Also attached to the shaft of the bearing is the core of the LVDT, a device which gives a DC signal proportional to linear motion. The air bearing pulley is essentially frictionless and allows the use of a hanging weight to exert axial force on the main shaft.

The plates are made from acrylic plastic for convenience in observing the samples, but transparency is not a requirement and metal plates can be used for high temperature work. Although the plates have an overlapping surface of almost 10 in. sq., most samples used so far have occupied only about one-tenth of the available area. The clearance between outer and moving plates is adjustable. The sample is loaded into the viscometer in two equal pieces, one on either side of the central plate. Temporary spacers 0.050 in. thick are placed so that the outer plates can squeeze the sample down to the thickness of the spacers. The outer plates then are bolted rigidly to the base and the spacers slipped out.

The linear air bearing operates with no measurable friction on an air supply of 25 lb./sq. m. gauge. The shaft is 10 in. by 1/2 in. in diameter. Since the core of the LVDT does not touch the walls of the cavity, there is no friction introduced. There is a solenoid force exerted in the LVDT which is not negligible under all circumstances. However, if the core is held to within 0.05 in. of the center position and the voltage to the coil is 2.9 v. AC (about one-fourth the maximum), a linear demodulated signal of 2.2 mv. DC/0.01 in. core displacement is obtained with little background noise. The most convenient method for varying the temperature in the range of 3° to 53°C. was to place the entire apparatus in a room or box at the desired temperature. A greater range could be obtained by using cored metal plates, but this has not been necessary yet.

Because of the geometry, the total shear is limited to several units. The rate of shear ranges from 10^{-5} to 1 sec.$^{-1}$, shear stresses from 10^2 to 10^5 dynes/sq. cm. The use of larger samples (greater area) and horizontal rather than vertical plates could lower the measurable viscosity by a factor of about 10.

OPERATING PROCEDURE

After the sample is placed in the apparatus, the air supply to the air bearings is turned on. A relaxation period comparable to that observed in subsequent creep recovery is allowed before the sample is stressed. A sample is sheared by hanging a weight over the pulley and by attaching it to a hook on the end of the main shaft. When the distortion which is recorded becomes linear with time, the weight is removed and the recovery followed. The time required to achieve linearity varies with the molecular weight of the sample in any series. With high molecular weight samples, visual inspection of the recorder tracing may be deceptive. It is more satisfactory to measure the recoverable shear after increasing times of creep until a constant level is reached (Figure 2). For the highest molecular weight sample used in the present study, creep times of over 10 hr. were required (Figure 3). Because of the finite sample area, the question of end effects arises. The simplest test is to run increasing sample sizes at the same shear stress. When this is done, there is no discernible effect on the measured viscosity or recoverable shear strain for samples in the range of 1 in. sq. in area.

HOOKEAN BEHAVIOR

There are basic disagreements among workers who have measured the elastic modulus by various means. Recoil in a rotational viscometer has been used by some (*5* to *7*) and in a parallel plate viscometer by another (*2*). It has been difficult for most workers to get into an authentic Hookean range where the modulus G, defined as the ratio of shear stress τ to recoverable shear strain γ_r, is a constant. This, then, is the first problem to which the present apparatus has been applied. Philippoff et al. (*6*) found that recoil measurements in a cup-and-bob viscometer indicated a Hookean region for polyisobutylene up to a shear stress of about 10^4 dynes/sq. cm. The modulus G was 5.5×10^4 dynes/ sq. cm., and the Newtonian viscosity η_0 in the same range was 1.12×10^6 poise. By using a similar sample, the behavior has been qualitatively reproduced with the present apparatus (Figure 4). The new measurements yield $G = 7.0 \times 10^4$ dynes/sq. cm. and $\eta_0 = 0.80 \times 10^6$ poise. The departure from Hookean elasticity and New-

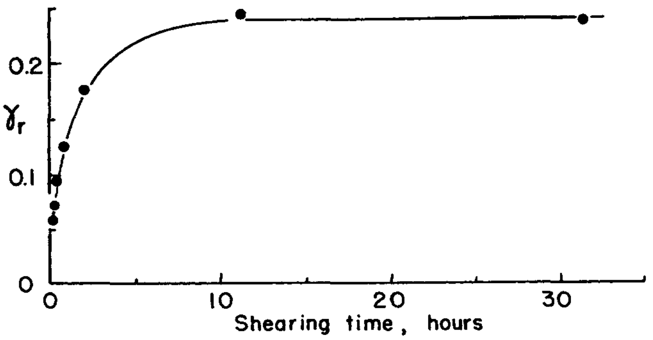

Fig. 3. Variation of recoverable shear strain γ_r with total strain time for sample F-4 at a stress 1,555 dynes/sq.cm.

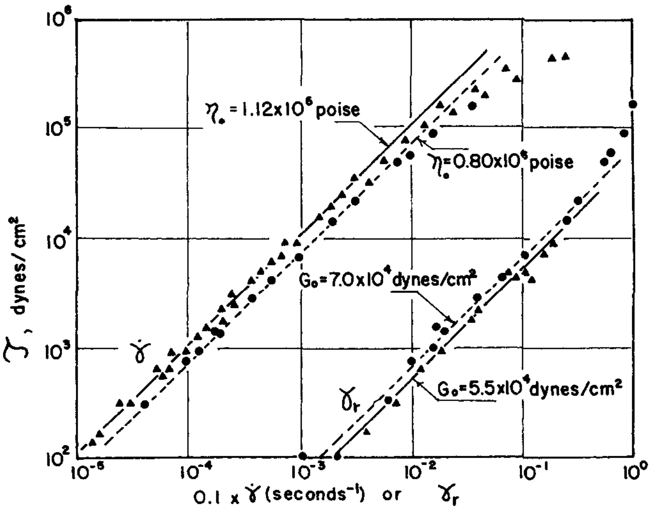

Fig. 4. Creep ($\dot{\gamma}$) and recovery (γ_r) for Vistanex LM-S (▲, data of Philippoff et al.) and Vistanex LM-MH (●, present work).

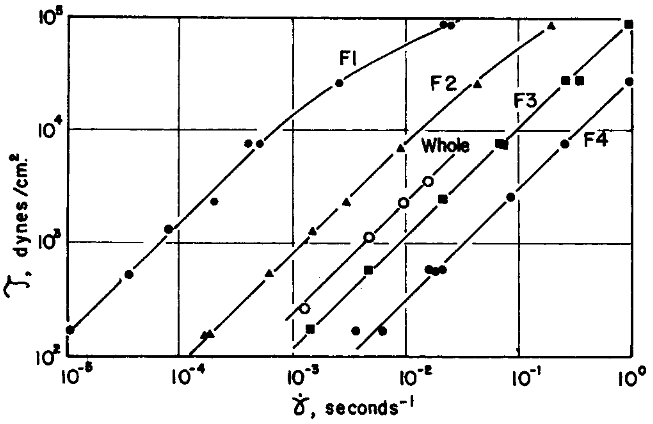

Fig. 5. Flow curves for siloxanes of Table 1.

tonian flow occur at about the same stress.

A series of poly(dimethyl siloxane) fractions were precipitated sequentially from a toluene solution by additions of methanol. The molecular weights, low shear viscosities, and Hookean moduli are summarized in Table 1 and Figures 5 and 6. There are several notable features:

1. There is a definite Hookean range for each material within the Newtonian flow range.
2. This Hookean behavior does not extend to the non-Newtonian flow range.
3. The modulus at low stresses decreases with increasing molecular weight.

The first point seems unquestionably confirmed. Benbow (*9*) and Rosen (*5*) seemed less confident in the existence of such a range, since their measurements did not extend to stresses much below 10^4 dynes/sq. cm. Their data fall in the cross-hatched area of Figure 6.

The second point is consistent with the aforementioned work of Benbow and of Rosen. However, workers using somewhat less direct measures of elasticity have concluded the converse. Die-swell measurements and end-effects plots from capillary extrusions may be cited. Bagley (*10*) postulates Hookean behavior for the linear plots of end-correction vs. shear stress. For both linear and branched polyethylene he indicates a Hookean region up to the point of melt fracture which is far into the non-Newtonian flow range and where the stresses exceed 10^6 dynes/sq. cm. Spencer (*11*) states that die-swell measurements for molten polystyrene can be interpreted as confirming Hookean behavior well into the non-Newtonian flow region. This latter observation is the more pertinent to the present work because the measuring technique is similar, even though the quantity measured differs. In some techniques, normal stress measurement and elastic-end-correction analysis, for example, the numbers are obtained while the stress is being applied. However, shear recovery and die-swell (the ratio of extrudate diameter to capillary diameter) both are measured after the stress has been removed. A disadvantage of the die-swell measurement is that most workers have dealt with materials that crystallize (polyethylene, polypropylene) or form glasses (polystyrene) shortly after extrusion. The long times of creep recovery so easily tolerated in the present apparatus are not feasible for unsupported, rod shaped melts. Consequently, most workers freeze the extrudate within a few seconds of extrusion, and the total recovered strain measured by die-swell is attenuated. In this light, the parallel plate data must be regarded as the more reliable. The conclusion is unescapable that Hookean behavior defined in terms of recovered strain certainly does not obtain at high stresses where flow is no longer Newtonian.

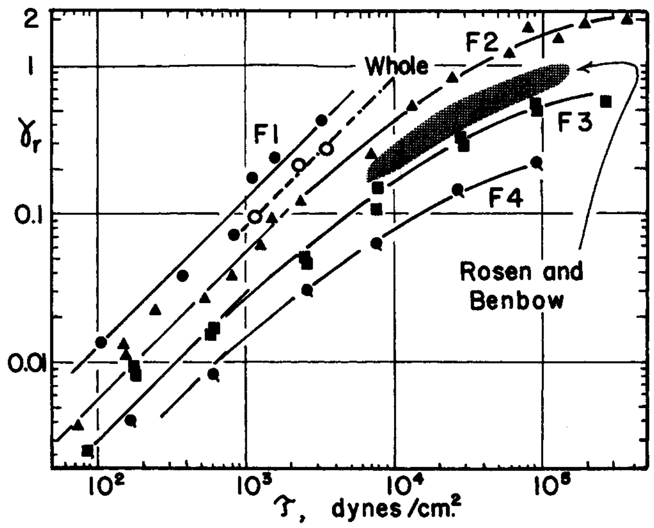

Fig. 6. Creep recovery curves for siloxanes of Table 1 (data of Benbow and Rosen lie in cross-hatched area).

TABLE 1. PARAMETERS OF SILOXANES

Designation	M_w* × 10^{-6}	M_w/ M_n*	$\eta_0 \times 10^{-4}$ poise	$G_0 \times 10^{-4}$ dynes/ sq. cm.
F-1	1.3	1.7	1,600 (25°C.)	0.8 (25°C.)
F-2	0.78	1.7	87	1.9
F-3	0.55	1.5	12.5	3.5
F-4	0.37	1.4	3.1	6.6
Whole polymer	0.70	2.4	25	1.2

* Established by gel permeation chromatography (*7*) and intrinsic viscosity (*8*).

A point even more in controversy is the effect of molecular weight on the elastic modulus. Both Bagley and Spencer invoke the theory of rubber elasticity to explain that modulus G should be inversely proportional to the molecular weight according to

$$G = \tau/\gamma_r = RT\rho/M \qquad (1)$$

Although disagreeing with these workers on the constancy of the modulus at high stresses, we support the idea of a decrease in modulus with increasing molecular weight although not according to Equation (1) (Figure 7). Van Holde, who also used a parallel plate viscometer on polyisobutylenes, found no effect of molecular weight on modulus. Benbow, with a cone plate viscometer and siloxanes, found no great effect.

Comparing die-swell for various molecular weights at a constant shear stress, Spencer (*11*) found an increase in swell for polystyrenes with increasing molecular weight as did Johnson and Baer (*12*) with low, molecular weight siloxanes. On the other hand, Arai and Aoyama (*13*) found die-swell decreased slightly with increasing molecular weight for linear polyethylenes. Although the normal stress differs fundamentally from recoil and die-swell in that it is measured during stressing, it should be mentioned that most workers conclude that a modulus based on normal stress measurements is independent of molecular weight.

Watkins (*14*) followed an earlier idea of Ferry (*15*) and proposed an equation for elastic creep compliance which takes into account variations in the molecular weight distribution. The suggestion of Watkins can be cast in a form for G, the shear modulus, in terms of a parameter p which is defined as

$$1/p = (M_w/M_n) - 1 \qquad (2)$$

Then

$$G = (5/2)\,\frac{(p+1)^2}{(p+3)(p+2)}\,(\rho RT/M_w) \qquad (3)$$

It can be seen in Figure 8 that Equation (1) would apply only when M_w/M_n is a little less than 2. The experimental data for the silicones do not fit Equation (3) (Figure 8). However, the downward trend in $GM/\rho RT$ with increased M_w/M_n is consistent with the prediction of Equation (3) in a qualitative sense.

The conclusion from the present work is that the increase in γ_r with molecular weight at constant stress is so large as to be beyond the range of experimental uncertainty, and that, when defined in terms of the recovered strain, the modulus decreases with increasing molecular weight. Even Van Holde, who finds no significant change in modulus with molecular weight, concludes that modulus decreases with increasing broadness of molecular weight distribution. This observation makes sense only if the high molecular weight end of a broad distribution is imparting greater recoverable shear strain than a lower molecular weight would. This is consistent with the present work. When we compare fraction F-2 and fraction F-3 with the whole polymer (Table 1), we find that the modulus for the whole polymer is smaller than that for fractions of even higher viscosity average molecular weight and, therefore, that the recoverable strain at constant shear stress is greater.

ACKNOWLEDGMENT

The authors are grateful to the Union Carbide Corporation and Enjay Chemical Company for providing samples.

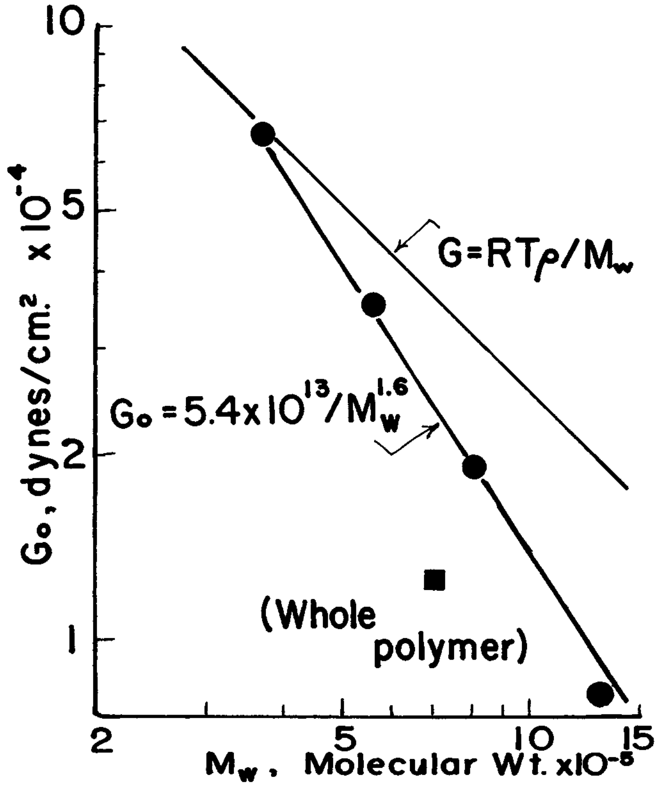

Fig. 7. Modulus based on recoverable shear strain.

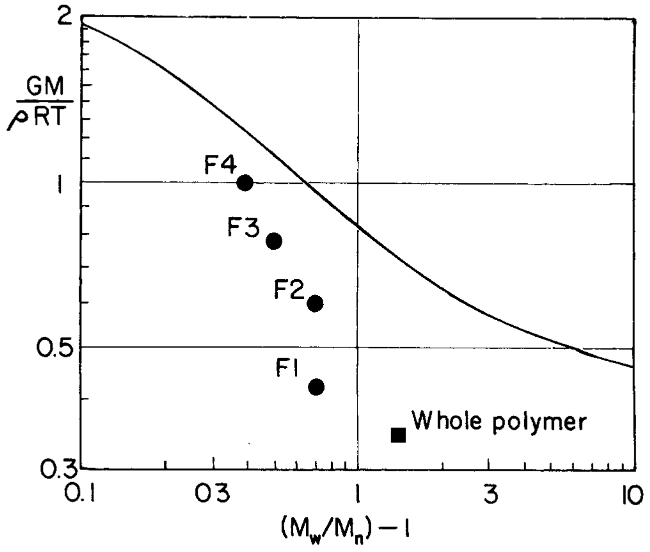

Fig. 8. Dimensionless modulus $GM/(\rho RT)$ as a function of polydispersity index M_w/M_n for silicones of Table 1. Solid line corresponds to Equations (2) and (3).

NOTATION

G = shear modulus, dynes/sq.cm.
G_0 = shear modulus in Hookean regime
M = molecular weight, g./mole
M_w = weight average molecular weight
M_n = number average molecular weight
R = gas constant, consistent units
T = absolute temperature, °K.

Greek Letters

$\dot{\gamma}_r$ = recoverable shear strain
γ = rate of shear, sec.$^{-1}$
η_0 = Newtonian viscosity, poise
ρ = density, g./cc.
τ = shear stress, dynes/sq. cm.

LITERATURE CITED

1. Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," p. 302, Interscience, New York (1963).
2. Van Holde, K. E. and J. W. Williams, *J. Polymer Sci.*, 9, 243 (1953).
3. Gibbs, D. A., and E. W. Merrill, "Proceedings of the Fourth International Congress on Rheology," Part 2, p. 183, E. H. Lee, ed., Interscience, New York, (1965).
4. Wyman, D. P., L. J. Elyash, and W. J. Frazer, *J. Polymer Sci.*, A3, 681 (1965).
5. Rosen, S. L., and F. Rodriguez, *J. Appl. Polymer Sci.*, 9, 1601, 1615 (1965).
6. Philippoff, W., F. H. Gaskins, and J. G. Brodnyan, *ibid.*, 28, 1118 (1957).
7. Rodriguez, Ferdinand, R. A. Kulakowski, and O. K. Clark, *Ind. Eng. Chem. Prod. Res. Develop.*, 5, 121 (1966).
8. Barry, A. J., *J. Appl. Phys.*, 17, 1020 (1946).
9. Benbow, J. J., and E. R. Howells, *Polymer* (*London*), 2, 429 (1961).
10. Bagley, E. B., *J. Appl. Phys.*, 31, 1126 (1960).
11. Spencer, R. S. and R. E. Dillon, *J. Colloid Sci.*, 3, 163 (1948); 4, 241 (1949).
12. Johnson, D. L. and E. Baer, *J. Appl. Polymer Sci.*, 7, 1359 (1963).
13. Arai, T. and H. Aoyama, *Trans. Soc. Rheol.*, 7, 333 (1963).
14. Watkins, J. M., *J. Appl. Phys.*, 27, 419 (1956).
15. Ferry, J. D., M. L. Williams, and D. M. Stern, *J. Phys. Chem.*, 58, 987 (1954).

Manuscript received October 8, 1968; revision received March 17, 1969; paper accepted March 19, 1969.