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Falling Coaxial Cylinder Viscometer for Polymer Solutions

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Synopsis

A simple, inexpensive glass viscometer can be constructed to time the rate at which a rod falls into a liquid held in a concentric closed-end glass cylinder. This equipment can be used to measure absolute values of apparent viscosities of Newtonian and non-Newtonian fluids. Calibration is not required. The technique is an adaptation of a method used previously with polymer melts at elevated temperatures. The present article describes the modifications needed for lower-viscosity fluids, such as paints, and validates the flow analysis with results of study of a characterized Newtonian fluid.

INTRODUCTION

Falling coaxial cylinder viscometers are of considerable antiquity.[1,2] Numerous attempts have been made to apply such instruments[2–6] because of their inherent simplicity, but the major uses have been for semiempirical studies of bitumens, rosins, and other vaguely characterized commercial products.

An adaptation of this technique for polymer melts was described several years ago.[7] The equipment consists simply of a weighted rod falling into a closed-end thermostated concentric cylinder. The velocity of the moving rod can be measured with an ordinary dial gauge. The rate of descent decreases and the immersion depth increases with time of fall in this apparatus. The rod velocity, driving weight (W), rod radius (r_i), and inner radius of the containing cylinder (r_a) yield corresponding values of shear rate and shear stress in the immersion fluid at the rod wall.

There are several key features in the operation of the new falling coaxial cylinder viscometer with polymer melts. The polymer must be free of entrapped air to avoid spurious dilatant flow curves when the falling piston compresses the melt. Such samples can be provided by compression molding thermoplastic specimens.[7–9] Location of the unperturbed polymer surface is also critical to the validity of the subsequent measurements, but experience has shown that the melt surface can be located precisely be feeling the resistance as the rod is lowered into the relatively viscous melt.[7,10,11] Different solutions are presented here to these problems, for use with a transparent vis-

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cometer and relatively fluid solutions at lower experimental temperatures than are characteristic of polymer melts.

The third key feature of the present instrument is the observation that the piston position relative to the initial liquid surface can be represented accurately by a logarithmic relation[7]

$$H^{\delta} = \beta t \tag{1}$$

where H (cm) is the position of the top of the piston at time t (sec) and δ (unitless) and β (cm^{δ}/sec) are constants established by the experimental results for given liquid, temperature, rod and reservoir diameters, and driving weight. This relation is equivalent to a power law expression in apparent viscosity and shear rate at the rod wall, with the power law exponent n given by[10]

$$\frac{1}{n} = \delta - 1. \tag{2}$$

Equation (1) has been established empirically for all polymers which have been investigated. The initial consolidation of the raw data from a single experiment serves automatically as a check on the validity of this expression. It is not surprising that such a relation should be applicable, in any event, since power law expressions are generally valid over shear rate ranges at least as extended as those in a single falling-rod experiment. If the fluid being studied is Newtonian, $\delta = 2$ ($n = 1$); and if it is shear thinning, $\delta > 2$ ($n < 1$).

Classical Poiseuille flow is assumed in the flow analysis.[7,10,11] Although end effects due to flow below the level of the bottom of the moving rod can be estimated quantitatively,[12] such effects are absent for most of the polymer melts which have been studied to date. The rheometer appears to provide true values of shear rate and shear stress at the surface of the falling rod, as judged by the observations that falling coaxial cylinder results are consistent with those from other measurement techniques with non-Newtonian polymeric fluids.

This article reports a confirmation of the validity of the rheometer data and flow analysis from a study of a characterized Newtonian fluid. This liquid has a lower viscosity than the polymer melts which have been studied to date, and a modified apparatus and technique are described for characterization of relatively low-viscosity fluids. The apparatus described is very simple and inexpensive to build and operate and requires no calibration to provide accurate viscosity data.

EXPERIMENTAL

The apparatus is sketched in Figure 1. The outer cylinder is made of heavy-wall glass tubing. The inner radius of this reservoir (r_a) can be measured with glass blowers calipers before the tube end is sealed or with a vernier bore gauge inserted through the open end. The falling rod in this case was a glass stirring rod ground to fit the ground-glass sleeve shown. The radius of this rod is r_i. Other lighter rods, such as sealed hollow glass tubing or rigid plastic rods, can be used with fluids which are even less viscous than the sam-

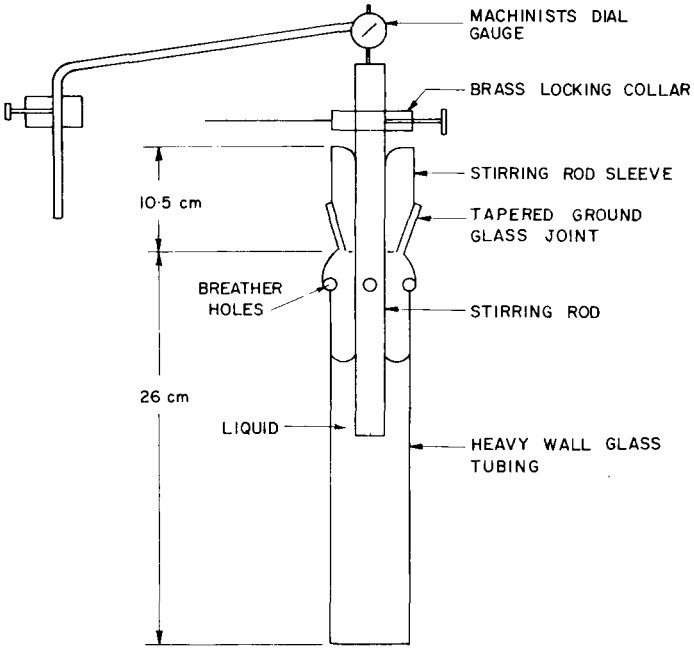

Fig. 1. Apparatus.

ple reported here. It is necessary that the fluid wet the rod surface, and this may restrict the use of plastics, in general.

The rod diameter can be varied at will, so long as a suitable ground-glass guiding sleeve is available. A polytetrafluorethylene sleeve will also be suitable. The rate at which the rod descends is determined by the characteristics of the liquid into which it falls and the driving weight on the rod. Added weights were not necessary in this work, but these can be readily provided, if needed, as described in earlier work with steel rods and polymer melts.[7] In the present case, different driving weights were provided by using rods of different lengths. The reservoir is mounted vertically in a transparent constant-temperature bath and is partly filled with the test fluid. The rod is carefully lowered onto the surface of the liquid and locked into this position with the set screw and locking collar shown in Figure 1. The initial rod position can be determined accurately with a cathetometer. The position (H, cm) of the top of the rod was registered on a dial gauge, which can be read to 0.0002 cm. The dial gauge must be firmly mounted. Its position is located with a sliding lock sleeve, as shown.

Machinists dial gauges are normally spring loaded so that the force exerted by the needle depends on the spring compression. One of the two springs in our gauge was removed, and it was determined that the probe exerted a constant load of 28 g, regardless of position of the needle on the gauge. This load was added to the weight of the glass rod to give W, the driving load.

The rod was released from its locking collar, and zero time was recorded on a stopwatch. Corresponding position and time readings were taken at appropriate intervals. The raw data consist of heights of the top of the shaft (rela-

tive to the initial reading with the rod at the liquid surface) and corresponding times.

The fluid studied here was a Newtonian liquid (S30000, Cannon Instrument Company, State College, Pa.) with a reported viscosity of 461 poises at 30°C. Our experiments were at 30.0°C.

FLOW ANALYSIS

The flow analysis has been given in detail elsewhere.[7,11,12] If the mass of the rod and the load delivered by the dial gauge is W (g), then the effective mass W_e of the descending rod will be

$$W_e = W - \pi r^2_i \alpha H \rho \tag{3}$$

where the second term on the right hand side of eq. (3) is a buoyancy correction. In this equation, α is a dimensionless ratio relating the piston position H to the corresponding immersion depth L[7]:

$$L = \alpha H \tag{4}$$

$$\alpha = \frac{r^2_a}{r^2_a - r^2_i}. \tag{5}$$

Experimentally, L (and H) are set to zero at $t = 0$. The density of the test liquid (0.8910 g/cm^3 at 30.0°, in this case) is denoted ρ. The coordinate system and flow analysis are detailed in reference 7, where it is shown that the velocity of the flow of the liquid at radial position r, V_z (z is the axial coordinate), is

$$V_z(r) = \frac{P}{4\eta L}(r^2_a - r^2) + \frac{\left[\ln\left(\frac{r}{r_a}\right)\right]\left[-V_i + \frac{P}{4\eta L}(r^2_a - r^2_i)\right]}{\ln\left(\frac{r_a}{r_i}\right)} \tag{6}$$

where P is excess pressure at the level of the bottom of the rod, η is the coefficient of viscosity of the liquid, and V_i is the instantaneous velocity of the falling rod. It can then be shown[12] that the shear rate in the fluid at the rod wall is

$$\dot{\gamma}_i = -V_i \frac{(r^2_a - r^2_i)}{r_i\left[(r^2_a + r^2_i)\ln\left(\frac{r_a}{r_i}\right) - (r^2_a - r^2_i)\right]}. \tag{7}$$

The experimental H–t data are fitted to eq. (1), from which the coefficients β and δ are derived for each experiment. Also, since[7]

$$-V_i = \frac{\beta \alpha^{\delta-1}}{\delta L^{\delta-1}} \tag{8}$$

eqs. (7) and (5) will then yield $\dot{\gamma}_i$ at any experimental value of H.

The corresponding shear stress τ_i at the rod wall is given by[12]

$$P_i \equiv \frac{W_e g}{\pi r^2_i} = \tau_i\left[\frac{L}{r_i} + \frac{r^2_a + 3r^2_i}{(r^2_a - r^2_i)}\frac{L}{r_i}\left(\frac{1}{\delta - 1}\right)\right] \tag{9}$$

TABLE I
Values of Coefficients of Equation (1) for Standard Viscosity Fluid

W, g	δ	β, cm$^{\delta}$/sec
98	1.940	0.1169
	2.224	0.1805
	2.013	0.1277
	2.083	0.1489
138	1.961	0.1703
	1.976	0.1781
192	2.044	0.2439
	2.018	0.2426
231	2.052	0.2799
	2.057	0.2933
296	2.033	0.3413
	2.037	0.3487

or

$$P_i \equiv \tau_i l \tag{10}$$

where P_i and l are defined by eqs. (9) and (10). To allow for possible end effects, eq. (10) can be written

$$P_i = \frac{W_e g}{\pi r_i^2} = \tau_i [l + \lambda] \tag{11}$$

where λ is a dimensionless correction term for shearing of the fluid over a depth greater than L, as assumed in the flow analysis. It is expected from previous studies on polymer melts that λ will be zero for Newtonian fluids.

In any event, both P_i and l are experimental values for any H (or L) during an experiment. From eq. (9) or (10), a plot of P_i against l will have a slope equal to τ_i. This line will pass through the origin if end effects are absent.

The values of β and δ, eq. (1), for various rod lengths (and therefore weights) are listed in Table I. The figures for replicate experiments show the

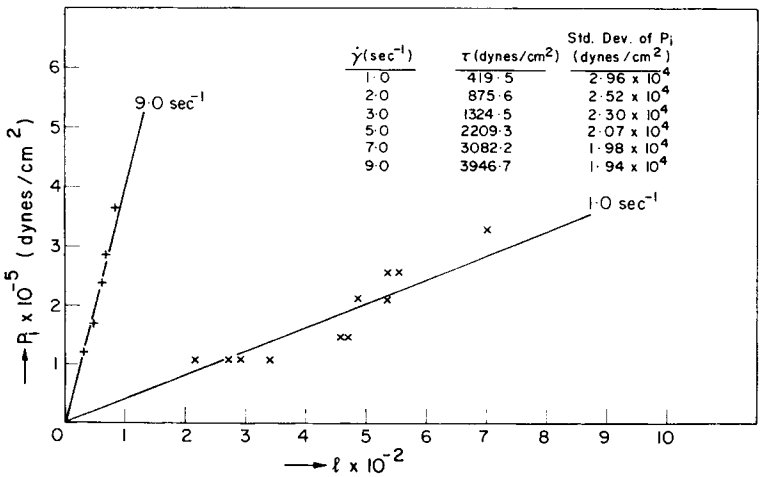

Fig. 2. Plot of eq. (10).

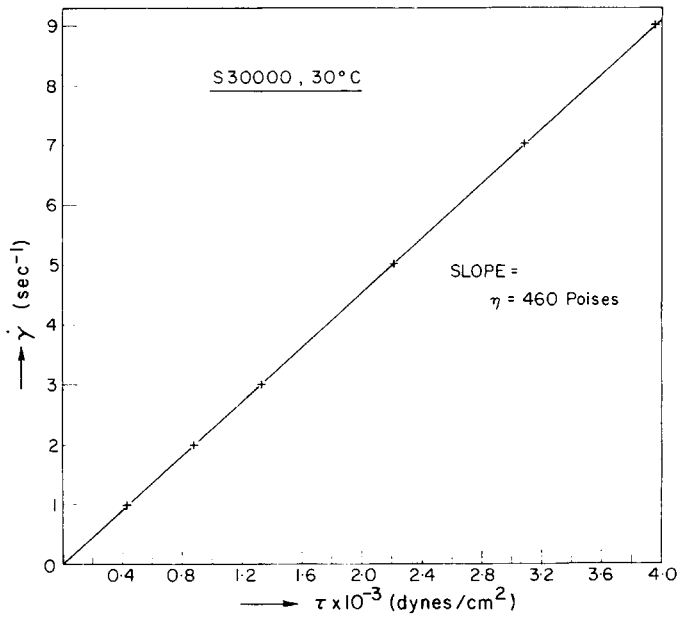

Fig. 3. Flow curve.

reproducibility of the measurements. All experimental δ figures are close to the Newtonian value of 2.

A plot of eq. (9) at given shear rate is shown in Figure 2. This figure includes the $\dot{\gamma}_i$ (sec^{-1}) and corresponding τ_i ($dynes/cm^2$) values for the six integral shear rates covered. Not all the plots are shown, for the sake of clarity. The P_i–l experimental data were fitted by linear least squares. The figure legend also records a measure of the goodness of this fit, in terms of the standard deviation of P_i about the least-square line. Standard deviations of P_i are of the order of 3×10^4 $dynes/cm^2$. The range of this parameter included values up to about 40×10^4 $dynes/cm^2$. All plots seem to be linear through the origin, as predicted.

The shear rate–shear stress flow curve is shown in Figure 3. The liquid is Newtonian, with a viscosity of 460 poises. The supplier quotes a value of 461.4 poises at 30.0°C. The two values coincide.

DISCUSSION

This comparison supports the validity of the technique and flow analysis. The simple glass viscometer described produces accurate viscosity measurements without calibration or correction for instrument parameters. It can evidently be used with non-Newtonian as well as Newtonian fluids.[7,10–12]

Opaque liquids can be studied so long as the apparatus above the liquid level can be cleaned to permit placement of the rod base at the liquid surface.

Entrapped air must be removed from the liquid before testing. This can be accomplished where necessary by subjecting the material to a reduced pressure or by freezing and thawing in the glass reservoir, if the liquid is stable to this operation.

The shear rates attained will depend on the fluid viscosity and weight of the falling rod. Shear rates lower than 0.05 sec^{-1} have been measured with viscous polymeric melts.[7,10–12] In the present case, the lowest value of $\dot{\gamma}_i$ attained was 1 sec^{-1}, but this could be reduced by using a lighter, hollow rod. The maximum shear rate attainable is limited by the operator's ability to read corresponding values of H and t. Shear rates at least as high as 10 sec^{-1} are conveniently reached. A separate publication[13] describes an extension of this technique to higher shear rates, with a motordriven piston.

The instrument described here and in earlier reports[7,10,11] can be used to study the thixotropic nature of solvent- and water-based paints. In this case, the logarithmic relation given by eq. (1) may fail to hold over the entire measurement range. However, values of δ and β at a particular value of L (or H) can be obtained from the tangent line to that point on the ln H–ln t plot. Hence, values of δ versus H and β versus H can be determined for a given applied weight W_e. Then, with the help of eqs. (7), (8), and (9), values of τ_i and $\dot{\gamma}_i$ for the same driving weight can be calculated. These shear stress and shear rate data correspond to a particular total shear strain γ_i at the rod wall, given by[7]

$$\gamma_i = K'H \tag{12}$$

where K' is an instrument constant given by

$$K' = \frac{r^2_a - r^2_i}{r_i\left[(r^2_a + r^2_i)\ln\left(\frac{r_a}{r_i}\right) - (r^2_a - r^2_i)\right]} \tag{13}$$

Variations of r_i and W_e can thus provide a plot of τ_i versus $\dot{\gamma}_i$ at given γ_i. A cross relationship yields the spectrum of apparent viscosities at given $\dot{\gamma}_i$ or τ_i and selected values of γ_i. This analysis, for which examples have been given elsewhere,[7,10] implies that shear history effects can be related to the total shear strain which the polymer has undergone at the rod wall.

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