Measurement of Dynamic Viscoelastic Properties of Polymer Melts and Liquids by the Modified Rheovibron

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Synopsis

A new technique is presented which permits the quantitative characterization of the dynamic viscoelastic properties of polymer melts and liquids. A new sample holding system with oscillatory shear platen and modification of the amplifier and oscillating unit made it possible to measure rheological properties of the viscous liquids using the Rheovibron. The dynamic shear modulus, viscosity, and internal friction of acrylic dope, and silicone fluids are obtained by using the new procedure and developed mathematical expressions. This technique will be useful in studies on the rheological properties characterization of polymer melts and liquids in conjunction with process parameters.

INTRODUCTION

The Rheovibron viscoelastometer (Toyo measuring instrument) is useful for obtaining dynamic mechanical properties of films and fibers over a wide temperature range of −160°C–250°C in an atmosphere of 0% relative humidity.[1] In recent years a modification which makes possible measurement on materials in the shear, compression, and bending modes has been reported.[2–6] However, no studies exist which show the measurement of dynamic viscoelastic properties of polymer melts and liquids using the Rheovibron instrument.

In this paper a new method for investigating dynamic viscoelastic properties of melts is presented and shows the effects of temperature on viscosity, dynamic shear modulus, and internal friction of polymer melts (acrylic dope, Quadrol) and silicone fluids.

ANALYTICAL DEVELOPMENT

In order to determine the dynamic shear modulus and viscosity of polymer melts under dynamic condition, the following mathematical analysis is carried out. Consider a shear plate submerged in the viscous liquid of density ρ, viscosity μ, and kinematic viscosity ν, with a forced sinusoidal oscillation at one end ($x = 1$) and fixed at the other ($x = 0$). We obtain the simplified Navier–Stokes equation and illustrate relationships in Figure 1:

$$\frac{\partial u}{\partial t} = \nu \frac{\partial^2 u}{\partial y^2} \tag{1}$$

where u = velocity of the liquid in the x direction; t = time; y = coordinate perpendicular to the film; and ν = kinematic viscosity.

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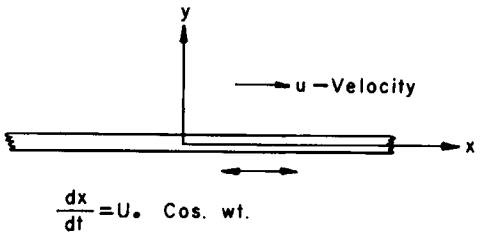

Fig. 1. Relationships between viscosity and a forced sinusoidal oscillation: $dx/dt = U_0 \cos \omega t$.

For infinite fluid, the boundary conditions are as follows: at $y = 0$,

$$u(0, t) = U_0 \cos \omega t \tag{2}$$

where U_0 is the complex velocity amplitude and ω is the frequency.
The solution is

$$u(y, t) = U_0 e^{-ky} \cos (\omega t - ky) \tag{3}$$

where

$$k = \sqrt{\omega/2\nu}$$

Velocity dies off exponentially as y increases:

$$\text{at } ky = 3\ e^{-ky} = 1/e^3 = 0.049$$

$$\text{at } ky = 4\ e^{-ky} = 1/e^4 = 0.018$$

$$\text{at } ky = 5/e^5 = 0.006$$

$$\text{at } ky = 6/e^6 = 0.002$$

At $y = 6/k$, where velocity is within 0.5% of zero, existence of another wall at this point will not significantly affect an infinite expanse solution.

Investigate:

$$y = 6/k$$

$$y = 6\sqrt{2\nu/\omega} = 8.48\ \sqrt{\mu/\rho\omega}$$

As viscosity increases, y increases, but y is decreased by an increase in ρ. Assume infinite solution can be applied. Now calculate shear stress (τ) at the surface of the plate.

$$\tau = \mu \left.\frac{\partial u}{\partial y}\right|_{y=0} \tag{4}$$

$$\frac{\partial u}{\partial y} = -kU_0 e^{-ky} \cos (\omega t - ky) - U_0 e^{-ky} k \sin (\omega t - ky) \tag{5}$$

$$\frac{\partial u}{\partial y} = -kU_0 e^{-ky} [\cos (\omega t - ky) + \sin (\omega t - ky)]$$

or

$$\frac{\partial u}{\partial y} = -k\sqrt{2}\, U_0 e^{-ky} [\sin (\omega t - ky + \pi/4)] \tag{6}$$

At $y = 0$

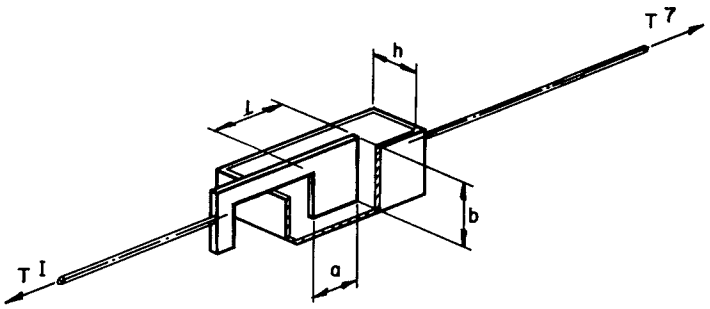

Fig. 2. The shear grip.

$$\partial u/\partial y = -k\sqrt{2}\, U_0 \sin(\omega t + \pi/4) \tag{7}$$

$$\tau = -\sqrt{\omega/2\nu}\,\sqrt{2}\,\mu\, U_0 \sin(\omega t + \pi/4)$$

$$\tau = -\sqrt{\omega\rho\mu}\, U_0 \sin(\omega t + \pi/4)$$

$$\tau_{\max} = \sqrt{\omega\rho\mu}\, U_0 \tag{8}$$

Equation (8) of the shear stress of liquid is incorporated with the dynamic mechanical parameters.

$$\tan\delta = E''/E' \tag{9}$$

where $\tan\delta$ is internal friction, E' is dynamic modulus, and E'' is loss modulus

$$E'' = \eta\omega \tag{10}$$

where η is viscosity of the viscoelastic system and ω is the frequency.

$$\eta\frac{dx}{dt} = 2\tau l \tag{11}$$

$$\eta\frac{dx}{dt} = 2\sqrt{\omega\rho\mu}\, U_0 l \tag{12}$$

where l is the length of the shear plate

$$\tan\delta\, E' = \eta\omega \tag{13}$$

$$\tan\delta\, E' = 2\sqrt{\omega\rho\mu}\,\omega l \tag{14}$$

$$(\tan\delta\, E')^2 = 4\,\omega^3\rho\mu l^2 \tag{15}$$

TABLE I
Dynamic Shear Modulus (G'), Viscosity (μ), and Internal Friction ($\tan\delta$) of Various Liquids

				(at 11 Hz)	
Sample		Silicone fluid 1 (25°C)	Silicone fluid 2 (25°C)	Acrylic dope (100°C)	Quadrol (25°C)
Dynamic shear modulus (G') (dynes/cm^2)		3.12×10^3	3.65×10^3	4.82×10^3	3.43×10^3
Internal friction ($\tan\delta$)		0.120	0.690	0.350	0.490
Viscosity (μ) cp	known	12,500	57,000	—	52,000
	measured	12,580	57,120	3.100	52,150

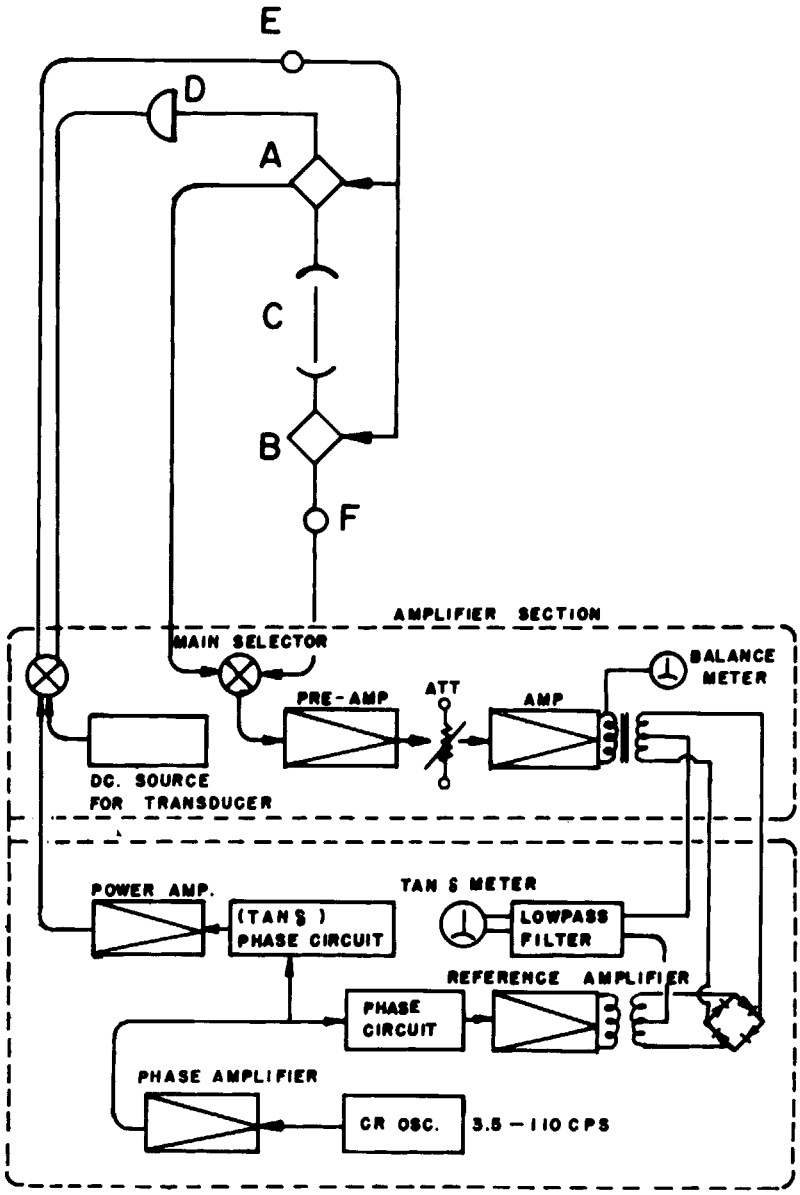

Fig. 3. Block diagram of apparatus: (A) Displacement transducer, (T-7) gauge; (B) load transducer, (T-1) gauge; (C) sample; (D) driver unit; (E, F) controller.

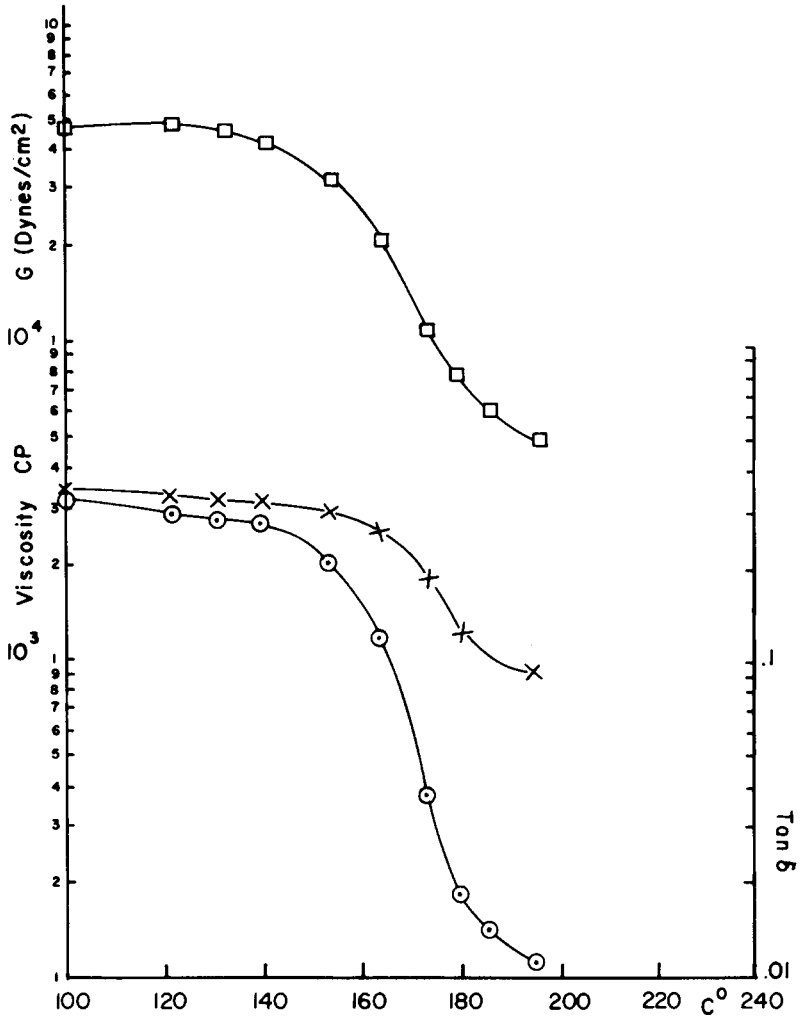

Fig. 4. Viscosity (⊙), dynamic shear modulus (□), and internal friction of acrylic dope: (×) tan δ.

$$\boxed{\mu = \frac{(\tan \delta\, E')^2}{4\,\rho\omega^3 l^2}} \left(\frac{\text{dyne} \cdot \text{s}}{\text{cm}^2}\right) \tag{16}$$

Viscosity μ of liquid can be determined by eq. (16). The necessary parameters in this equation are obtained except the dynamic modulus E'. In this analysis E' should be the dynamic shear modulus of liquids. The determination of the shear modulus is developed by using a new grip, as seen in Figure 2, with the modification of the amplifier and oscillating unit of the Rheovibron. The dynamic shear modulus G' is

$$G' = \frac{F/a \times b}{\Delta L/h} \tag{17}$$

where F is the dynamic shear force, ΔL is the dynamic displacement, a and b are dimensions of the shear plate, and h is the thickness of liquid in the sample container.

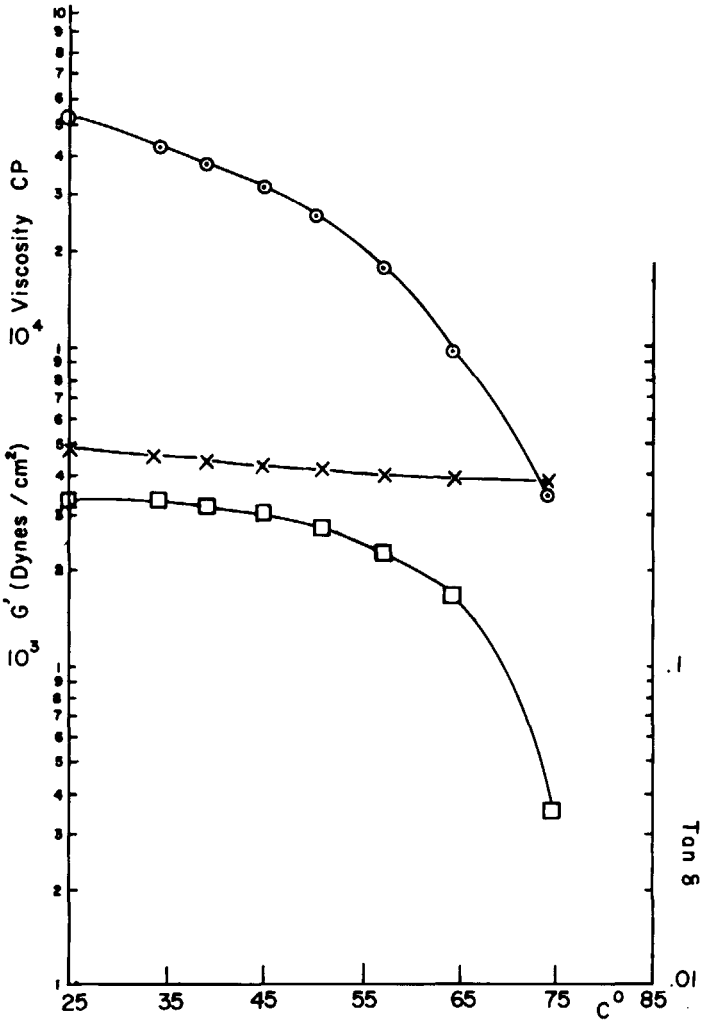

Fig. 5. Viscosity (⊙), dynamic shear modulus (□), and internal friction of quadrol (×).

Equation (17) is combined with the operational equation of the Rheovibron.

$$\boxed{G' = \frac{2}{A \times D} \times 10^9 \frac{h}{(a \times b)}} \frac{\text{dynes}}{\text{cm}^2} \tag{18}$$

where A is the amplitude factor of the instrument and D is the value of the dynamic force dial. Thus, the dynamic shear modulus and viscosity of liquids are obtained by using eqs. (18) and (16). The required values for these equations, such as the loss tangent, tan δ, the oscillating load, and displacement of liquid can be measured directly by the Rheovibron.

EXPERIMENTAL

The Rheovibron applies a sinusoidal tensile strain to one end of a sample and measures the stress output at the other end. The instrument operates at frequencies of 3.5, 11.0, 35.0, and 110 Hz. Two transducers are used to read di-

rectly the absolute dynamic modulus $|E^*|$ (the ratio of maximum stress amplitude to maximum strain amplitude) and the phase angle δ between stress and strain. From these two quantities, the real part E' (dynamic modulus) and the imaginary part E'' (loss modulus) can be calculated from the complex dynamic tensile modulus E^*.

In order to measure the dynamic viscoelastic properties of polymer melts using a Rheovibron viscoelastometer, it was necessary to develop a new sample holder and shear platen to permit characterization of liquids in a dynamic shear mode. The sample holder is shown in Figure 2. A small amount of liquid is installed in the sample container (2 cm × 1 cm × 1 cm or 2 cm × 0.5 cm × 1 cm). The sample holders consist of one liquid sample container and shear platen with 15-cm-long rods; the weight of this unit is 13.0 g.

The tensile clamp is replaced by these grips at the connector of T_1 and T_7 of the strain gage. A sample of melt is placed at the holder of T_7.

The operating procedure for dynamic testing of liquids with the Rheovibron is as follows: With the tan δ range switch at 30 and amplitude factor switch at 30:

1. Calibrate stress gage T_1 and strain gage T_7 using the calibration procedure of the Rheovibron.
2. Set the main selector to stress T_1 gage position.
3. Turn the handle of slider of the driving section and set the shear platen in the center of the sample container.
4. Set the main selector switch to "Amp. F" position and turn the tan δ meter switch to 40 and the amplitude factor switch to 30.
5. Adjust "Amplitude Adjust" for full scale indication on the tan δ meter.
6. Set the main selector switch to "Dyn. F" position.
7. Adjust the "Phase Adjust" control for the correct Lissajou's pattern on the oscilloscope (straight line at approximately a 45° angle to horizontal).
8. Adjust the "Dynamic Force" potentiometer for full scale indication on the tan δ meter and read the value on the dial of "Dynamic Force." In case of measurement on low viscous liquid, adjust the "Dynamic Force" potentiometer for 500 scale.
9. Turn the main selector switch to the "tan δ" position and read tan δ.
10. Turn the tan δ meter switch to 30 and the amplitude factor switch to 30. Set the main selector switch to the stress T_1 gage position and read stress.

In order to determine the dynamic viscoelastic properties of liquids, the amplifier and oscillating unit of the Rheovibron are modified as shown in Figure 3. A new controller (E, F) is built to adjust the resistor of T_1 and T_7 gages since the arrangement of the driving unit and sample grips are changed. Acrylic dope and Quadrol (N,N,N',N'-tetrakis (2 hydroxypropyl) ethylenediamine), prepared by A. A. Armstrong, and silicone fluids were used to test this new procedure. Dynamic measurements were made at 3.5, 11, 35, and 110 Hz. Samples were heated at 1°C/min in a nitrogen atmosphere, and measurements of the dynamic shear modulus G' and internal friction tan δ were made at 5°C or 10°C increments. Samples were allowed to equilibrate at temperature for 15 min before measurements were made.

RESULTS AND DISCUSSION

The dynamic shear modulus (G'), along with the loss tangent and viscosity of three liquids at room conditions and acrylic dope at 100°C, is shown in Table I. The dynamic viscoelastic properties of acrylic dope as a function of temperature are shown in Figure 4. Figure 5 shows results of Quadrol (N,N,N',N'-tetrakis (2 hydroxypropyl) ethylenediamine). Two standard silicon fluids are used for calibration of the new technique. The measured viscosities of these fluids are 12,500 and 57,000 cp. There is good agreement between measured viscosity and standard viscosity.

The dynamic shear modulus, viscosity, and internal friction of acrylic dope are shown in Figure 4. The dynamic shear modulus and viscosity of polymer melt are decreased greatly in a temperature range of 140–180°C. This shows the higher molecular mobility in polymer chains in this temperature range.

The dynamic shear modulus and viscosity of Quadrol are decreased with increasing temperature. However, the internal friction shows small changes in the temperature range of 25–75°C. The dynamic shear modulus of Quadrol was lower than that of the acrylic dope. This difference is that the Quadrol has lower molecular weight as compared with high molecular weight of acrylic dope. The difference in internal friction of these materials could be related to the degree of molecular cohesion in the chain structure. The new method for measurement of the dynamic shear modulus, viscosity, and internal friction of polymer melts and liquids is useful for characterization of the melt properties of polymers in connection with process parameters.

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