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Stress Growth and Relaxation of a Molten Polyethylene in a Modified Weissenberg Rheogoniometer

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Synopsis

A Weissenberg rheogoniometer was modified[1–3] to improve sample temperature uniformity and constancy (to within ±0.5°C) and to give a quicker response to normal thrust changes (estimated gap change ≤0.1 μm/kg thrust; gap angle = 8.046°; gap radius = 1.2 cm; servomechanism replaced by an open-loop cantilever spring of 10 kg/μm stiffness). Low-density polyethylenes (IUPAC samples A and C, melt index at 190°C = 1.6) at 150°C were used in step-function shear rate experiments. Inspection of marked sectors in the samples showed substantial uniformity of shear at values of $\dot{S}$ = 0.1, 2, and 5 sec^{-1}; for $\dot{S}$ = 10 sec^{-1} and $S \leq 2$ shear units ($S = \dot{S}t$), the shear was highly nonuniform at and near the free boundary. Using selected premolded samples A, scatter in seven replicate tests at $\dot{S}$ = 1.0 sec^{-1} did not exceed ±6% for $N_1(t)$ and ±5% for $\sigma(t)$ (N_1 = primary normal stress difference; σ = shear stress; t = time of deformation from the initiation of experiment at zero time). $N_1(t)$ and $\sigma(t)$ data agreed with Meissner's[1]; for $\dot{S}$ = 0.1, 2.0, 5.0, and 10.0 sec^{-1}, torque maxima occurred at S = 6 shear units, and thrust maxima occurred in the range of 10 to 20 shear units. $\sigma(t)$ and $N_1(t)$ data do not satisfy the van Es and Christensen[4] test for rubber-like liquids with strain rate invariants included in the memory function. On cessation of shear (after a shear strain S at constant shear rate $\dot{S}$), initial values of $-d\sigma(t)/dt$ and $-dN_1(t)/dt$ were found to depend strongly on S, in some cases passing through maxima as S was increased. After shearing at $\dot{S}$ = 0.1 sec^{-1} for 500 sec, such that stresses became constant, stress relaxation data satisfied Yamamoto's[5] equation of $dN_1(t)/dt = -2\dot{S}\sigma(t)$.

INTRODUCTION

In obtaining the transient stress data on molten polymers, rheogoniometers with cone/plate geometry have presumably provided an attractive advantage of a uniform shear rate across the gap and up to the free surface of the sample.[6] Pollett[7] verified this assumption of shear uniformity in the gap, except near the free boundary of the sample. Hence, many researchers used cone/plate apparatus,[7–16] in particular the commercial Weissenberg rheogoniometer,[14–16] for measuring the transient shear $\sigma(t)$ and primary normal $N_1(t)$ stresses of polymers. However, there are objections to the use of the

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commercial Weissenberg rheogoniometer (WRG) in obtaining stress growth and stress relaxation data for molten polymers of high viscosity.[1,17–19]

Mills[18] replaced the usual normal thrust measurement system of the commercial WRG[20] by a piezoelectric force transducer, claiming to improve the response time from 0.2 sec to 5 μ sec. Yet, a calculation by Lodge[21] reveals a 700% error in Mill's measured value and questions the validity of some of Mill's conclusions attributing the cause to the lack of stiffness in the upper section of the WRG. Meissner[1] increased the vertical stiffness of his apparatus by a factor of 10 in comparison to the commercial version of the WRG and replaced the spring-servomechanism of the thrust-measuring system with an open-loop cantilever beam spring of high stiffness. We have adapted some of Meissner's modifications[1] to our WRG and obtained transient $\sigma(t)$ and $N_1(t)$ data on a molten polyethylene identical to Meissner's IUPAC sample C. We obtained both the $\sigma(t)$ and $N_1(t)$ growth and relaxation as function of shear rate $\dot{S}$ in the range of 0.1 to 10.0 sec^{-1} and shear strain S in the range of 2 to 300 units, where $S = \dot{S}t$.

Trapeznikov and his colleagues studied the dependence of the initial rate of shear stress relaxation $-d\sigma(t)/dt$ on the strain prior to relaxation.[22–24] Because of anomalies,[24] the dependence of the initial rate of normal stress relaxation $-dN_1(t)/dt$ on strain could not be determined. We have obtained $-dN_1(t)/dt$-versus-strain data on a molten polyethylene which appears similar to our $-d\sigma(t)/dt$-versus-strain curve.

A simple experimental test is proposed by Yamamoto[5] to check the applicability of a class of constitutive equations having the second invariant of shear rate tensor in the memory function. More recently, van Es and Christensen[4] proposed another method for checking the same type of constitutive equations. Using the data obtained in our research, the equations of Yamamoto and van Es and Christensen were evaluated. The data satisfied Yamamoto's condition (eq. 22, ref. 5), but not van Es and Christensen's criterion (eq. 6, ref. 4).

EXPERIMENTAL

Equipment

We have used a modified WRG similar to Meissner's,[1] and a more detailed account of the apparatus is given elsewhere.[2]

The heating system of our apparatus was different from that of the original WRG and the new system controlled the sample temperature more accurately. A schematic drawing of the heating system is illustrated in Figure 1, which incorporates heaters H1 and H4 in each shaft to give a more uniform radial temperature distribution in the specimen. The general configuration of the heating chamber can be thought of as three concentric shell-like enclosures. Heaters H2 and H3 form the innermost enclosure, insulating rock wool of $\frac{3}{4}$-in. wall thickness surrounds the enclosure, and a water jacket enclosure functions as a heat sink for heaters H2 and H3 by supplying 25°C cooling water into the jacket.

As shown in Figure 1, five platinum resistance thermometers (T1, T2, T3, T4, and T5) in conjunction with a bridge of ±0.208°C accuracy were used to

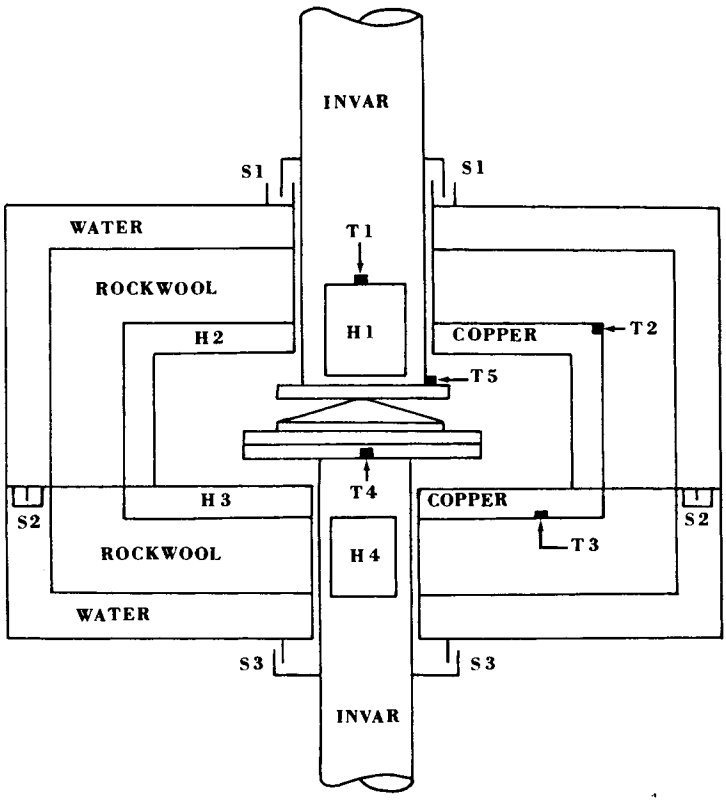

Fig. 1. Heating system for the modified WRG. H1, H2, H3, and H4 heaters (H2 and H3 spirally wound on the surface of the copper); T1 to T5 are platinum resistance thermometers; S1, S2, S3 are silicone seals.

detect the sample temperature. Correlations between the readings of the temperature sensors (PRT) and the gap temperature were established and a radial temperature deviation of less than ±0.5°C in the gap was obtained with the molten polyethylene attributing a negligible resistance.

Materials

We used a low-density polyethylene with the following properties: density (at 20°C) = 0.919 gm/cm^3; melt index (ASTM D 1238; 190°C; 2.16 kgf piston load) = 1.6; viscosity η at 150°C (low shear rate limit) = 5.0×10^5 poise; $d(\ln \eta)/dT$ = 0.04/°C; M_w = 800,000 to 900,000; M_n = 20,000. To determine the flow field in the samples, polyethylene similar to the above but containing an additional 2.5 vol-% spherical carbon black particles was also employed.

Polyethylene samples were made by compression molding at 145°C and applying 1.4×10^9 dynes/cm^2 pressure for 20 min using an especially designed cavity mold to provide samples for fitting the gap in the WRG. Black samples were similarly made from the carbon containing polymer. Next, a small sector of the unfilled polyethylene sample (white in color) was cut and replaced with an equal sector from the carbon-containing sample, and this new specimen was further compression molded (at 145°C, 1.4×10^9 dynes/cm^2

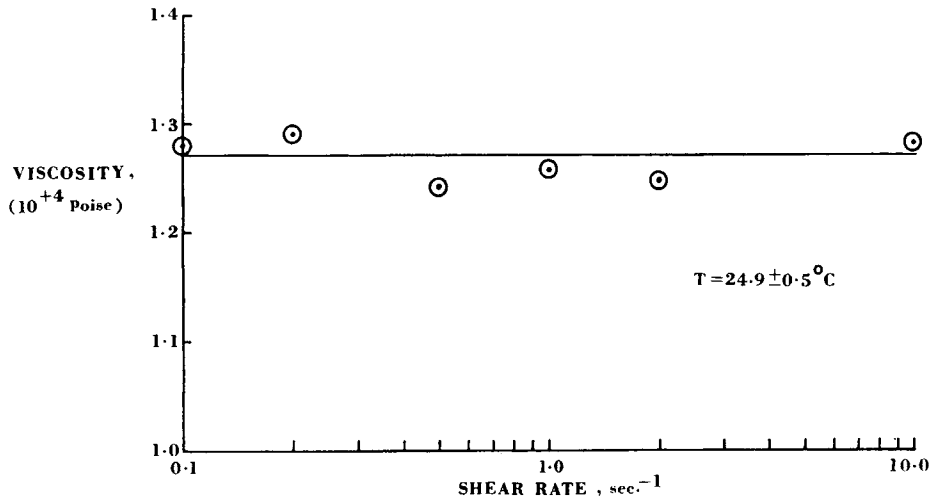

Fig. 2. Viscosity–shear rate data for polybutene standard. Extrapolated zero-shear rate viscosity using WRG = $(1.27\pm0.03)\times10^4$ poises at 24.9° ± 0.5°C, given zero-shear rate viscosity = 1.25×10^4 poises at 25°C.

pressure for 20 min) to use in our experiment. Only samples free from bubbles, with straight boundaries between the white and black sectors, and with smooth surfaces, were employed for testing. All samples were stored in a dry desiccator until tested.

Experimental Procedure

Our experimental procedure was similar to the common procedure of shearing the test specimen in a WRG[20]; however, the gap setting was performed at the steady-state test temperature and the sample was placed in the heated gap afterward. In placing the sample, attention was given to the concentricity of the sample in the gap and to the absence of bubbles between the surfaces of the sample and the surfaces of the cone and plate. To prevent possible degradation of the polyethylene, 150°C-heated nitrogen gas was blown into the heated chamber throughout the experiment.

After the sample reached the steady-state temperature of 150° ± 0.5°C, the sample was sheared by keeping the plate stationary and rotating the cone with a set angular velocity. A "strain function generator" [2] was operated to override the clutch of the WRG after a desired amount of shear strain in the sample and to stop further rotation of the cone for obtaining stress relaxation data. While the sample was being sheared and relaxed, the torque and thrust of the test fluid were continuously monitored. After each experiment, the test piece was allowed to cool in the gap overnight at the ambient condition. The solidified sample was then removed from the gap and inspected for the uniformity in deformation (to be discussed later).

Conditions

With a few exceptions (noted later), the experiments in this paper were performed at 150° ± 0.5°C using an 8.046° cone, 1.2-cm gap radius, 10 kgf/μm cantilever spring, 2.1×10^{12} dyne·cm/radian torsion bar, and a maximum

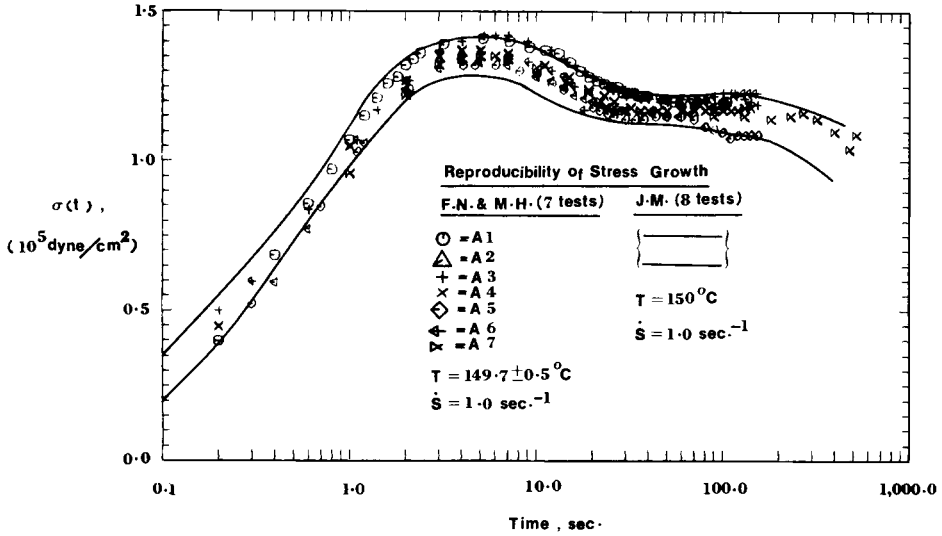

Fig. 3. Reproducibility of the shear stress $\sigma(t)$ growth data (F. N. & M. H., 7 tests) and their comparison with Meissner's data (J. M., 8 tests). Polyethylene sample A, $\dot{S} = 1.0\ \text{sec}^{-1}$.

possible gap separation change during shear ≤ 1 μm. The accuracy of the strain function generator to override the clutch system was less than 0.01 sec. Experimentally, the clutch and brake engagement times were found to be 0.07 sec, and the time required for the angular velocity of the cone to reach the desired constant value or for the cone to be stopped from rotation was less than 0.005 sec.

Preliminary Tests

The torque measuring system of our modified WRG was checked using a polybutene standard[25] with a given zero shear rate viscosity of 1.25×10^4 poises at 25°C. The experimental viscosity-versus-shear rate results at 24.9° ± 0.5°C obtained from our apparatus is presented in Figure 2. The extrapolated zero shear rate viscosity from Figure 2 is $(1.27 \pm 0.03) \times 10^4$ poises.

In measuring the generated thrust when shearing a viscoelastic fluid in a cone/plate rheogoniometer, Meissner,[1] Chang,[26] and Crawley[27] have found possible undesirable artifacts due to the gap angle smallness and spring softness. Recently, Hansen and Nazem[3] provided experimental data pointing out the influence of the fluid viscosity and the radius of the gap as well as gap angle and spring stiffness on the response time of the thrust measuring system. Using a magnetic system,[28] we have found 0.03 sec for the response time of the thrust measuring system (including less than 0.01 sec for the magnetic coils) when using an 8.046° cone gap filled with a 150° ± 0.5°C molten polyethylene, as opposed to 1.6 sec corresponding to a gap angle of 1.92°. Therefore, in agreement with Meissner,[1] only nominal 8° cone with 1.2-cm gap radius was employed hereafter.

Data Reproducibility

Stress growth experiments were performed on IUPAC polyethylenes (samples A and C) at 0.1 and 1.0 sec^{-1} shear rates. Figures 3 and 4 illustrate the

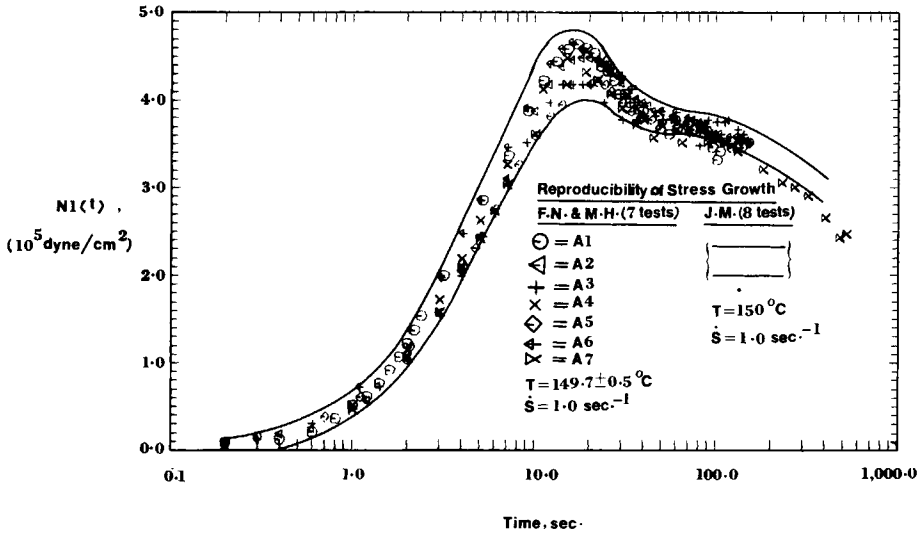

Fig. 4. Reproducibility of the primary normal stress difference $N_1(t)$ growth data (F. N. & M. H., 7 tests) and their comparison with Meissner's data (J. M., 8 tests). Polyethylene sample A, $\dot{S} = 1.0\ \text{sec}^{-1}$.

shear and primary normal stress growths, respectively, for seven repeated experiments at 1.0 sec^{-1} shear rate using a fresh sample A for each test. For these experiments, $\sigma(t)$ and $N_1(t)$ data lay within ±5% and ±6%, respectively, of the mean values in seven replicate tests and within the reproducibility bands given by Meissner for eight of his replicate tests. Meissner's reproducibility bands are shown by the solid lines in Figures 3 and 4. Similarly, Figures 5 and 6 represent the stress overshoot phenomena for IUPAC polyethylene samples A and C at 0.1 sec^{-1} shear rate obtained at our laboratory. These data also agree with Meissner's and show that samples A and C have almost the same $\sigma(t)$ growth yet different $N_1(t)$ growth.

To determine the possible influence of the apparatus on the stress relaxation data, the following was performed. A load of 1624 g was applied to the cone assembly of our WRG (air in gap) using the magnetic system[28] and subsequently by the sudden removal of the load (simulating a stress relaxation experiment), the response of the thrust system was recorded on an oscilloscope screen. We found that the thrust system was capable of detecting 1.8×10^8 dynes/cm^2 sec (initial rate of drop), yet the maximum initial rate of $N_1(t)$ relaxation for our experiments (to be presented later) was less than 2.2×10^6 dynes/cm^2 sec, indicating the reliability of the thrust system in providing sound stress relaxation data. However, for the stress growth and relaxation in this research a chart recorder (Model 7100 B, Hewlett-Packard) was employed instead of an oscilloscope. We incurred negligible error (less that ±3% difference) in determining the initial rate of $N_1(t)$ relaxation using the chart recorder. A similar conclusion was reached for the initial rate of $\sigma(t)$ relaxation. In addition, the agreement between our stress growth data and that of Meissner (Meissner obtained data in a digital form via a computer directly connected to $\sigma(t)$ and $N_1(t)$ measuring systems), illustrated in Figures 3 and 4, testifies the absence of significant influence from the chart recorder on the data of our research.

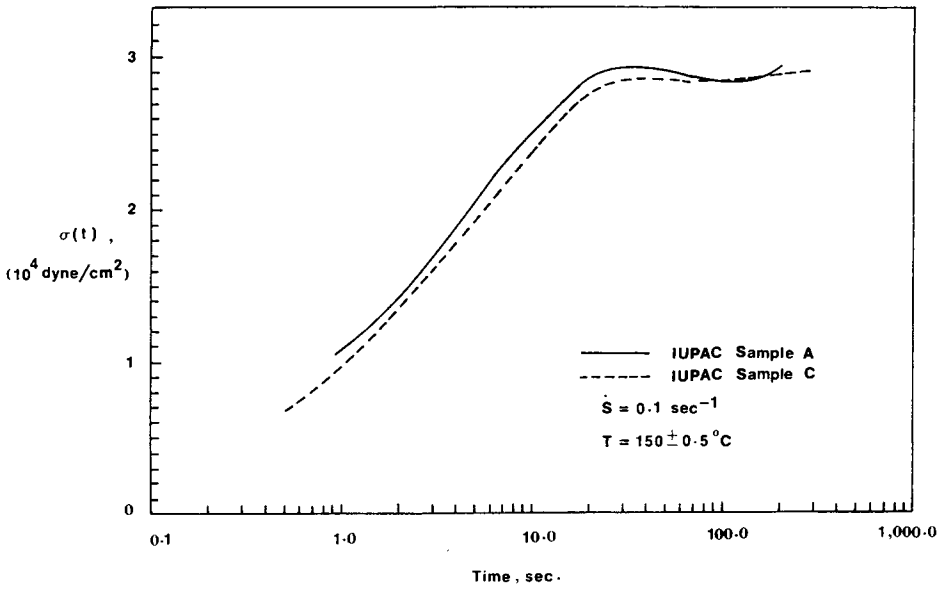

Fig. 5. Comparison of the shear stress growths for polyethylene samples A and C, $\dot{S} = 0.1$ sec^{-1}.

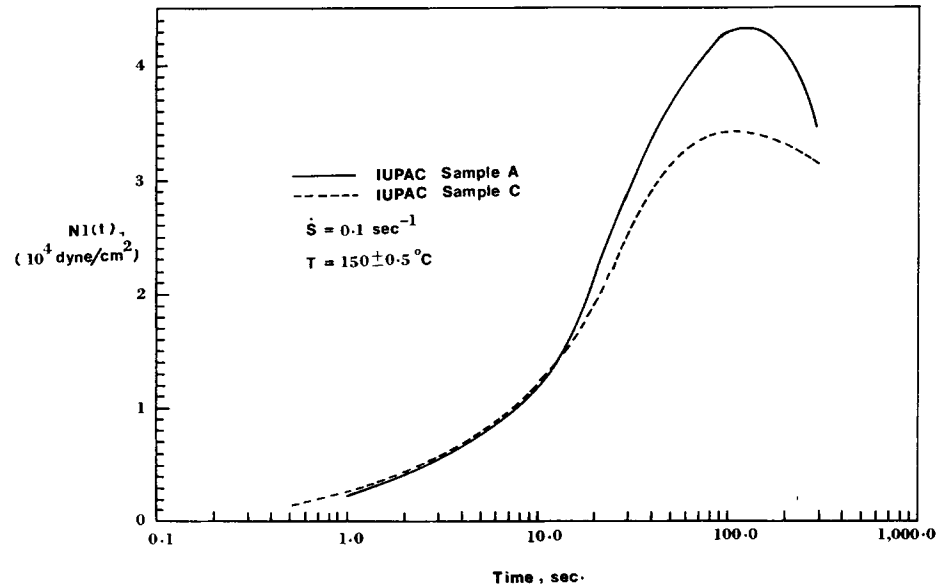

Fig. 6. Comparison of the primary normal stress growths for polyethylene samples A and C, $\dot{S} = 0.1$ sec^{-1}.

TEST PLAN AND EXPERIMENTAL RESULTS

In the light of the information presented in previous sections, we judged that our modified WRG was capable of providing reliable transient $\sigma(t)$ and $N_1(t)$ data for molten polyethylenes using an 8.046° cone, gap radius of 1.2 cm, 10 kg/μm cantilever spring, and 2.1×10^{12} dyne·cm/radian torsion rod.

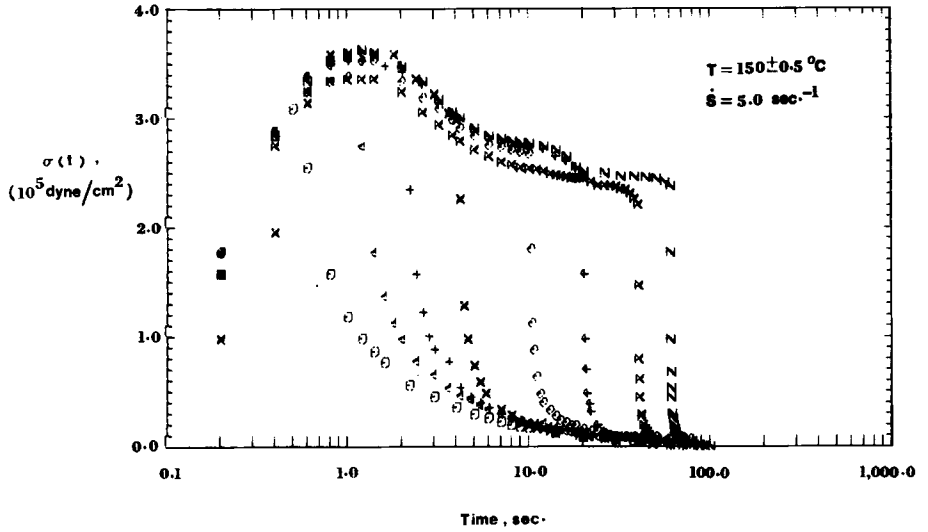

Fig. 7. Typical shear stress growth and relaxation for polyethylene sample C, $\dot{S} = 5.0$ sec^{-1}: relaxation after: (⊖) 2 strain units; (▲) 5 strain units; (+) 10 strain units; (×); 20 strain units; (◊) 50 strain units; (▲) 100 strain units; (▷◁) 200 strain units; (⋀⋁) 300 strain units.

Stress growth and relaxation data on polyethylene sample C at 150° ± 0.5°C were obtained at 0.1, 2.0, 5.0, and 10.0 sec^{-1} shear rates. For $\dot{S} = 0.1$ sec^{-1}, five experiments were performed which differed only by the shear deformation, namely, 2, 5, 10, 20, and 50 units of strain, prior to the onset of stress relaxation. The shear deformation for 2.0, 5.0, and 10.0 sec^{-1} experiments prior to stress relaxation were chosen to be 2, 5, 10, 20, 50, 100, 200, and 300 units. The data of $\dot{S} = 5.0$ sec^{-1} experiments are shown in Figures 7 and 8 representing typical stress growth and relaxation for $\sigma(t)$ and $N_1(t)$, respectively.

The striking but well-known features of Figures 7 and 8 are the presence of maxima in $\sigma(t)$ and $N_1(t)$-versus-time curves. We have made similar observations for 0.1, 2.0, and 10.0 sec^{-1} experiments. Controversy exists as to whether or not stress overshoot is a true material behavior consequence of homogeneous shearing of a viscoelastic liquid. Hence, we have given special attention to the shear field of the sample upon shearing. Figure 9 displays a comparison of 0.1 and 10.0 sec^{-1} shear rate samples (both sheared 2 units of strain, and looking at the free boundaries of the samples). Illustrated in Figure 9, a nonuniformity in $\dot{S} = 10.0$ sec^{-1} sample (upper sample) exists which is absent in $\dot{S} = 0.1$ sec^{-1} sample (lower sample). To detect the possible shear nonuniformity inside the samples, cuts were made circumferentially as function of the distance from the center of the samples and inspected under a microscope with a magnification of 7×. Attempts so far have indicated nonuniformity of shear only at the free boundary of the test piece, yet it warrants future studies of the flow profile inside the samples.

In attempting to explain the shear nonuniformity, the following points were considered: (a) viscous heating; (b) inertial forces due to the sudden start-up of shear flow, and (c) the "slip stick" condition at the surfaces of the sample in contact with the surfaces of the gap. Using the Bird-Turian[29] equation, the possible temperature rise due to viscous heating in the sample

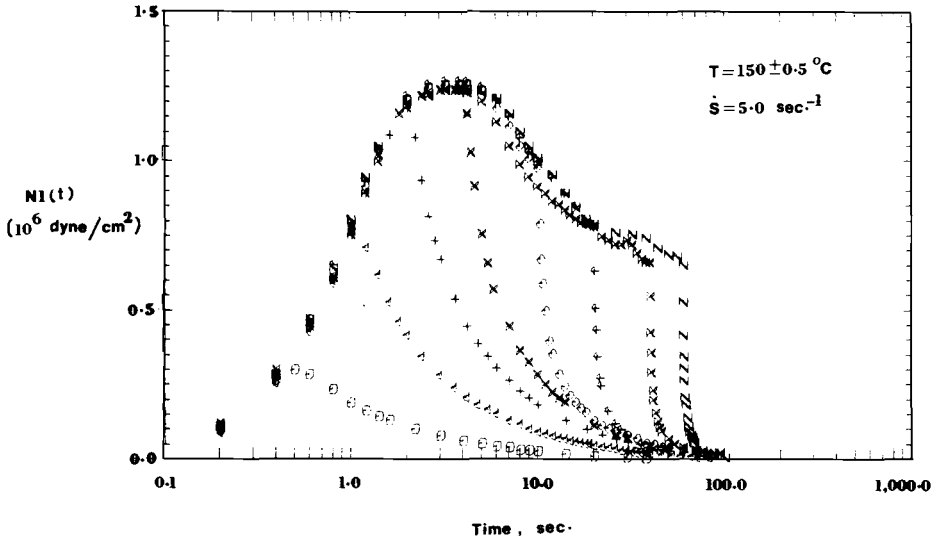

Fig. 8. Typical primary stress growth and relaxation for polyethylene sample C, $\dot{S}$ = 5.0 sec^{-1}: relaxation after (⊖) 2 strain units; (▲) 5 strain units; (+) 10 strain units; (×) 20 strain units; (◇) 50 strain units; (▲) 100 strain units; (▷◁) 200 strain units; (▽△) 300 strain units.

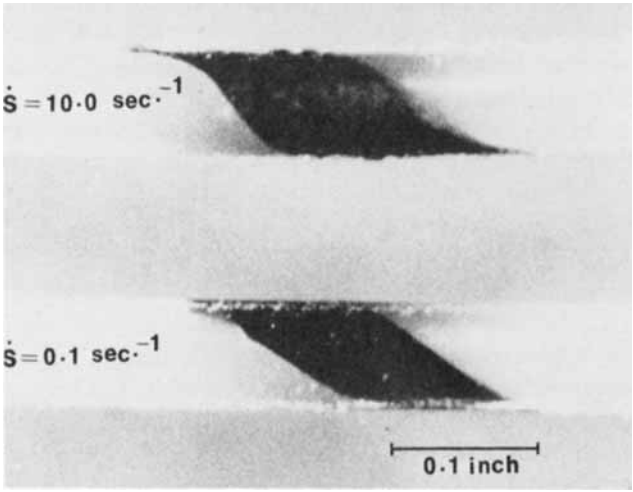

Fig. 9. Comparison of uniform shear profile ($\dot{S}$ = 0.1 sec^{-1}, lower sample) and nonuniform shear profile ($\dot{S}$ = 10.0 sec^{-1}, upper sample) looking at the free boundary of the marked samples. Polyethylene sample C, both sheared 2 strain units, T = 150° ±0.5°C, cone angle = 8.046°, gap radius = 1.2 cm.

was calculated and found to be only 0.3°C for $\dot{S}$ = 10.0 sec^{-1}. Furthermore, the effect of viscous heating is expected to lead to a larger shear strain near the gap center, contrary to our observation. The inertial force effect is expected to produce an unsymmetrical shear nonuniformity about the gap center (instead of symmetrical, upper sample in Fig. 9). By placing marks on the edges of the cone and plate in line with the marked sector of the sample prior to the experiment and after shearing the sample at 10.0 sec^{-1} for 300 units of strain, no slip condition at the surfaces of the sample could be detect-

ed. Moreover, the calculation of strain in the sheared sample corresponded to the time of shearing and substantiated the absence of "slip stick" condition in our experiments. Therefore, we cannot explain the cause of shear nonuniformity at the free boundary of the samples at $\dot{S} = 10.0\ \text{sec}^{-1}$ experiments.

In our experiments, as the shear rate $\dot{S}$ increased, we observed that both $\sigma(t)$ and $N_1(t)$ became larger and reached their maximum values with a steeper slope from the initiation of the experiment, producing a more pronounced stress overshoot. Table I displays the maximum values of $\sigma(\max)$ and $N_1(\max)$ as a function of $\dot{S}$ along with the values of time $t_{\max}$ and shear strain $S_{\max}$ where the maxima occurred. As $\dot{S}$ increases, Table I shows that both $\sigma(\max)$ and $N_1(\max)$ become larger and in shorter times. The $N_1(\max)$ of 2.0, 5.0, and 10.0 sec^{-1} experiments appear approximately at 16–20 strain units; however, for 0.1 sec^{-1}, experiment $N_1(\max)$ occurs at approximately 10 units of strain. Irrespective of the imposed shear rate on the sample, all $\sigma(\max)$ appear at approximately 6 units of strain.

The initial rates of stress relaxation for $\sigma(t)$ and $N_1(t)$ are obtained from the raw data and are illustrated in Figures 10 and 11 as a function of $\dot{S}$ and S prior to the onset of relaxation. One observes that as $\dot{S}$ increases, both $-d\sigma(t)/dt$ and $-dN_1(t)/dt$ increase. Figures 10 and 11 further show that the initial rates of relaxation for $\sigma(t)$ and $N_1(t)$ are dependent on S, increasing at the beginning up to a maximum value and subsequently decreasing rapidly to a steady state or a slowly decreasing region. For 2.0, 5.0, and 10.0 sec^{-1} experiments, we found that the strains where $\sigma(\max)$ and $N_1(\max)$ occur are, approximately, the same strains where $-d\sigma(t)/dt$ and $-dN_1(t)/dt$ display maximum values respectively. However, for 0.1 sec^{-1} experiment, the strains where maximum $-d\sigma(t)/dt$ and $-dN_1(t)/dt$ occur do not correspond to the strain values of $\sigma(\max)$ and $N_1(\max)$, respectively.

DISCUSSION

A major advancement in the development of constitutive equations, to describe the deformation behavior of flowing materials, has been achieved theoretically with Lodge's elastic liquid model[30] and its subsequent modifications of the memory function.[31–33] Yet, these theoretical attempts still cannot adequately describe many of the experimental observations. A popular class of constitutive equation is

$$\sigma(\mathrm{t}) = -P\mathbf{I} + \int_{-\infty}^{t} \mu(t - t', II_d(t')) \times \left[\left(1 + \frac{\epsilon}{2}\right)(\mathbf{C}^{-1}(t - t') - \mathbf{I}) + \frac{\epsilon}{2}(\mathbf{C}(t - t') - \mathbf{I})\right] dt' \quad (1)$$

where $\sigma(\mathrm{t})$ denotes the stress tensor, $P\mathbf{I}$ is the isotropic stress tensor, μ is the memory function, $II_d(t')$ is the second invariant of the deformation rate tensor at past time t', ϵ is an empirical parameter, and $\mathbf{C}^{-1}$ and $\mathbf{C}$ are the relative Finger and Cauchy strain tensors.

TABLE I
Data on Maximum Shear and Normal Stresses

Shear rate, sec^{-1}	Time of maximum shear stress, sec	Strain of maximum shear stress, strain units	Maximum shear stress, 10^4 dyne/cm^2	Time of maximum normal stress,[b] sec	Strain of maximum normal stress, strain units	Maximum normal stress, 10^4 dyne/cm^2
0.1	60[a]	6[a]	3.2	100	10	3.7
2	3[a]	6[a]	23	10	20	54
5	1.2	6	35	3.3	16.5	125
10	0.6	6	48	2.0	20	220

[a] Average values.

[b] Using eq. (20) of ref. 3, the normal thrust response time for a Newtonian fluid of 5×10^5 poises viscosity using the apparatus geometry employed in this paper is 0.041 sec. Note that this calculation for the Newtonian fluid represents the upper limit of the apparatus response time, and one expects a smaller value of the response time for a viscoelastic fluid of equivalent zero shear rate viscosity.

Using eq. (1), Yamamoto[5] provides the following relation for stress relaxation after the cessation of steady ($\dot{S}$ = constant) shear flow:

$$-\frac{dN_1(t)}{dt} = 2\dot{S}\sigma(t); \tag{2}$$

where $-dN_1(t)/dt$ is the rate of primary normal stress relaxation, $\sigma(t)$ is the shear stress, and $\dot{S}$ is the constant shear rate prior to relaxation. Yamamoto suggests using eq. (2) as a check for the applicability of eq. (1) in describing the flow behavior of viscoelastic fluids. Using our stress relaxation data of 0.1 sec^{-1} shear rate experiment for polyethylene sample C sheared 50 units of strain, eq. (2) was evaluated. To determine the left-hand side of eq. (2), the

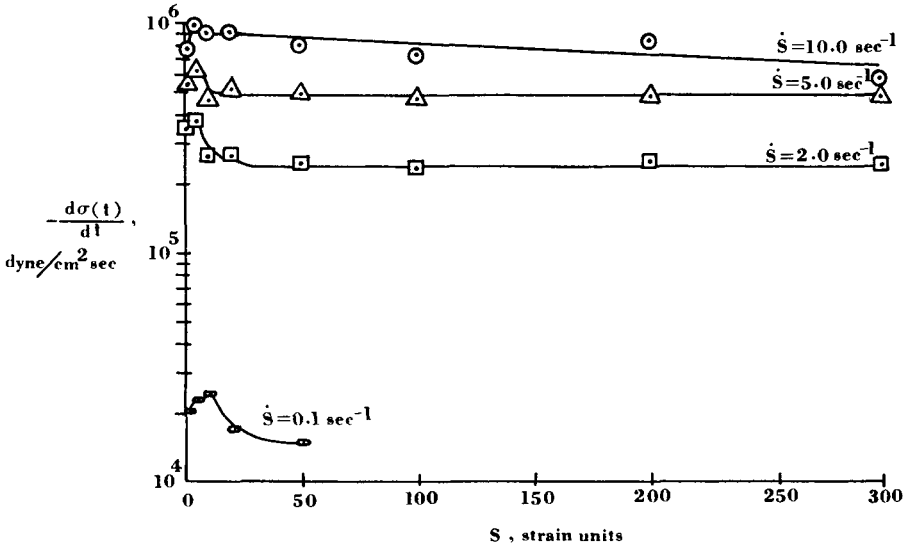

Fig. 10. Initial rate of shear stress relaxation $-d\sigma(t)/dt$ vs. strain S and as a function of shear rate $\dot{S}$. Polyethylene sample C, T = 150° ± 0.5°C.

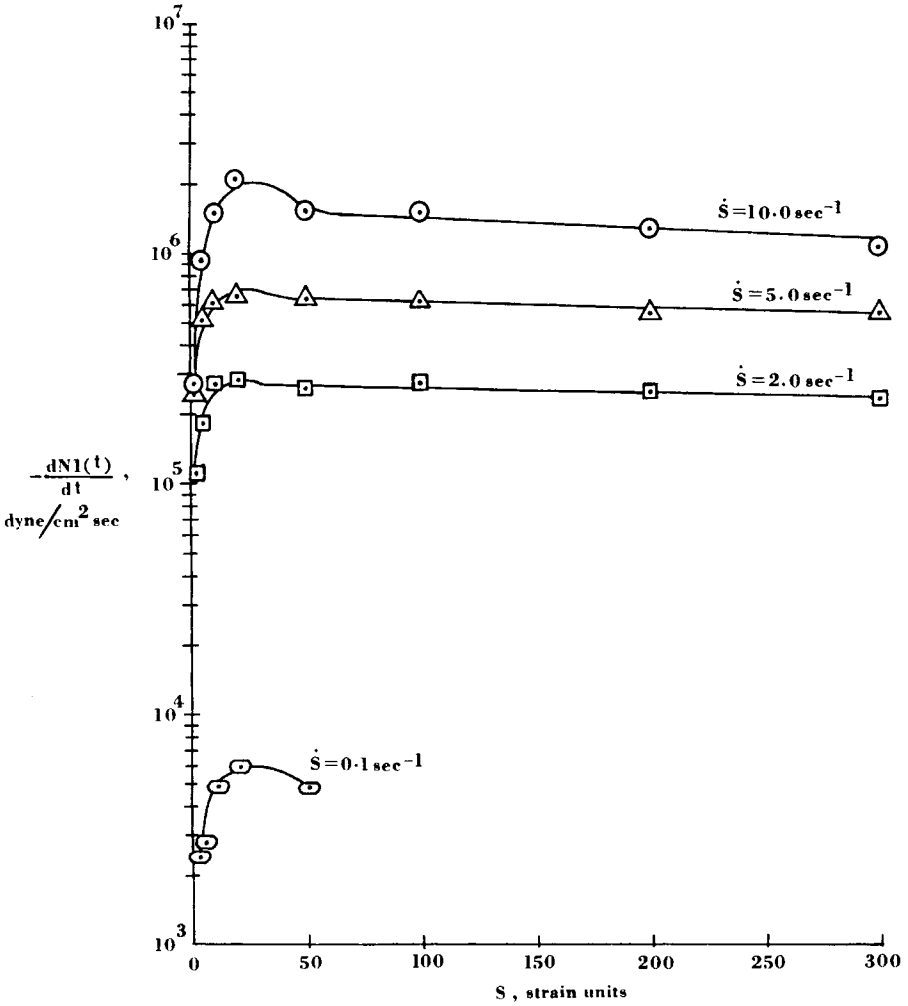

Fig. 11. Initial rate of primary normal stress relaxation $-dN_1(t)/dt$ vs. strain S and as a function of shear rate $\dot{S}$. Polyethylene sample C, T = 150° ± 0.5°C.

experimental $N_1(t)$ relaxation vs time data was fit with a third-order polynominal using the least-squares technique, which subsequently was employed for determining $-dN_1(t)/dt$. A comparison of calculated $[(-\frac{1}{2}\dot{S})dN_1(t)/dt]$ and measured $\sigma(t)$ shear stress relaxation is displayed in Figure 12 indicating the validity of eq. (2) for our data.

Recently, van Es and Christensen[4] proposed yet another method for checking the applicability of eq. (1) and they present

$$\int_0^t \lambda\left[\int_0^\infty \mu_0(\lambda+\xi)d\xi\right]d\lambda = -t\eta(t) + \int_0^t \eta(\lambda)d\lambda + \theta(t) \qquad (3)$$

where $\theta(t) = N_1(t)/\dot{S}^2$ and all the other terms of eq. (3) are defined in reference 4. For eq. (1) to be applicable, van Es and Christensen conclude, the right-hand side of eq. (3) should be determined from the experimental $\sigma(t)$ and $N_1(t)$ data and must be independent of shear rate and monotone increasing function of time. Using stress growth data for a monodisperse poly α-

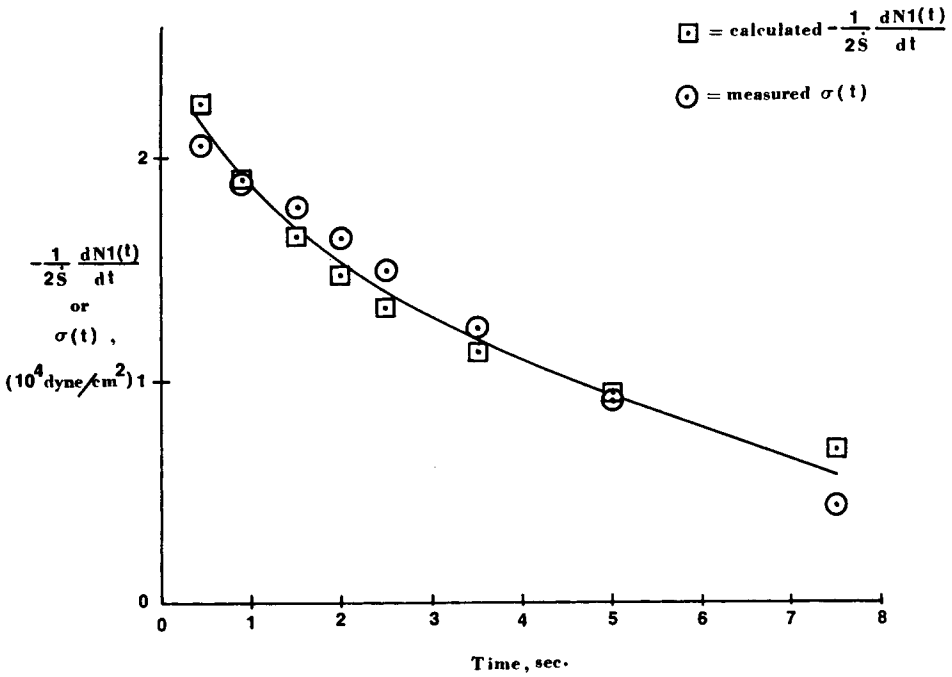

Fig. 12. Relationship between calculated $[(-1/2\dot{S})dN_1(t)/dt]$ and measured $[\sigma(t)]$ shear stresses for $\dot{S} = 0.1$ sec^{-1} experiment. Polyethylene sample C sheared 50 strain units prior to relaxation: (□) calculated $(-1/2\dot{S})dN_1(t)/dt$; (⊙) measured $\sigma(t)$.

methylstyrene dissolved in diphenyl chloride, Sakai et al.[34] have shown that eq. (2) holds, yet the two conditions of shear rate independence and the monotone increasing of the right-hand side of eq. (3) are not always satisfied.

Employing the stress growth data from our research, the right-hand side value of eq. (3) is evaluated. Figure 13 displays these values (for $\dot{S} = 0.1$, 2.0, 5.0 and 10.0 sec^{-1} experiments) as a function of time. Except for a small range at the beginning of the curves, these values were found to be $\dot{S}$ dependent and not always monotonically increasing with time. Thus, our data do not satisfy the van Es and Christensen's criterion. Without a need for detail discussion, at large times, the $-t\eta(t) + \int_0^t \eta(\lambda)d\lambda$ term is negligible compared with $\theta(t)$; and when $N_1(t)$ is still decreasing, the monotone increasing condition of van Es and Christensen's criterion will not be met. In fact, the stress growth data of $\dot{S} = 0.1$ sec^{-1} experiment presented in Figure 13 confirmed this point. However, we observe that the right-hand side values of eq. (3) for $\dot{S} = 2.0$, 5.0, and 10.0 sec^{-1} experiments are monotonically increasing functions of time. Yet, for these high shear rate experiments, the shearing of the samples was not pursued far enough to reach the steady stress regions. If we would have continued our $\dot{S} = 2.0$, 5.0, and 10.0 sec^{-1} experiments further, we suspect a similar behavior as for the $\dot{S} = 0.1$ sec^{-1} experiment. Similarly, due to the dependence of $\theta(t)$ on $\dot{S}$, the right-hand side of eq. (3) should be expected to be shear rate dependent.

Hence, eq. (1) seems unsuitable for describing the stress growth behavior of the polyethylene sample C employed in our measurements, except for the region where $S \leq 0.06$ shear units. Moreover, Figures 10 and 11 indicate that

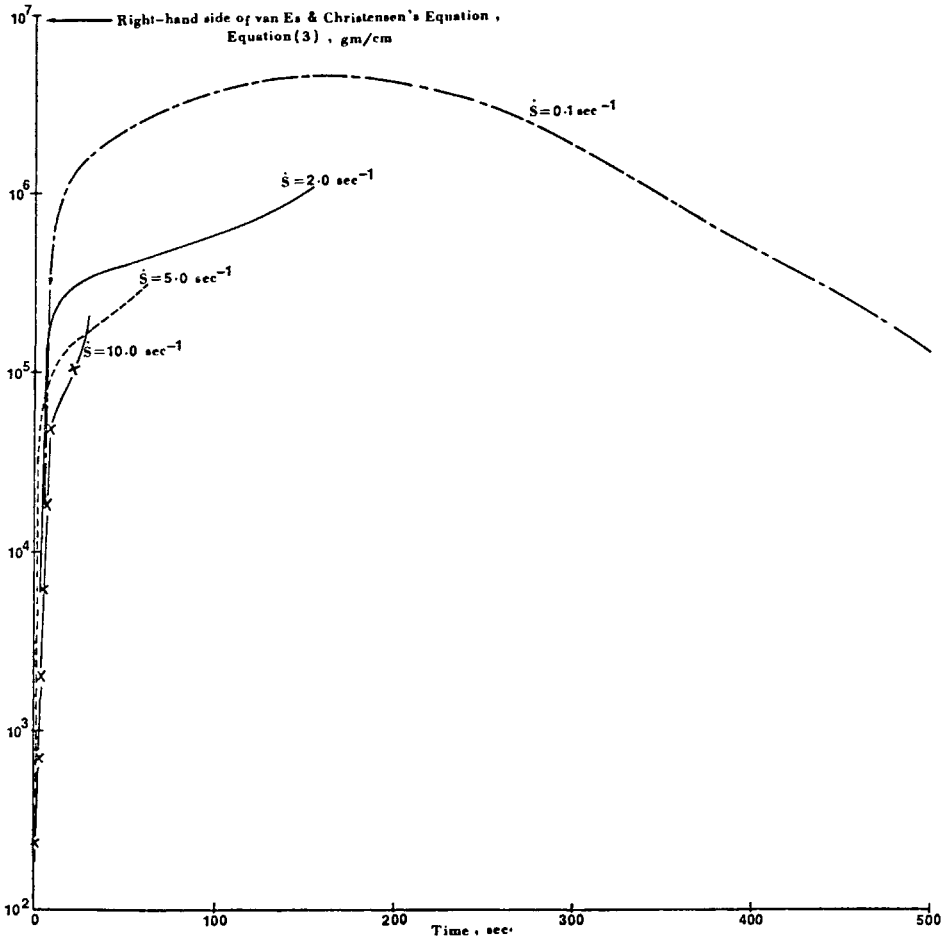

Fig. 13. Experimental evaluation of van Es and Christensen's equation (eq. 3). Polyethylene sample C data at various shear rates: (— — —) $\dot{S}$ = 0.1 sec^{-1}; (—) $\dot{S}$ = 2.0 sec^{-1}; (– – –) $\dot{S}$ = 5.0 sec^{-1}; (— × —) $\dot{S}$ = 10.0 sec^{-1}.

the choice of a memory function depending only on the second invariant of the shear rate (as a function of past time t') might not be adequate. From Figures 10 and 11, one observes that the initial rates of shear and normal stress relaxations are very much dependent on the strain, supporting the belief that the memory function should embody information on strain as well as on shear rate.

CONCLUSIONS

We have reached the following conclusions:

1. The agreements of our $\sigma(t)$ and $N_1(t)$ stress growth data with those of Meissner confirm Meissner's findings and indicate the soundness of Meissner's modifications of the WRG for the transient normal thrust measurements of molten polymers.

2. Using the above WRG (gap angle = 8.046°, gap radius = 1.2 cm), the shear is substantially uniform at low shear rates ($\dot{S} \leq 5.0$ sec^{-1}), but at $\dot{S}$ =

10.0 sec^{-1} and shear strain as low as 2 units, shear nonuniformity was observed at the free boundary of the sample. Attempts to determine the possible degree of nonuniformity inside of the samples from 10.0 sec^{-1} experiments have been unsuccessful and warrants further research to provide an answer to this fundamental question. However, we believe that the shear nonuniformity at the free boundary of the sample for $\dot{S}$ = 10.0 sec^{-1} experiment cannot be due to (i) viscous heating in the sample, (ii) inertial forces associated with sudden start-up of shear flow, or to (iii) the "slip stick" condition at the surfaces of the test specimen in contact with the surfaces of the gap.

3. The time of maximum shear stress $t_{12}(\max)$ and that of the maximum primary normal stress difference $t_1(\max)$ are both decreasing function of $\dot{S}$ (see Table I). We found that the ratio $t_1(\max)/t_{12}(\max)$ for $\dot{S}$ = 0.1 to 10.0 sec^{-1} experiments to be in the range of 1.7 to 3.4, illustrating the need for a broad distribution of relaxation times in the memory function.

4. Using the experimental data obtained in this work, we found Yamamoto's relation, eq. (2) holds; yet the conditions of van Es and Christensen, eq. (3), are not always satisfied. From the evaluation of the right-hand side of eq. (3), we found these values were $\dot{S}$ dependent and not always monotone increasing with time. Hence, the class of constitutive equations with the second invariant of deformation rate tensor (depending on past time t') in the memory function is not suitable to describe our experimental stress growth data.

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