# Equibiaxial Extension of Two Polymer Melts: Polystyrene and Low Density Polyethylene

PAUL R. SOSKEY* and H. HENNING WINTER, *University of Massachusetts, Department of Polymer Science and Engineering* and *Department of Chemical Engineering, Amherst, Massachusetts 01003*

## Synopsis

Stress relaxation after rapid extensional strain was measured to obtain the extensional relaxation modulus. The research had the objectives of developing the lubricated squeezing technique for molten polymers, of applying the technique to two different polymers, and of testing the "separability hypothesis." Equibiaxial extensional flow was generated with a Rheometrics RDS-LA, using the lubricated squeezing technique. The *time* dependence of the relaxation modulus was found to be the same in extension as in shear, given by the relaxation modulus of linear viscoelasticity. The *strain* dependence was markedly different than in shear. Separation of time and strain dependence into a product of two functions is suggested by the experimental results. This is a strong support for the separability hypothesis and simplifies the formulation of rheological constitutive equations. A polymer with linear macromolecules (PS) exhibited stronger strain dependence than a polymer with long chain branched macromolecules (LDPE). The parameters of an integral constitutive equation were determined in rapid strain experiments and the constitutive equation was tested experimentally with stress growth at start-up of equibiaxial extension.

## INTRODUCTION

Biaxial extensional flows occur in several polymer processing operations such as film blowing, blow molding, and vacuum forming. The rheological behavior of viscoelastic polymers in biaxial extension is of prime importance in understanding and improving such processes. Biaxial extensional data would also be useful as guidance during the development of rheological constitutive equations. Research in extensional rheology has occurred primar-

ily in the last two decades, and several reviews have appeared in the literature.[1-3] To date four methods have been used to study biaxial extension: sheet inflation, axisymmetric stagnation flow, sheet stretching, and lubricated squeezing.

Sheet inflation involves the extension of a thin polymer sheet by means of an inert gas[4-8] or a silicone oil.[9-10] A hemispherical bubble was inflated by applying gas at different pressure on both sides of a sheet. The deformation was measured optically and the stress in the sheet was determined from the local bubble curvature and the pressure difference. Both stress and strain rate were changing with time. The use of an incompressible silicone oil as the inflating medium and a control system for the inflation rate has enabled constant rate experiments to be performed using this technique. Controlled biaxial extension, however, is restricted to the area near the pole of the bubble.

Constant biaxial strain rates were achieved in an axisymmetric stagnation flow device[11,12] in which two impinging fluid streams are guided by lubricated trumpet shaped walls.[13] Flow birefringence was measured in the plane of symmetry and the force which tended to separate the trumpets was measured simultaneously. Polystyrene melts were investigated at constant strain rates.

A sheet stretching device consisting of eight rotary clamps has also been used to obtain biaxial extensional data.[14,15] The biaxial deformation with this device is homogeneous throughout the sample. Constant strain rate data for polyisobutylene at room temperature have been reported. High temperatures, as needed for polymer melt rheology, will be difficult to obtain and to control due to the bulky design of the rheometer.

These techniques require very sophisticated equipment, large samples, careful sample preparation, and are limited to certain temperature ranges. The experiments are also limited to constant stress and/or constant strain rates.

Recently, the lubricated squeezing technique has been developed to generate equibiaxial extensional flow.[16,17] A small sample of viscous material is compressed between two lubricated parallel disks as shown in Figure 1. This technique has the advantages of simple geometry, small sample size, fast experiments, and a broad range of temperature control. Another important advantage and the main focus of this study is the ability to perform step
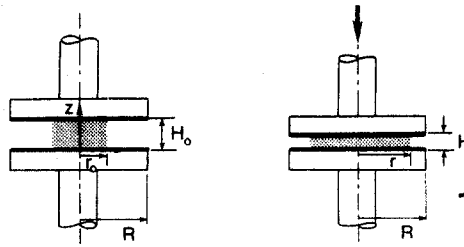
Fig. 1.  Sketch of lubricated squeezing geometry.

strain in equibiaxial extension[18] in addition to constant stress and constant strain rate experiments.

## KINEMATICS OF EQUIBIAXIAL EXTENSION

Equibiaxial extension is a special case of axisymmetric extension which is defined by a velocity field

$$\mathbf{v} = \left( \dot{\epsilon}_a x_1, \ - \frac{\dot{\epsilon}_a}{2} x_2, \ - \frac{\dot{\epsilon}_a}{2} x_3 \right). \tag{1}$$

The components are written in principal coordinates with the 1-axis being the symmetry axis of the flow. The density is assumed to be constant. The axisymmetric extension rate

$$\dot{\epsilon}_a \equiv \dot{\epsilon}_1(t) = \partial v_1 / \partial x_1 \tag{2}$$

and extensional strain

$$\epsilon_a \equiv \epsilon_1(t',t) = \int_{t'}^{t} \dot{\epsilon}_1(t'') dt'' \tag{3}$$

are positive for *uniaxial extension* and negative for *equibiaxial extension*. The Finger strain tensor of axisymmetric extension has the components

$$\mathbf{C}^{-1}(t',t) = \begin{pmatrix} \exp(2\epsilon_a) & 0 & 0 \\ 0 & \exp(-\epsilon_a) & 0 \\ 0 & 0 & \exp(-\epsilon_a) \end{pmatrix}. \tag{4}$$

The invariants of $\mathbf{C}^{-1}(t',t)$ are

$$I_1 = \text{trace } (\mathbf{C}^{-1}) = \exp(2\epsilon_a) + 2\exp(-\epsilon_a) \qquad (5)$$

$$I_2 = \{I_1{}^2 - \mathbf{C}^{-1}{:}\mathbf{C}^{-1}\}/2 = \exp(-2\epsilon_a) + 2\exp(\epsilon_a) \qquad (6)$$

$$I_3 = 1; (\rho = \text{const}). \qquad (7)$$

The equibiaxial extension (axisymmetric compression) data are presented in terms of the biaxial extensional strain

$$\epsilon_b \equiv \epsilon_2(t',t) = -\epsilon_a/2. \qquad (8)$$

One can see from Eqs.(4), (5), (6), and (8) that the first invariant of axisymmetric extension (uniaxial extension) is equal to the second invariant of axisymmetric compression (equibiaxial extension) and the second invariant of axisymmetric extension is equal to the first invariant of axisymmetric compression when the invariants are functions of a negative $\epsilon_a$,

$$I_1(\epsilon_a) = I_2(-\epsilon_a) \qquad (9)$$

$$I_2(\epsilon_a) = I_1(-\epsilon_a). \qquad (10)$$

These strain invariants are used to describe the strain dependence of the stress in transient experiments. One of the most informative of these experiments is the step strain experiment.

## STEP STRAIN IN SHEAR AND EQUIBIAXIAL EXTENSION

The step strain experiment is a direct means of measuring the strain dependent rheology of polymeric liquids. In the experiment, a test sample is placed into the rheometer and the system is kept at rest until the sample is completely relaxed to the stressfree state. At time $t = 0$, a finite strain is "instantaneously" applied and held constant thereafter. The resulting stress is measured as it relaxes with time. The analysis of step strain data is especially easy since only two states of strain are involved, assuming that the finite rise time of the strain has negligible influence. The result of the measurement is the time and strain dependent relaxation modulus.

For step *shear*, the relaxation modulus is commonly defined as

$$G_s(t,\gamma) = \frac{\tau_{21}(t,\gamma)}{\gamma_{21}} \qquad (11)$$

with shear stress, $\tau_{21}$, and shear strain, $\gamma_{21}$, described in a shear coordinate system. For step *axisymmetric extension*, the relaxation modulus may be defined as

$$G_e(t,\epsilon_a) = \frac{[\sigma_{11} - \sigma_{22}](t,\epsilon_a)}{C_{11}^{-1} - C_{22}^{-1}} = \frac{\sigma_{11} - \sigma_{22}}{e^{2\epsilon_a} - e^{-\epsilon_a}}. \qquad (12)$$

If the strain is a compression (equibiaxial extension) then the extensional relaxation modulus can be written in terms of the equibiaxial extensional strain as defined in Eq. (8):

$$G_e(t,\epsilon_b) = \frac{\sigma_{11} - \sigma_{22}}{e^{-4\epsilon_b} - e^{2\epsilon_b}}. \qquad (13)$$

In the limit of small strain, the extensional relaxation modulus becomes equal to the relaxation modulus of linear viscoelasticity

$$\lim_{\epsilon_b \to 0} G_e(t,\epsilon_b) = \frac{\sigma_{22} - \sigma_{11}}{6\epsilon_b} = \overset{o}{G}(t). \qquad (14)$$

The relaxation modulus of linear viscoelasticity can be described by a spectrum of relaxation times, $\lambda_i$, and associated relaxation moduli, $g_i$,

$$\overset{o}{G}(t) = \sum_{i=1}^{N} g_i \exp(-t/\lambda_i). \qquad (15)$$

This relation allows one to check the novel extensional flow experiments against well-known small strain shear data. The relaxation modulus of linear viscoelasticity can, of course, be obtained from several different experiments.[19] The relaxation time spectra of the polymers in this study appear in Table I.[20]

## SEPARABILITY OF TIME AND STRAIN DEPENDENCE

Many authors have suggested that the time and strain dependence of the relaxation modulus can be expressed as a product of two independent functions, the time dependent relaxation modulus of linear viscoelasticity, $\overset{o}{G}(t)$, and a strain function, $h$. The separability hypothesis has been based on phenomenological arguments[21-24] and on a molecular theory.[25] Shear data support this hypothesis for molten polymers.[26,27,20] However, no step

TABLE I
Discrete Relaxation Time Spectra of LDPE and PS Samples

| LDPE $T_o = 150°C$ | | PS $T_o = 180°C$ | |
|---|---|---|---|
| $\lambda_i$ [s] | $g_i$ [Pa] | $\lambda_i$ [s] | $g_i$ [Pa] |
| $5.913 \times 10^1$ | $3.776 \times 10^1$ | $5.152 \times 10^1$ | $7.763 \times 10^1$ |
| $1.817 \times 10^1$ | $3.710 \times 10^2$ | $8.669 \times 10^0$ | $1.338 \times 10^3$ |
| $3.680 \times 10^0$ | $1.952 \times 10^3$ | $5.135 \times 10^0$ | $9.275 \times 10^2$ |
| $6.606 \times 10^{-1}$ | $1.085 \times 10^4$ | $1.018 \times 10^0$ | $1.762 \times 10^4$ |
| $1.073 \times 10^{-1}$ | $2.806 \times 10^4$ | $1.107 \times 10^{-1}$ | $5.004 \times 10^4$ |
| $2.060 \times 10^{-2}$ | $6.040 \times 10^4$ | $1.065 \times 10^{-2}$ | $6.978 \times 10^4$ |
| $3.026 \times 10^{-3}$ | $1.371 \times 10^5$ | $9.927 \times 10^{-4}$ | $1.009 \times 10^5$ |
| $3.381 \times 10^{-4}$ | $3.027 \times 10^5$ | $5.821 \times 10^{-5}$ | $5.558 \times 10^5$ |

strain data were available for testing the separability hypothesis in extensional flow. Wagner[28] calculated an uniaxial strain function from stress growth experiments at constant rate, using a particular constitutive equation and data from the literature. The uniaxial strain function was found to depend on the strain as well as on the rate of extension.

With lubricated squeezing, a method is now available to perform step strain experiments in equibiaxial extension. If the separability hypothesis holds, the extensional relaxation modulus can be decomposed

$$G_e(t,\epsilon_a) = \overset{o}{G}(t)h_e(\epsilon_a), \quad h_e \leqslant 1 \qquad (16)$$

in the same manner as the shear relaxation modulus

$$G_s(t,\gamma) = \overset{o}{G}(t)h_s(\gamma), \quad h_s \leqslant 1. \qquad (17)$$

We therefore propose, as a test of the separability hypothesis, that the extensional relaxation modulus and the shear relaxation modulus have the *same shape*, i.e., the ratio of the moduli is independent of time. At small strain, both strain functions, $h_e$ and $h_s$, adopt a value of 1 and the relaxation modulus in shear and extension is equal. This will be discussed further along with the experimental results.

The strain functions can be combined by expressing them in terms of a generalized strain invariant $I$:[29]

$$I = \alpha I_1 + (1 - \alpha)I_2; \quad 0 \leqslant \alpha \leqslant 1 \qquad (18)$$

where $\alpha$ is a constant. For axisymmetric extension (positive $\epsilon_a$), this strain invariant becomes

$$I(\epsilon_a) = \alpha I_1(\epsilon_a) + (1 - \alpha)I_2(\epsilon_a)$$
$$= \alpha[\exp(2\epsilon_a) + 2\exp(-\epsilon_a)] \tag{19}$$
$$+ (1 - \alpha)[\exp(-2\epsilon_a) + 2\exp(\epsilon_a)]$$

while for equibiaxial extension (negative $\epsilon_a$), $I_1$ and $I_2$ become functions of a negative axisymmetric strain. The invariant $I$ can be rewritten in terms of $\epsilon_b$ as defined in Eq. (8),

$$I(\epsilon_b) = \alpha[\exp(-4\epsilon_b) + 2\exp(2\epsilon_b)]$$
$$+ (1 - \alpha)[\exp(4\epsilon_b) + 2\exp(-2\epsilon_b)]. \tag{20}$$

In shear flows, $I$ is independent of $\alpha$ since $I_1(\gamma)$ and $I_2(\gamma)$ are identical

$$I(\gamma) = I_1(\gamma) = I_2(\gamma) = \gamma^2 + 3. \tag{21}$$

Possible generalized strain functions can then be written as a sigmoidal function[20]

$$h(I) = (1 + a(I - 3)^{b/2})^{-1} \tag{22}$$

or as the sum of two exponential functions[24]

$$h(I) = f\exp(-n_1\sqrt{I - 3}) + (1 - f)\exp(-n_2\sqrt{I - 3}). \tag{23}$$

The parameter $\alpha$ in the strain invariant, Eq. (18), can be determined from extensional step strain experiments. Values of $a$, $b$, $n_1$, $n_2$ and $f$ were determined from shear step strain experiments[20] and appear in Table II. In comparison, Papanastasiou et al.[18]

TABLE II
Parameters for Approximation of Measured Strain Function

| Approximation function | Parameters | LDPE 150°C | PS 180°C |
|---|---|---|---|
| $h(\gamma) = f\exp(-n_1\gamma) +$ | $f$ | 0.67 | 0.88 |
| $(1 - f)\exp(-n_2\gamma)$ | $n_1$ | 0.304 | 0.377 |
| | $n_2$ | 0.070 | 0.073 |
| $h(\gamma) = \dfrac{1}{1 + a\gamma^b}$ | $a$ | 0.172 | 0.302 |
| | $b$ | 1.39 | 1.57 |

suggested a sigmoidal strain function, Eq. (22), with $b = 2$ for all materials.

## EXPERIMENTAL

### Apparatus and Materials

A linear rheometer (Rheometrics RDS-LA) was used for the experiments. The rheometer has a linear motor mounted for vertical displacement on which various test fixtures can be attached. Disks of 25 mm and 10 mm diameter were used. The test fixtures are surrounded by an air convection oven and temperatures up to 250°C are easily obtainable. The temperature can be controlled to $\pm 0.5$K. A transducer with selectable ranges of 0.1 Nm, 0.2 Nm and 0.5 Nm was used to measure the axial forces. A microprocessor controls the strain signal to the motor. A data handling system stores the measurement of the resulting strain and force for transfer to laboratory computers and subsequent analysis.

A linear polymer, PS (Dow Styron 666, polystyrene at 180°C) and a branched polymer, LDPE (duPont Alathon 20, low density polyethylene at 150°C) were studied. Samples for the lubricated squeezing experiments were melt pressed into disks of 25.4 mm diameter and approximately 2.5 mm thick at 190°C for four minutes then quenched in water. The polystyrene was melt pressed under vacuum and slowly cooled to below 100°C before removal from the press to eliminate bubble formation in the sample upon reheating. Smaller diameter samples were cut from these pressed disks.

Silicone oils (General Electric, "Viscasil" silicones) were used as the lubricating medium. The choice of a suitable lubricant is essential in generating a homogeneous extensional deformation. The ratio of zero shear viscosities between sample and lubricant was the criterion for selecting a suitable lubricant. A ratio of 500 to 1000 seems to give the best lubrication.[30] Polymer and lubricant viscosities appear in Figure 2. Viscasil 600,000 and Viscasil 300,000 were used as lubricants for PS and LDPE, respectively.

### Experimental Procedure

A sketch of the lubricated squeezing test geometry is shown in Figure 1. A disk-shaped sample of polymer is placed between two
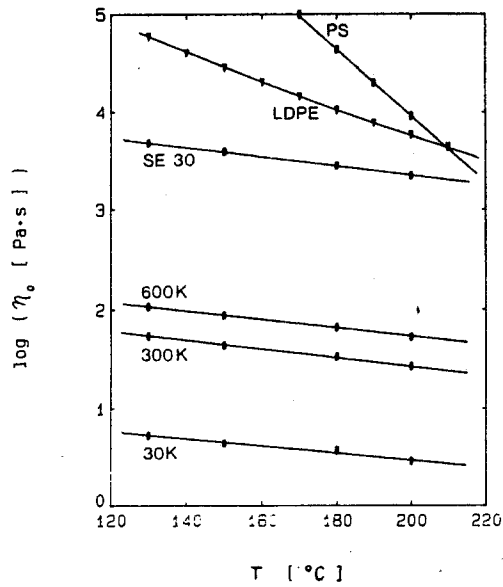
Fig. 2. Zero shear viscosities of samples and lubricants.

lubricated parallel disks. Assuming that the material is incompressible and that the deformation is homogeneous (i.e., the shear deformation occurs only in the lubricant layer and the polymer melt undergoes only equibiaxial extensional flow), the axisymmetric strain rate and strain are

$$\dot{\epsilon}_a = \frac{1}{H}\frac{dH}{dt} \tag{24}$$

$$\epsilon_a = \ln(H/H_o) \tag{25}$$

where $H_o, H$ are the initial and instantaneous sample thicknesses, respectively. The equibiaxial strain, $\epsilon_b$, is obtained from Eq. (8). The normal stress difference is obtained from the relations

$$\sigma_{rr} - \sigma_{zz} = F/[\pi r^2(t)] \qquad \text{for } r \leq R \qquad \text{(partial filling)} \tag{26}$$

$$\sigma_{rr} - \sigma_{zz} = F/\pi R^2 \qquad \text{for } r \geq R \tag{27}$$

where $F$ is the squeezing force on the disks, $r$ is the instantaneous sample radius and $R$ is the radius of the disks.

The instantaneous sample radius is determined assuming constant density:

$$r = r_o \sqrt{H_o/H(t)}; \quad r_o = r(t = 0). \tag{28}$$

The actual experiments proceeded as follows. The parallel disk fixtures were heated to the desired temperature, the oven was opened and a layer of lubricant approximately 0.06 mm thick was applied to the top and bottom disks by means of a wooden spatula. The lubricant layer thickness was about 1% of the sample thickness. The sample thickness can therefore be approximated by the separation of the disks. The polymer sample (consisting of two preformed disks, stacked to give a total initial sample thickness, $H_o \approx 5$ mm) was centered on the bottom disk and the top disk was lowered until it just contacted the sample. The sample was heated to the desired temperature and held there for at least eight minutes before the test was started to ensure complete melting and relaxation of any residual stresses present due to the sample preparation. The initial disk separation, $H_o$, was measured and the test begun. The resulting transient axial force was then recorded.

Two types of experiments were performed: 1) stress relaxation after a step in equibiaxial extensional strain and 2) stress growth at constant equibiaxial extension rate.

Stress relaxation experiments after a step in equibiaxial extensional strain were performed up to $\epsilon_b = 2.3$. The 25-mm disks were used for $\epsilon_b < 0.47$ and the 10-mm disks for $0.35 < \epsilon_b < 2.30$. The equibiaxial extensional strain was measured by removing the deformed sample after the stress had relaxed to below the accuracy of the force transducer (after approximately 200 s), wiping any remaining lubricant from the disk surfaces, bringing the disks into contact and measuring the change in disk displacement after the temperature re-equilibrated to the test value.

For the step strain experiment, a rapid rise time is desired in order to avoid corrections to the resultant stress relaxation.[26] The motor response for a step in strain was extremely fast as seen in Figure 3. Rise times of less than 20 ms were obtained for even the highest strain of $\epsilon_b = 2.3$. Rise times of this magnitude do not significantly affect the stress response at $t \geq 0.4$ s. These rise times are considerably faster than those obtained in shear step strain experiments of the same polymers.[20]
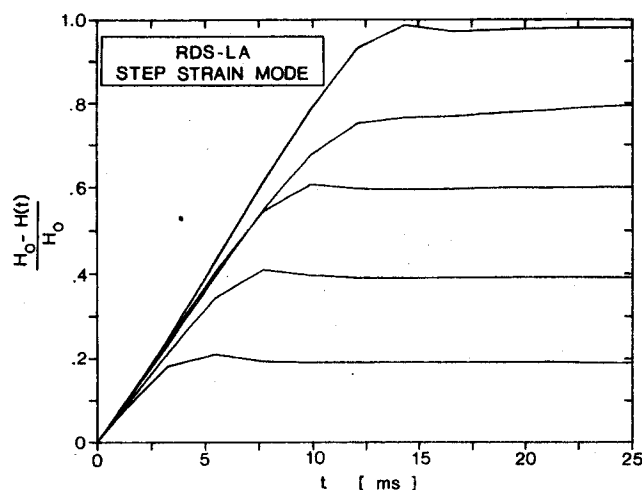
Fig. 3. Measured disk separation as a function of time for step strain experiment on RDS-LA.

The stress response after various steps in strain is shown in Figure 4. The horizontal regions at short times are due to the force transducer range being exceeded at the start of the experiments. Even though the transducer range was exceeded during some tests, there was not an appreciable offset at long times. However, at long times and small strains, some scatter in the data occurs due to the inaccuracy of the transducer at force levels less than $5 \times 10^{-4}$ Nm. This scatter is more pronounced for the LDPE than for the PS. For $\epsilon_b > 1.6$, the effectiveness of the lubrication is seen to diminish as evidenced by the very high force levels at short times and abrupt dips in the force at longer times. Also any slight disk movements at very high strains, $(H_o - H)/H_o > 0.96$, showed up as instabilities in the force measurements. Therefore, due to the limits of the transducer range and the loss of effective lubrication, stress relaxation data over two time decades, $0.1 \leq t \leq 10$ s, and for strains $\epsilon_b \leq 1.5$ were considered reliable.

Stress growth at constant equibiaxial strain rate experiments were also performed. In order to generate a constant rate in the lubricated squeezing experiment, the disks must approach each other in a logarithmic manner based on the initial separation of
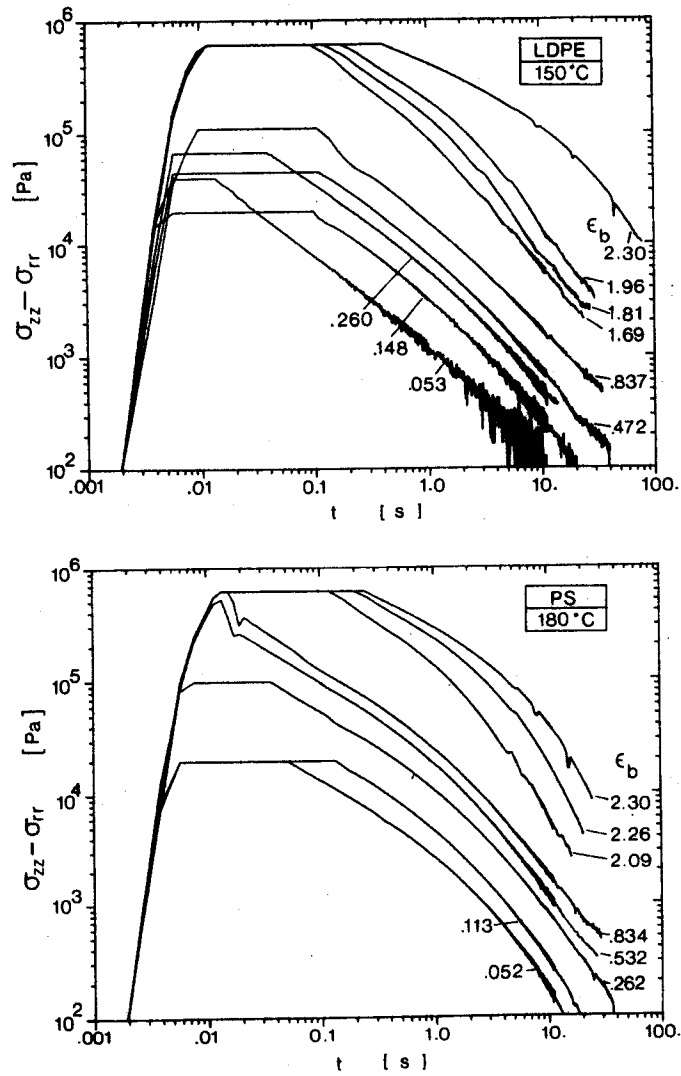
Fig. 4.  Transient stress relaxation measured by RDS-LA for various equibi-axial strains using lubricated squeezing technique. (a) LDPE, $T$ = 150°C, (b) PS, $T$ = 180°C.
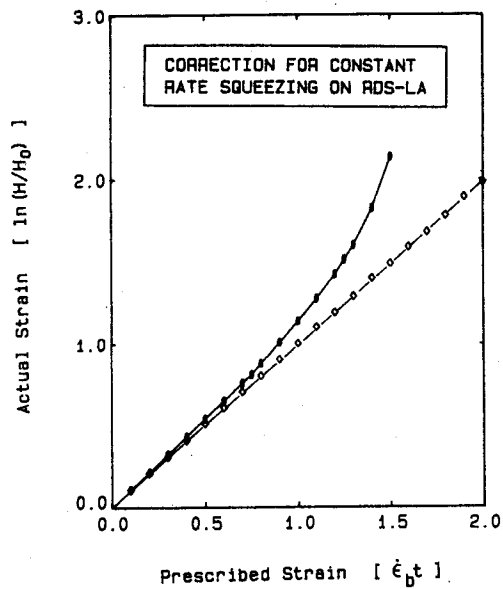
Fig. 5. Actual plate separation vs. prescribed strain for constant strain rate squeezing experiments on RDS-LA. (●————●) before corrections, (◇————◇) after correction according to Eq. (29).

the disks, see Eqs. (24) and (25). A substantial discrepancy was found between the true strain and the required strain for any particular prescribed strain rate. The true strain is obtained from the actual disk separation, $\ln(H/H_o)$, while the prescribed strain is obtained from the prescribed strain rate at a particular time, $\dot{\epsilon}_b t$, see Figure 5. This problem in the motor displacement response prohibits the attainment of a constant strain rate without some modification of the experimental procedure. This deviation from constant strain rate is especially severe at higher strains and is due to the incorrect programming of the motor displacement based on the initial disk separation, $H_o$. Fortunately, this error can be resolved and a constant strain rate obtained by inputting a corrected sample height for the motor control according to the following relation:

$$H_{o,corr} = 0.9467 \, H_o. \tag{29}$$

This correction method allows a constant strain rate to be generated and is the same for all strain rates.

Constant strain rate experiments were performed for $0.01 \leq \dot{\epsilon}_b \leq 0.5\ s^{-1}$. A changing area technique similar to the one described by Frank[17] was used. The technique involves using a sample that has an initial diameter less than the disk diameter and taking into account the changing area of the sample on the disk surface when calculating the stress from the force measurements as the experiment progresses. Figure 6 shows the transient equibiaxial extensional viscosity

$$\eta_b(t,\dot{\epsilon}_b) = \frac{[\sigma_{rr} - \sigma_{zz}](t)}{\dot{\epsilon}_b} \tag{30}$$

measured for LDPE and PS using this technique.

## RESULTS AND DISCUSSION OF STEP STRAIN EXPERIMENTS

The strain and time dependent extensional relaxation modulus, Eq. (13), was determined from the transient stress relaxation data of Figure 4. The results appear in Figure 7 where only the data at a few strains are presented for clarity. The solid line in Figure 7 is the relaxation modulus of linear viscoelasticity, Eq. (15), as calculated from the relaxation spectrum of Table I. The data clearly show that, indeed, the extensional relaxation modulus is equal to the linear viscoelastic relaxation modulus as the equibiaxial strain approaches zero.

The lubrication is effective in removing the shear stress at the top and bottom surfaces of the polymer sample as evidenced by the shape of the relaxation modulus curves. This is argued with the following observations: The measured *extensional* relaxation moduli exhibit the same time dependence as their respective *shear* relaxation moduli obtained from shear step strain experiments and from linear viscoelastic experiments. One would not expect the same shapes for the shear and extensional relaxation modulus curves if the lubrication was poor in the squeezing experiment. Furthermore, the time dependent modulus differs significantly between the two samples, LDPE and PS. The data, up to moderate strains, indicate that a true material response was measured in the equibiaxial extensional step strain experiment
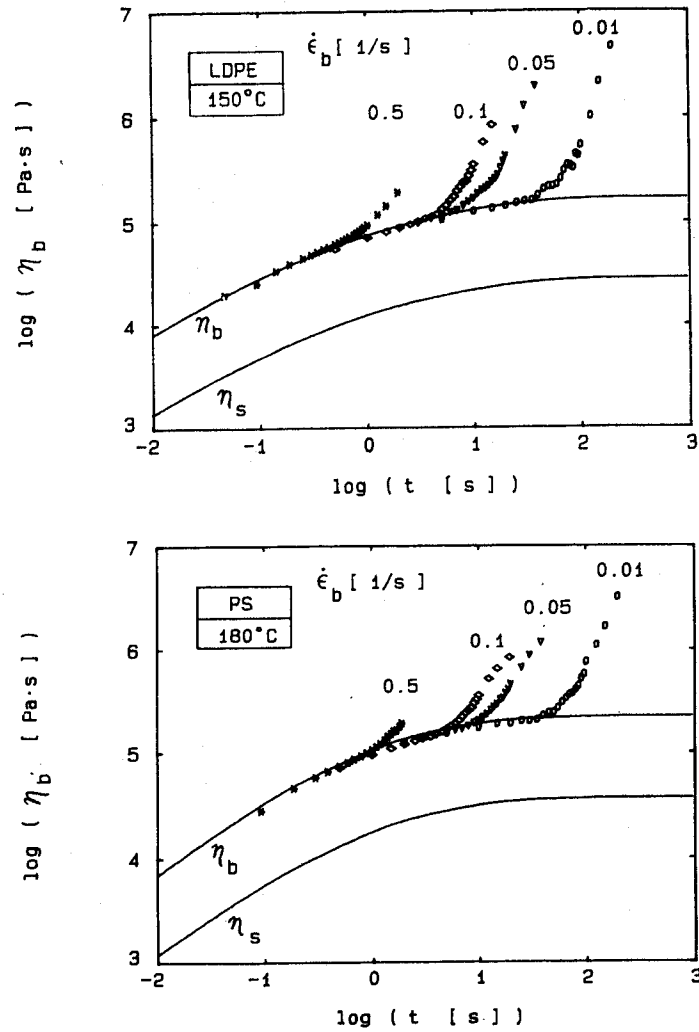
Fig. 6. Transient equibiaxial extensional viscosity measured with RDS-LA utilizing changing area lubricated squeezing technique. (a) LDPE, $T = 150°C$, (b) PS, $T = 180°C$. The linear viscoelastic limit for start-up in shear (lower solid line) and in extension (upper solid line) is calculated from data of Table I.
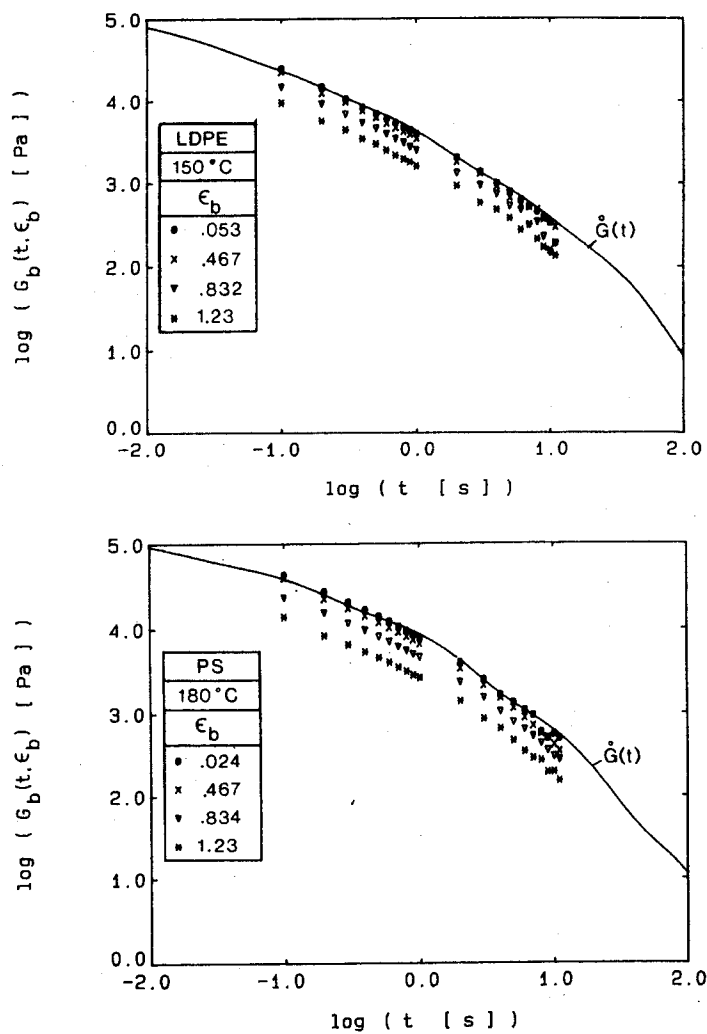
Fig. 7.   Transient extensional relaxation modulus at different equibiaxial extensional strains. The solid line is the transient linear viscoelastic relaxation modulus calculated from Eq. (15) using the constants of Table I. (a) LDPE, $T =$ 150°C, (b) PS, $T =$ 180°C.

and equibiaxial extension was indeed achieved through effective lubrication. However, some loss in effectiveness of lubrication was seen at high strains, $\epsilon_b > 1.6$ (very small final disk separations), where the shapes of the stress relaxation curves change significantly as seen in Figure 4. The curves exhibit unexpectedly high stress levels at short times along with several small dips in the curves at long times. These features are attributed to the loss of effective lubrication as the sample thickness is reduced below 4% of its initial value. The small dips are caused by small movements of the linear drive system, i.e., by small changes in the disk separation, $H(t)$.

The extensional modulus curves not only have the same shape but decrease as the strain increases. This suggests the separability of the extensional relaxation modulus into a product of two independent functions of time and strain, Eq. (16). The strain function, $h_e$, for equibiaxial extension has been obtained by shifting the modulus data of Figure 7 vertically upwards until they coincide with the linear viscoelastic modulus. The resultant values for the extensional strain function versus strain appear in Figure 8 and are seen to monotonically decrease as the equibiaxial strain increases. Due to the nonparallelism of the relaxation modulus curves at high strains, accurate values for the extensional strain function for equibiaxial extension could not be obtained beyond $\epsilon_b = 1.5$ or $\epsilon_a = -3$.

As already observed with the shear strain function $h_s$,[20] the extensional strain function decreases more rapidly for the polymer with linear macromolecules (PS) than for the polymer with branched macromolecules (LDPE) although the difference between the two is not as great as for the shear strain function.

A generalized strain function that describes both shear and extension, Eq. (18), was used to analyze the extensional strain function for equibiaxial extension. The prediction of the extensional strain function using the proposed generalized strain functions, Eqs. (22) and (23), along with the generalized strain invariant for equibiaxial extension, Eq. (20), and the parameters of Table II has also been plotted in Figure 8. Data from the shear step strain experiments predict an extensional strain function for equibiaxial extension between the curves $\alpha = 0$ and $\alpha = 1$. The measured extensional strain function for equibiaxial extension, $h_e(\epsilon_b)$, although lying slightly above, is described best by the
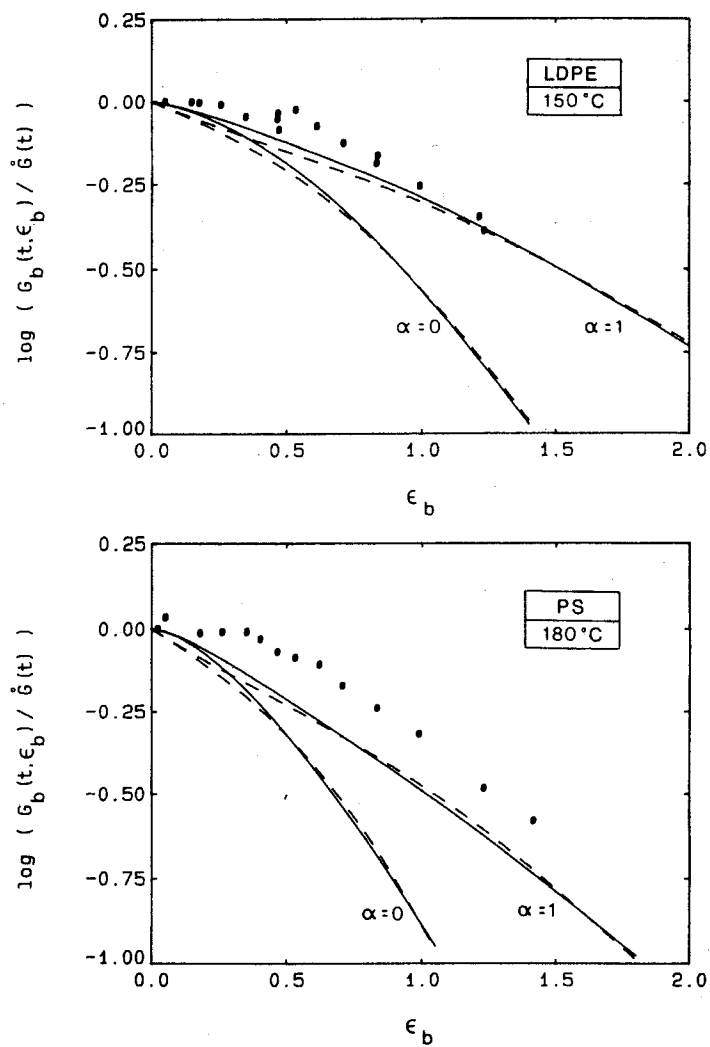
Fig. 8. Extensional strain function, $h_e$, in equibiaxial extension (axisymmetric compression). (———) from Eq. (22) and (-------) from Eq. (23) using constants of Table II.

curve with $\alpha = 1$. Just as with the shear strain function, the sigmoidal form of the extensional strain function, Eq. (22), approaches the small strain limit asymptotically. For intermediate strains, the sigmoidal form is therefore better than the form having a sum of two exponentials, Eq. (23).

The extensional strain function for uniaxial extension of a LDPE melt was found to be described best by $\alpha \approx 0$ for a generalized strain invariant given by Eq. (19), $h_e[I(\epsilon_a)]$.[28] Because of the relation between the strain invariants for axisymmetric extension and axisymmetric compression as discussed in Eqs. (9) and (10), the extensional strain function for equibiaxial extension, $h_e[I(-\epsilon_a)]$ with $\alpha = 1$ is identical to the extensional strain function for uniaxial extension, $h_e[I(\epsilon_a)]$, with $\alpha = 0$. This identity is easily seen when one plots the extensional strain function for equibiaxial extension in terms of the axisymmetric strain along with the extensional strain function for uniaxial extension as shown in Figure 9.

This leads to the conclusion that the strain function as given in Eqs. (22) or (23) can be used to describe both shear and uniaxial extension or it can be used to describe both shear and equibiaxial extension. However, the same strain function cannot describe all
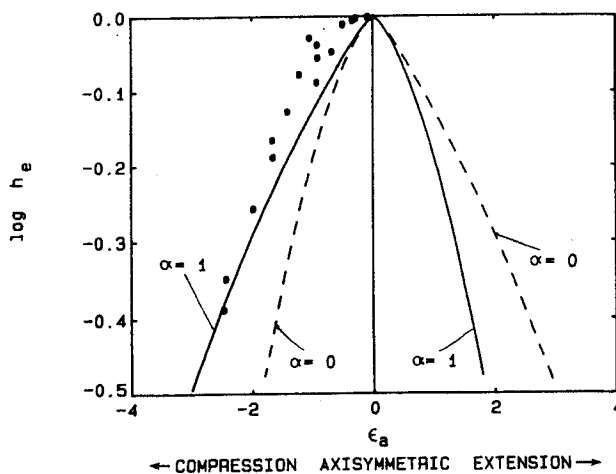


Fig. 9. Extensional strain function, $h_e$, in terms of an axisymmetric strain, $\epsilon_a$. The data points are for LDPE, $T = 150°C$. Lines are calculated from Eqs. (19) and (22) and the constants of Table II, with (————) $\alpha = 1$ and (--------) $\alpha = 0$.

three modes of deformation. Further investigations are needed for finding a suitable form of the strain function.

This same problem occurred to Wagner and Stephenson[29] during the elastic recoil after uniaxial extension. The kinematics of the recoil is that of equibiaxial extension. A best fit of the recoil data was found with $\alpha = 1$ while the uniaxial extensional data was described with $\alpha \approx 0$. They proposed to fit the data with a strain function

$$h_e[I(|\epsilon_a|)] \text{ with } \alpha = 0 \left\{ \begin{array}{ll} h_e[I(\epsilon_a)] & \text{with } \alpha = 0 \\ h_e[I(-\epsilon_a)] & \text{with } \alpha = 1 \end{array} \right. \quad (31)$$

making use of the symmetry between uniaxial extension and equibiaxial extension. No biaxial extension data was available for their LDPE sample.

## RESULTS AND DISCUSSION OF STRESS GROWTH EXPERIMENTS

The results of the stress growth during start-up of flow at constant equibiaxial extension rate, $\dot{\epsilon}_b$, were analyzed by applying a single integral constitutive equation based on the Lodge rubber-like-liquid equation[31,23,26]

$$\sigma(t) = -p(t)\mathbf{1} + \int_{-\infty}^{t} \mu(t - t')h(I)\mathbf{C}^{-1}(t',t)dt' \quad (32)$$

where $\sigma(t)$ is the stress tensor at the instant of observation, $p$ is an isotropic stress contribution, $\mu$ is the linear viscoelastic memory function, $h$ is the strain function, and $\mathbf{C}^{-1}$ is the relative Finger strain tensor between the states $t$ and $t'$. The memory function is chosen in discrete form

$$\mu(t - t') = \sum_{i=1}^{N} \frac{g_i}{\lambda_i} \exp\left(- \frac{t - t'}{\lambda_i}\right). \quad (33)$$

For equibiaxial extension at constant volume, the relative Finger strain tensor is given in Eq. (4). The start-up experiment with constant equibiaxial extension rate $\dot{\epsilon}_b$ is defined by

$$\epsilon_b(t',t) = \left\{ \begin{array}{ll} \dot{\epsilon}_b(t - t') = \dot{\epsilon}_b s & \text{for } s < t \\ \dot{\epsilon}_b t & \text{for } s \geqslant t \end{array} \right. \quad (34)$$

where $s = t - t'$. A normal stress difference can be determined from the memory integral constitutive equation, Eq. (32), and the kinematics of equibiaxial extension as prescribed with Eq. (34):

$$[\sigma_{22} - \sigma_{11}](t) = \int_0^t \mu(s)h[I(s)][e^{-4\dot{\epsilon}_b s} - e^{2\dot{\epsilon}_b s}]ds$$
$$+ \overset{o}{G}(t)h[I(t)][e^{-4\dot{\epsilon}_b t} - e^{2\dot{\epsilon}_b t}]. \qquad (35)$$

The transient equibiaxial extensional viscosity, Eq. (30), was then calculated by numerical integration of Eq. (35) for different extension rates and forms of the strain function.

The measured equibiaxial viscosity appears in Fig. 6 where the solid lines are the predictions of Eq. (32) in the linear viscoelastic limit using the material parameters of Table I. The lower solid line represents the transient shear viscosity $\eta_s(\dot{\gamma} = 0.0001 \text{ s}^{-1})$ and the upper solid line is $\eta_b(\dot{\epsilon}_b = 0.0001 \text{ s}^{-1})$. It can be shown from linear viscoelastic theory that the two transient viscosities are related by a factor of six, $\eta_b = 6\eta_s$. At low extensional strains and for all the measured extension rates, the measured equibiaxial viscosity becomes slightly less than the linear viscoelastic limit. At $\epsilon_b \approx 0.85$, the measured equibiaxial viscosity begins to rise above the linear viscoelastic limit and continues to rise to very high values at large strains. The strain at which this deviation occurs increases slightly as the extension rate increases. This rise in stress at large strain may be attributed to the loss of effective lubrication and is seen for several different polymer melts. Two other lubricants having shear viscosities a decade higher and lower than the Viscasil 300,000 and 600,000 were used and the measured equibiaxial viscosity at low strains was considerably higher than those reported in Figure 6, but approached the same measured viscosity at high strains indicating that, regardless of the lubricant, the effectiveness of the lubrication may be lost and the response at high strains is due to the extra force needed to shear the polymer sample.

This possible loss of effective lubrication in the constant rate experiment occurs at a slightly lower strain than in the step strain experiment. It seems that at these relatively low extension rates the lubricant has a chance to squeeze out at lower strains, whereas for the step strain experiment, the extension occurs so fast (very short rise times) that the lubricant does not have

enough time to be squeezed out and therefore the effectiveness of the lubrication remains until higher strains.

This rise in biaxial viscosity at large strains has also been seen by others who have not used the lubricated squeezing technique. Both Stephenson and Meissner[14] with the sheet stretching device and Rhi-Sausi and Dealy[10] with a sheet inflation biaxial rheometer, where lubrication effects are absent, report biaxial viscosities which increase at high strains. However, other experimental difficulties at high strains makes it difficult to analyze the data. Better methods of obtaining high strain data are needed.

Even though experimental data at large strains are difficult to obtain it is instructive to look at the predictions of the equibiaxial viscosity for the various forms of the strain function obtained from the step strain experiments. The predictions of the equibiaxial viscosity appear in Figure 10 for $\dot{\epsilon}_b = 0.1 \text{ s}^{-1}$. The three curves marked $L$, $S$, and $E$ correspond to the following choice of $h(I)$:

$L$—Lodge[31] rubberlike-liquid constitutive equation; $h(I) = 1$.
$S$—Sigmoidal form of strain function; $h(I)$ as given by Eqs. (22) and (20) with $\alpha = 1$.
$E$—Exponential form of strain function; $h(I)$ as given by Eqs. (23) and (20) with $\alpha = 1$.

The prediction of $\eta_b(t)$ from the Lodge rubberlike-liquid equation is seen to follow the linear viscoelastic limit at small strains then rise sharply at $\epsilon_b \approx 1$ and continue to rise to an infinite viscosity similar to the uniaxial extensional viscosity.[31] The prediction with the sigmoidal form of $h(I)$ is seen to follow the linear viscoelastic limit at small strains, level off to a viscosity below the linear viscoelastic limit at intermediate strains and then rise in a dramatic manner to an infinite viscosity at large strains. The form of $h(I)$ containing the sum of two exponential functions predicts an equibiaxial viscosity similar to the sigmoidal form up to intermediate strains as would be expected from Figure 8 where the functions are nearly identical up to $\epsilon_b = 2$. However, at $\epsilon_b > 4$ the exponential form of $h(I)$ predicts a constant value of $\eta_b$ that is less than the linear viscoelastic limit. This feature occurs because the exponential form of $h(I)$ decreases much more rapidly at large strains than the sigmoidal form and is able to cancel out the exponentially increasing part of Eq. (35) due to the equibiaxial
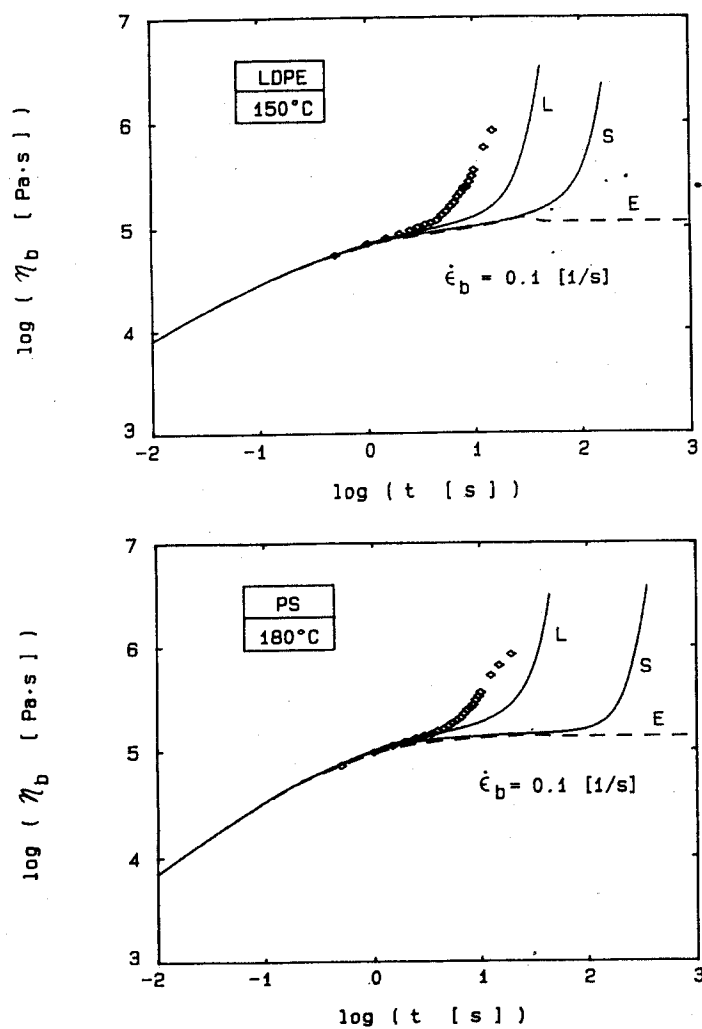
Fig. 10. Predictions of the transient equibiaxial extensional viscosity according to Eq. (36) for various forms of the strain function. $L - h(I) = 1$, $S - h(I)$ given by Eqs. (20) and (22) with $\alpha = 1$, $E - h(I)$ given by Eqs. (20) and (23) with $\alpha = 1$. (a) LDPE, $T = 150°C$, (b) PS, $T = 180°C$.

strain. The measured equibiaxial viscosity is described well by the memory integral constitutive equation up to intermediate strains.

## CONCLUSIONS

A step strain experiment using the lubricated squeezing technique has provided a means of directly measuring the extensional strain function of polymer melts in equibiaxial extension. The maximum strain with sufficient lubrication was found to be about $\epsilon_b = 1.6$. The novel extensional data support the separability of the extensional relaxation modulus into time and strain dependent functions. The transient equibiaxial viscosity measured at constant extension rates with the lubricated squeezing technique agrees well at low and intermediate strains with the predictions of a memory integral constitutive equation using the extensional strain function determined from the step strain experiments. Improved experimental methods are required to accurately determine the rheological behavior of polymer melts at high equibiaxial extensional strains.

## References

1. F. N. Cogswell, *Trans. Soc. Rheol.*, **16**, 383 (1972).
2. J. M. Dealy, *J. Non-Newtonian Fluid Mech.*, **4**, 9 (1978).
3. C. J. S. Petrie, *Elongational Flows*, Pitman, London, 1979.
4. C. D. Denson and R. J. Gallo, *Polym. Eng. Sci.*, **11**, 174 (1971).
5. D. D. Joye, G. W. Poehlein, and C. D. Denson, *Trans. Soc. Rheol.*, **16**, 421 (1972); *ibid.*, **17**, 287 (1973).
6. E. D. Baily, *Trans. Soc. Rheol.*, **18**, 635 (1974).
7. J. M. Maerker and W. R. Schowalter, *Rheol. Acta*, **13**, 627 (1974).
8. A. J. DeVries, C. Bonnebat, and J. Beautemps, *J. Polym. Sci. Polym. Symp.*, **58**, 109 (1977).
9. C. D. Denson and D. C. Hylton, *Polym. Eng. Sci.*, **20**, 535 (1980).
10. J. Rhi-Sausi and J. M. Dealy, *Polym. Eng. Sci.*, **21**, 227 (1981).
11. J. A. van Aken and H. Janeschitz-Kriegl, *Rheol. Acta*, **19**, 744 (1980).
12. J. A. van Aken and H. Janeschitz-Kriegl, *Rheol. Acta*, **20**, 419 (1981).
13. H. H. Winter, C. W. Macosko, and K. E. Bennett, *Rheol. Acta*, **18**, 323 (1979).

14. S. E. Stephenson and J. Meissner, *Proc. VIII Intl. Cong. Rheology,* Naples, p. 431 (1980).

15. J. Meissner, T. Raible, and S. E. Stephenson, *J. Rheol.,* **25,** 1 (1981).

16. S. Chatraei, C. W. Macosko, and H. H. Winter, *J. Rheol.,* **25,** 433 (1981).

17. A. J. P. Frank, Elongational Testing of Polymer Melts Using Uniaxial Extensional Flow and Lubricated Squeezing Flow Techniques, *Conf. Engineering Rheology,* London, 1983.

18. A. C. Papanastasiou, L. E. Scriven, and C. W. Macosko, *J. Rheol.,* **27,** 387 (1983).

19. R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids,* Vol. 1, John Wiley & Sons, New York, 1977.

20. P. R. Soskey and H. H. Winter, *J. Rheol.,* **28,** 625 (1984).

21. R. I. Tanner and G. Williams, *Trans. Soc. Rheol.,* **14,** 19 (1970).

22. H. C. Yen and L. V. McIntire, *Trans. Soc. Rheol.,* **18,** 495 (1974).

23. M. H. Wagner, *Rheol. Acta,* **15,** 136 (1976).

24. K. Osaki, *Proc. VIIIth Int. Congr. Rheology,* Gothenburg, p. 104, (1976).

25. H. Doi and S. F. Edwards, *J. Chem. Soc. Faraday II,* **74,** 1784 (1978); *ibid.,* **74,** 1818 (1978); *ibid.,* **75,** 38 (1979).

26. H. M. Laun, *Rheol. Acta,* **17,** 1 (1978).

27. Y.-H. Lin, *J. Rheol.,* **28,** 1 (1984).

28. M. H. Wagner, *J. Non-Newtonian Fluid Mech.,* **4,** 39 (1978).

29. M. H. Wagner and S. E. Stephenson, *J. Rheol.,* **23,** 489 (1979).

30. G. Tovstiga, M.S. Thesis, University of Massachusetts, 1983.

31. A. S. Lodge, *Elastic Liquids,* Academic Press, New York, 1964.