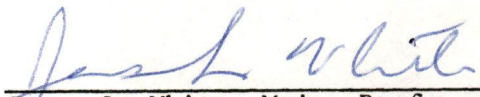
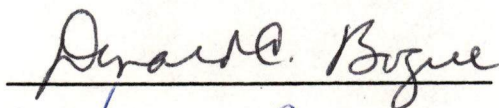


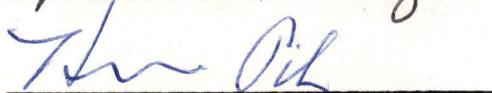
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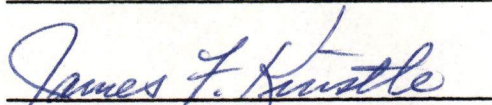
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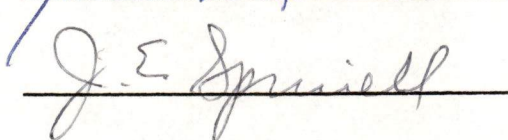

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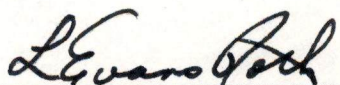

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INTERPRETATION OF THE RHEOLOGICAL PROPERTIES OF CARBON
BLACK REINFORCED POLYMER MELTS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Vincent M. Lobe

August 1980

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ABSTRACT

The rheological response of carbon black filled polymer systems were investigated using a broad range of experiments. Stress relaxation and dynamic experiments characterize the small strain behavior while steady state shear viscosity, normal stresses and elongational flow experiments describe the large strain response. Extrudate swell is also measured.

Highly filled systems exhibit yield values. This is seen in the dynamic experiments and in the shear and elongational viscosities. Viscosity does not level off at finite values with decreasing deformation rate but continues to increase approximately inversely proportional to the deformation rate. This corresponds to yield values of order 5×10^5 dynes/cm².

The storage modulus also does not tend to zero at low frequencies. The dynamic properties and stress relaxation results suggest high material memories for the highly filled systems. The extrudate swell values are small, however, and these systems exhibit very little delayed recovery.

The implications of these experimental results are interpreted in terms of a generalized "Schwedoff body," a single integral constitutive model with a yield value. The Von Mises yield criterion is used and alternative criteria are considered. Parameters of the model are evaluated and a unified constitutive model is found to describe the results observed from the diverse experiments. Extensions of the theory into transient phenomena are discussed.

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CHAPTER I

INTRODUCTION

Very few commercial polymer processing applications involve homogeneous polymers. Most polymer materials are compounded with reinforcing agents, colorants or fillers for various other purposes. The compounded material is then molded or shaped for a variety of end uses. The original reason for compounding carbon black in rubber materials was primarily to provide an inexpensive filler or extender in the costly natural rubber. This small particle filler was then found to have high reinforcing properties. The mechanical properties of tires are in good part due to carbon black reinforcement. Carbon black is also used in various plastics applications as a colorant.

While there have been extensive studies of the influence of carbon black on the mechanical behavior of reinforced rubber vulcanizates (83,84,131,167,169,188,190,192,193,219,220,221,222), there have been relatively few on the flow properties on unvulcanized elastomers and molten plastics. The importance of such rheological behavior to processing is widely recognized. While qualitative trends have been observed in certain types of rheological experiments, no comprehensive experimental studies in a wide range of geometries and deformation states has been carried out. No comprehensive 3-dimensional view of the rheological characteristics of filled systems has been developed. It is clear however that the nonlinear constitutive theories which

describe viscoelastic behavior cannot provide an adequate model of these filled systems.

In this dissertation, the rheological effects of fillers in polymer melt systems are studied, in particular the rheological effects of carbon black fillers in polybutadiene and polystyrene will be investigated in a wide range of experiments including shear and elongation, steady state and transients. Three-dimensional tensor constitutive equations for small and for large strains are developed for such systems and critically tested.

CHAPTER II

BACKGROUND

A. VISCOELASTIC CONSTITUTIVE THEORY

The response of a material to an applied stress varies from the ideal viscous fluid, in which the stress is proportional to the deformation rate, to the ideal elastic solid, in which the stress is proportional to the strain. Polymeric materials respond to strain in a manner which depends on a memory function, characteristic of the material, and on the extent and rate of the applied strain. The characteristic memory function relates stress to strain in such a way that the strains recently applied are more important than those applied in the distant past. When the stress is independent of the strain history, which is the case for a vanishingly small memory, the material is a viscous fluid. In the limit of a very large memory function the material stress depends on the sum of all of the previously applied strains, called the net strain, and the material behaves elastically.

Some materials show a change in stress response when repeat experiments are performed on the same sample. The amount of change in stress response decreases as the rest time between repeat tests increases. If this change diminishes the magnitude of the stress response the materials are called thixotropic.

Materials which demonstrate a response to an imposed strain which is between the viscous and elastic limits are called viscoelastic

materials. Combinations of these limiting ideals have been used to model the viscoelastic behavior in a one-dimensional framework (36). The Maxwell fluid (166), the Volgt solid (195), and the Jeffreys model (124) illustrate the simplest combinations. To properly model the material flow for large deformations in three dimensions (6,34,337) we must use time derivatives of stress that, at least, translate and rotate with the fluid motion instead of the simple time derivative of stress observed from a fixed coordinate system.

The simplest proper (rotational) time derivative, now called the Jaumann derivative, was first used by Zaremba (26,29,36,349) in 1903 to generalize the Maxwell model to a three-dimensional framework. This derivation with some modifications was essentially repeated by several researchers including Hencky (36), Fromm (29), Oldroyd (337), deWitt (70), and White and Metzner (328). The latter authors consider the time constants in the model to depend upon deformation rate. In an exposition on the mathematical theory of continuum mechanics, Noll (209) presents the principles of determinism, contiguous action and objectivity as basic invariance principles of mechanics from which constitutive equations may be formulated. He presents a very general constitutive equation which degenerates to a Maxwell model in small deformations.

Prior to Noll's work, Oldroyd (213) considered derivatives in which the coordinate system translates, rotates and deforms with the fluid motion. He also generalized a more complicated combination of ideal viscous and elastic elements (the Jeffreys model) to obtain a better description of the viscoelastic response (216). This model employed the complex convected (Oldroyd) derivative and the complex Jeffreys

model. Williams and Bird (338,339) simplified this model using a Jaumann derivative with the Jeffreys model.

The convected contravariant Maxwell model with a deformation rate dependent time constant provides the simplest model capable of qualitatively illustrating the important viscoelastic effects. It has been used to analyze simple flow situations by Metzner (7) in transient shear, White (121), and Denn (71) in the analysis of melt spinning and extensional flow.

The White-Metzner model has been generalized by Acierno et al. (1,2,3,4) to accommodate a spectrum of relaxation times and a time varying modulus and relaxation times. The time variation is introduced through a structure parameter which depends upon a stress measure. In simple shear then three simultaneous differential equations which are implicit in stress must be solved. As in the single element model this model predicts a zero second normal stress difference which is approximately true in many cases of polymer melt flow (140). This model has the attractive qualities of incorporating some of the important features of the viscoelastic flow but requires some approximation at the outset (Wiessenberg hypothesis) and leads to some rather involved computation.

Boltzmann (36,40) developed the most general (linear) theory of viscoelasticity for small strains based on the concept of an hereditary functional.

The result of the Boltzmann theory can be written in three-dimensional form as:

$$\underline{\underline{P}} = -p\underline{\underline{I}} + \int_{-\infty}^t 2\phi(t-s)\underline{\underline{\epsilon}}(s)ds \quad (\text{II-1})$$

where: $\underline{\underline{\epsilon}}$ is the infinitesimal strain tensor measured from the instantaneous (present) state of the material to the past time s . The function $\phi(t)$ which has generally been expressed as

$$\phi(t) = \int_{-\infty}^{+\infty} \frac{H(\tau)}{\tau} e^{-t/\tau} d\tau \quad (\text{II-2})$$

where $H(\tau)$ is a spectral distribution function of relaxation times τ . The function $\phi(t)$ can be expressed

$$\phi(t) = - \frac{dG(t)}{dt} \quad (\text{II-3})$$

where $G(t)$ is the relaxation modulus.

The Boltzmann linear theory for small deformations was generalized by Lodge (145,146,312) who used the convected coordinate framework of Oldroyd (to satisfy the "Principle of Material Indifference"). From the kinetic theory of (crosslinked) rubber elasticity we have

$$\underline{\underline{P}} = -p\underline{\underline{I}} + G\underline{\underline{C}}^{-1} \quad (\text{II-4})$$

where $\underline{\underline{C}}^{-1}$ is the Finger deformation tensor referred to the undeformed state and G is a modulus proportional to the crosslink density. The total stress tensor is denoted $\underline{\underline{P}}$ and $\underline{\underline{I}}$ represents a unit tensor.

Lodge uses mechanistic arguments to replace the permanent crosslink junctions with temporary "entanglement" junctions and obtains the relation

$$\underline{\underline{P}} = -p\underline{\underline{I}} + \int_{-\infty}^t \phi(t-s) \underline{\underline{C}}^{-1}(s) ds \quad (\text{II-5})$$

where $\underline{\underline{C}}^{-1}(s)$ is the finger strain tensor referred to the configuration at time t .

Here Lodge has used a suitable nonlinear deformation tensor but proper generalization also requires generalizing the hereditary functional to three dimensions for large deformations. This was first proposed by Green and Rivlin (98) and later developed by Coleman and Noll (48,209). The hereditary functional

$$\underline{\underline{P}} = -p\underline{\underline{I}} + F[\underline{\underline{e}}(z)]_{z=0}^{z=\infty} \quad (\text{II-6})$$

is written as a Frechet expansion of integrals

$$\begin{aligned} \underline{\underline{P}} = & -p\underline{\underline{I}} + \int_{-\infty}^t \phi(t-s) \underline{\underline{e}}(s) ds + \int_{-\infty}^t \int_{-\infty}^t \psi(t-s_1, t-s_2) \underline{\underline{e}}(s_1) \underline{\underline{e}}(s_2) ds_1 ds_2 \\ & + \int_{-\infty}^t \int_{-\infty}^t \beta(t-s_1, t-s_2) [t_r \underline{\underline{e}}(s_1)] \underline{\underline{e}}(s_2) ds_1 ds_2 + \dots \end{aligned} \quad (\text{II-7})$$

where $\phi(s)$, $\psi(s_1, s_2)$ and $\beta(s_1, s_2)$ are relaxation moduli and $\underline{\underline{e}}(s)$ is a suitable nonlinear strain tensor referred to the instantaneous state.

The strain tensor $\underline{e}(s)$ may be written as a Taylor expansion about the instantaneous value "t" using either the Cauchy type of strain tensor and obtaining the Rivlin-Erickson (245) acceleration tensors or using a Finger type of strain tensor to obtain another acceleration tensor (87,311).

It is important to note that there is no unique generalization of the linear (Boltzmann) theory to the nonlinear but this integral expansion is proper and is exact. It is exact only for an infinite number of terms in complex flows. An exact solution for a limited number of terms is only possible in viscometric shearing flows, elongational flows, and a "fourth order flow" (helical flow with an axial gradient). For very slow flows a limited number of terms may provide an adequate approximation to the exact solution.

The problem with the multiple integral expansion is its intractable complexity and computational difficulty (see also 91). With the hope that a truncated series of these integrals with some modification of memory function or strain measure would provide an adequate approximation of the stress a number of researchers have subsequently proposed constitutive models.

Based on experiments of multistep, large deformation, stress relaxation tests on bulk rubber, Zapas and Craft (347) have shown that the single integral is more appropriate than constitutive equations containing multiple integrals. They suggest a constitutive equation which can be written in the form

$$\underline{P} = -p\underline{I} + \int_{-\infty}^t \{ \mu_1 [(t-s), I_{C^{-1}}, II_{C^{-1}}] \underline{C}^{-1} - \mu_2 [(t-s), I_{C^{-1}}, II_{C^{-1}}] \underline{C} \} ds \quad (II-8)$$

This single integral form can be compared with the Lodge liquid in which $\mu_2=0$. Many of the researchers of the 1960s used this type of single integral model to represent stresses in large deformations of polymer fluids. A number of review articles discuss these models (26, 29, 34, 36, 57, 108, 180, 230, 263, 312). The idea of these models is to empirically devise some "memory function" (kernel of the integral) which is consistent with the principle of material indifference and can represent the response of the viscoelastic material to as many different types of applied strains as possible.

Bernstein, Kearsley, and Zapas (18, 21, 22, 23, 127, 346, 347, 348) represented the memory functions in their single integral theory by

$$\mu_1 = 2 \frac{\partial U}{\partial I_{C^{-1}}} \quad \mu_2 = 2 \frac{\partial U}{\partial II_{C^{-1}}} \quad (II-9)$$

The function U is an empirical relation which can be interpreted as the stored strain energy (Helmholtz free energy). Zapas and his co-workers (395) have proposed expressions for u in terms of the invariants $I_{C^{-1}}$ and $II_{C^{-1}}$. The authors also point out some of the nonisothermal implications of their theory (22). Their model is distinguished by the memory functions which depend on the extent of deformation or strain invariants.

Bird et al. (27,263) propose a model in which the memory functions μ_1 and μ_2 are functions of the second invariant of the rate of deformation tensor $\dot{II}_d$ (as opposed to the deformation invariants I_{-1}^C and II_{-1}^C in the BKZ model). This model was modified later by Bird and Carreau (27) and most recently by Carreau (48). The general case for this model is written

$$\mu_1 = (1 + \frac{\epsilon}{2}) \left(\sum_{p=1}^M \frac{\eta_p f_p(\dot{II}_d(s))}{\lambda_p^2} \exp \left\{ - \int_s^t \frac{ds'}{\lambda_p g_p(\dot{II}_d(s'))} \right\} \right) \quad (II-10)$$

$$\mu_2 = \frac{\frac{\epsilon}{2}}{(1 + \frac{\epsilon}{2})} \mu_1$$

A special case of this model defines the functions f_p and g_p

$$f_{p-1}(\dot{II}_d(s)) = \frac{1 + (\frac{1}{2}(2^\alpha t_1)^2 \dot{II}_d(s))^{S/2\alpha}}{[1 + \frac{1}{2} C^2 \dot{II}_d(s) \lambda^2]^{2R}} \quad (II-11)$$

$$g_{p-1}(\dot{II}_d(s)) = \frac{[1 + (\frac{C^2}{2}) \lambda^2 \dot{II}_d(s')]^R}{1 + (\frac{1}{2}(2^\alpha t_1)^2 \dot{II}_d(s'))^{S/2\alpha}}$$

Models of this type which have functions of the rate of deformation in the term multiplying the exponential term and in the exponential term are called rate-dependent viscoelastic models. Empirical variations of the rate-dependent model have been made (153,150,175) to improve the fit of the model predictions.

While rate-dependent models can fit the steady shear viscosity and normal stress data and dynamic oscillatory data very well (48,150) they require a large number of empirical constants to conform to the transient shear data. There exists a unique relation between the normal stress, shear stress, and memory function of a viscoelastic material which is verified by the experimental data (295). Using an unspecified memory function Van Es and Christensen show that these rate-dependent theories cannot conform to the requirements of the normal stress-shear stress relation for any (rate-dependent) memory function.

At the time the first model was proposed by Bird et al. (from which the Carreau model evolved) Bogue proposed a model which used the same nonlinear relaxation time function in both the exponential term and its coefficient. This model was later modified by Bogue and White (36) to the form

$$\mu_1(t-s, I) = \left(1 + \frac{\epsilon}{2}\right) \sum_{i=1}^n \frac{G_i}{\tau_{i\text{eff}}} e^{-\left(\frac{t-s}{\tau_{i\text{eff}}}\right)} \quad (\text{II-12})$$

$$\mu_2(t-s, I) = \frac{-\frac{\epsilon}{2}}{\left(1 + \frac{\epsilon}{2}\right)} \mu_1$$

where $\tau_{i\text{eff}}$ is some function of the motion invariants I such as II_d , I_C^{-1} , or II_C . Chen and Bogue (57) have demonstrated that one form of the effective relaxation time function using the time averaged second invariant of the rate of deformation tensor provides an adequate fit of flows exhibiting the development of normal stresses. The form is

$$\tau_{i\text{eff}} = \frac{\tau_i}{1 + b \langle II_d^{\frac{1}{2}} \rangle \tau_i} \quad (\text{II-13})$$

$$\langle II_d^{\frac{1}{2}} \rangle = \frac{1}{t} \int_0^z (II_d^{\frac{1}{2}}) dz$$

This model has been verified experimentally in shear flows (56,57, 89) and in extensional flows (58,119,122,276). The experiments show that an a priori prediction of transient normal stresses from shear stress data does not work as well (see 2) but with a single optimum fit parameter the model can conform reasonably precisely to the data (57). The Bogue-White is the most widely applied of all models to polymer melt systems. Generations of Tennessee students (Chen, Takaki, Ide) have shown its use for various polyethylene (low density and high density) and polystyrene melts. In the most recent work of Ide and White (123) its utility to elongational flow has been studied and it has been shown that the elongational flow behavior largely depends on the "b" parameter or Eq. (II-13).

Takahashi, Masuda, and Onogi (274,275) make comparisons of integral models according to the stress relaxation function. They claim that models using the second invariant of the deformation tensor are better able to fit more types of flow situations than those involving invariants of the strain tensor alone. They further point out (275) that none of the models involving rate of strain invariants (Bogue-White, Carreau, Macdonald, Meister, etc.) or those involving strain

invariants (BKZ) are able to fit the Christensen-Van Es test of constitutive equations. They find that only those involving stress invariants are capable of meeting the requirements of this test.

Marucci and Astarita (158) discuss theories involving rate of deformation (i.e., Carreau type) and time averaged rate of deformation (Bogue-White). They claim that any model using rate of deformation invariants and also the White-Metzner model violates some of the smoothness conditions by which the nonlinear models must approach the linear limits (as does the Second Order Fluid) for small strains.

Other models have been proposed which have not been included in these general reviews and critiques. Mainly for pedagogical reasons Bird et al. advocate a closer look at co-rotational models (29,91). This type of model removes some of the mystery of deforming coordinates by introducing an ambiguity into the element of rotation. It is not clear exactly what is rotating in a deforming polymer melt. While this offers a new point of view from which to examine constitutive theories, Bird indicates that it does not offer any improvements in the fit or predictions of the single integral constitutive equations.

Another different type of constitutive relation is that proposed by Phillips (229,230) in which a nonlinearity is introduced into the strain measure. An unspecified isotropic strain measure $I(\underline{C})$ or $I(\underline{C}^{-1})$ is used with a general fading memory function. This model requires a rather involved procedure in first determining the strain function and secondly specifying an appropriate memory function. The fit of experimental data and theory predictions do not appear to be a large improvement over present single integral constitutive equations.

It is clear that none of the published models can claim to best describe the behavior of all possible flows and that choice of the most appropriate model still depends, to a certain aspect, on the flow application.

We have seen that the stress of a viscoelastic material can be related to the imposed strain using an integral over the strain history. The memory function of the integral involves a modulus, which is a function of the relaxation spectrum, a relaxation time, which is a function of time and invariants of the motion, and an exponential decaying function which weights events in the recent past more heavily than those of the distant past. In the models proposed to date, the required complexity is related to the precision of the desired fit and the complexity of the imposed strain. The available models are phenomenological in nature and therefore they do not relate the molecular structures of the material to the response of the applied strain.

B. PLASTIC YIELDING CONSTITUTIVE THEORY

In 1923, Bingham (25) wrote that some materials, notably concentrated suspensions, exhibit an apparent yield stress in the shear stress-shear rate behavior. These materials behave as solids when the applied stress is less than the yield stress and flow as fluids with higher applied stresses. In contrast, polymer solutions appeared to flow as fluids under any applied shear stress, no matter how small. The apparent zero shear viscosity of the Bingham plastic

is infinite while that of the polymer solution is finite. The behavior of suspensions and of filled polymer systems varies from the limit of polymer solution-like behavior at low loadings to the Bingham plastic behavior (infinite zero shear viscosity) at high loadings. Carbon black filled polymers show this type of limiting behavior, that is, they indicate a yielding value at high loadings (300).

The yielding criteria must be expressed in a form which does not depend upon the particular coordinate reference selected for the material. In 1913, Von Mises (303,308) used such a coordinate invariant measure of the yielding stress of solid materials. The second invariant of the extra stress tensor is used. Ward (308) lists a number of alternate expressions of this second invariant. A preferred form is

$$II_p = 3(t_{r\sim}T^2) - (t_{r\sim}T)^2 = 6Y \quad (II-14)$$

The material yields when the contributions from the stress tensor exceed the value $6Y$. This particular form is appealing because the shearing stress yield criteria turns out to be three times the extensional yielding value.

The Bingham plastic model (25) was presented in a one-dimensional form. The model material was rigid below a yielding stress and deformed as a Newtonian fluid for stresses exceeding the yield value. Hohenemser and Prager (237) used the Von Mises yield criteria and the Newtonian fluid model to obtain a proper three-dimensional representation of the Bingham plastic.

One of the curious effects of rubber is the softening of the vulcanizate after a strain is applied (188). This softening, called the "Mullins' effect" approaches a limiting value after repeated strains. The effect occurs in both filled and unfilled vulcanizates, as well as in filled molten plastics, increasing with the extent of applied strain. Mullins attributes this effect to configurational changes in the molecular network. He attributes the increased effect seen in filled systems to the increase in apparent "strain amplification" due to the presence of the filler. The explanation applies to moderate and high deformations. At very small deformations the apparent softening is due to the breakdown of filler aggregates.

These time dependent effects are similar to the thixotropic properties of suspensions. Slibar and Pasley (257) propose a modification of the Bingham plastic model which represents this thixotropic behavior,

$$\left(\frac{\sqrt{II_p} - \underline{Y}}{\sqrt{II_p}} \right)^T = 2\eta d \quad \text{for } \sqrt{II_p} \geq \underline{Y} \quad (II-15)$$

$$\text{where } \underline{Y} = K_1 - \frac{\int_{-\infty}^t II_d e^{-\alpha(t-\xi)} d\xi}{\beta + \int_{-\infty}^t II_d e^{-\alpha(t-\xi)} d\xi} (K_1 - K_0)$$

$$\text{and } d = 0 \quad \text{for } \sqrt{II_p} < \underline{Y}$$

C. RHEOLOGICAL RESPONSE TO IMPOSED KINEMATICS

1. Simple Shear Flow

In simple shearing flows the imposed kinematics can be described by the relation:

$$\mathbf{v} = v(v_1(x_2), 0, 0) \quad (\text{II-16})$$

This type of deformation field arises in flow between parallel plates, flow between a rotating cone and fixed plate, and in flow between concentric cylinders in relative motion. The deformation rate in this deformation may be written

$$\tilde{\mathbf{d}} = \frac{1}{2} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) = \begin{vmatrix} 0 & \frac{dv_1}{dx_2} & 0 \\ \frac{dv_1}{dx_2} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} = \begin{vmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (\text{II-17})$$

The stresses which develop in a viscoelastic fluid are:

$$\tilde{\mathbf{P}} = -p\tilde{\mathbf{I}} + \begin{vmatrix} \beta_1 \dot{\gamma}^2 & \eta \dot{\gamma} & 0 \\ \eta \dot{\gamma} & \beta_2 \dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (\text{II-18})$$

The shearing stress, related to the shear rate through

$$P_{12} = \eta \dot{\gamma} \quad (\text{II-19})$$

The viscosity coefficient η is measured by the torque in rotational viscometric flows or by the force in the direction of flow in the parallel plate device. Unequal normal stresses arise in the direction and perpendicular to the direction of flow. The principal normal stress differences are

$$N_1 = P_{11} - P_{22} = \psi_1 \dot{\gamma}^2 = (\beta_1 - \beta_2) \dot{\gamma}^2 \quad (\text{II-20})$$

$$N_2 = P_{22} - P_{33} = \psi_2 \dot{\gamma}^2 = \beta_2 \dot{\gamma}^2$$

where ψ_1 and ψ_2 are the primary and second normal stress coefficients.

In the theory of nonlinear viscoelasticity the primary normal stress coefficient has been shown to be related to the viscosity coefficient in the slow flow asymptote by

$$\bar{\tau} = \frac{\sum G_i \tau_i^2}{\sum G_i \tau_i} = \frac{\psi_1}{2\eta} \quad (\text{II-21})$$

In higher shear rate flows for example using a Bogue-White constitutive model we have

$$\tau^* = \frac{\frac{\sum_{i=1}^n G_i \tau_{i\text{eff}}^2}{n}}{\frac{\sum_{i=1}^n G_i \tau_{i\text{eff}}}{n}} = \frac{\psi_1}{2\eta} \quad (\text{II-22})$$

While the values of η appear to have a finite limiting value in the case of polymer solutions and in melts this does not appear to be the case in filled systems (300). Filled polymer systems exhibit a yielding stress, a stress at which the apparent viscosity appears to increase indefinitely. This yield value in polymer systems may be an "apparent yield value" with another flow type of curve at very high viscosities (or low shear rates). This type of behavior is observed for polystyrene spheres suspended in a polystyrene-DEP solution (162).

2. Extensional Flow

In simple extensional flows the imposed kinematics can be described by the relation:

$$\underline{v} = \underline{v}(v_1(x_1), v_2(x_2), v_3(x_3)) \quad (\text{II-23})$$

The system is symmetric in the 2 and 3 directions and

$$v_2(x_2) = v_3(x_3) \quad (\text{II-24})$$

Since the individual velocities vary only with their own directions the deformation rate is given by

$$\underline{d} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) = \begin{vmatrix} \dot{E} & 0 & 0 \\ 0 & -\frac{\dot{E}}{2} & 0 \\ 0 & 0 & -\frac{\dot{E}}{2} \end{vmatrix} \quad (\text{II-25})$$

where $\dot{E} = \frac{\partial v_i}{\partial x_1}$ is the rate of elongation. The stresses which develop under this type of deformation can be expressed

$$\tilde{P} = -p\tilde{I} + \begin{vmatrix} T_{11} & 0 & 0 \\ 0 & T_{22} & 0 \\ 0 & 0 & T_{33} \end{vmatrix} \quad (\text{II-26})$$

The boundary conditions are

$$T_{11} = \frac{F}{\pi R^2} \quad T_{22} = T_{33} = 0 \quad (\text{II-27})$$

where F is the force applied in the axial direction, R is the radius of the deforming cylinder. Eliminating the pressure

$$\tilde{P} = \begin{vmatrix} T_{11} - T_{22} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (\text{II-28})$$

For a Newtonian fluid we have

$$P_{11} = + (T_{11} - T_{22}) = 3 E \quad (\text{II-29})$$

One can see that the extensional viscosity is then

$$\chi = \frac{P_{11}}{\dot{E}} = 3\eta \quad (\text{II-30})$$

This was first shown by Trouton (119,286) both theoretically and experimentally.

Nitschmann and Schrade (208) first suggested that extensional viscosity increases with increasing extension rate in 1948. Yamamoto was the first to develop an expression for the extensional viscosity in terms of a nonlinear viscoelastic fluid theory (342). Ide (119) compares the predictions of several viscoelastic constitutive theories. White (316) derives the steady state expression for the Bogue-White model:

$$\chi = \left(1 + \frac{\epsilon}{2}\right) \int \frac{3G_i \tau_{i\text{eff}}}{(1-2\tau_{i\text{eff}})(1+\tau_{i\text{eff}}\dot{E})} - \frac{\epsilon}{2} \int \frac{3G_i \tau_{i\text{eff}}}{(1+2\tau_{i\text{eff}}\dot{E})(1-\tau_{i\text{eff}}\dot{E})} \quad (\text{II-31})$$

for cases in which $\tau_{m\text{eff}}\dot{E} < \frac{1}{2}$.

D. REVIEW OF EXPERIMENTAL DATA OF FILLED SYSTEMS

1. Small Strain Experiments

The dynamic data of Matsumoto, Onogi et al. (162,163,214) on filled polymer solutions show the effect of increasing filler loading on the dynamic moduli G' and G'' . In general the filled systems have higher moduli and longer relaxation times. A large, rapid increase in moduli occur with increase in frequency between a low frequency plateau and a high frequency plateau for carbon black filled systems. A pronounced strain amplitude effect, similar to increasing frequency, is also observed in these systems. In contrast suspensions of polystyrene

spheres in polystyrene showed a lower strain amplitude effect and the change in modulus with frequency is much less than that observed with carbon black filled systems, i.e., the modulus-frequency curves are more flat. This change in response is due to the lower particle-particle and particle-polymer interaction.

Steady shear flow data (162) showed an apparent yielding behavior for the spheres in polystyrene. This behavior is characterized by a Newtonian response at high shear rates, a constant stress response in an intermediate region and a second Newtonian response at very low shear rates.

A relaxation spectrum was evaluated from G' at large (80%) and small (0.5%) strains. The large strain spectrum was divided into two parts: a large short relaxation time peak associated with the properties of the medium and a broad peak at long relaxation times associated with the particulate network. The short strain spectrum was independent of strain (.05, 1, and 2%). The long relaxation time peak of the large strain spectrum was very sensitive to strain but the short relaxation peak was insensitive to strain. We note here that the large strains have concomitant large stresses. The relaxation spectrum of filled systems consists of the wedge box distribution observed at lower relaxation times and a broad peak or extra box which increases in magnitude as the strain amplitude increases. The second plateau is claimed to originate from a three dimensional network structure formed by the suspending particles.

Vinogradov and his co-workers (300) have measured the shear relaxation modulus G for small stresses which is necessarily for small strains. He finds the shear relaxation modulus to be independent of stress level on both sides of the yield stress.

2. Large Strain Experiments

The most complete and careful study of filled polymer systems in shear is that of Vinogradov et al. (300) on carbon black filled polyisobutylene. Shear data were obtained in cone and plate, couette, parallel plate and capillary rheometers. The steady shear data show increasing viscosity with increasing loading of carbon black and definite yield values. The data of the several measurement geometries and the capillary data with different diameters is seen to superimpose indicating the absence of wall slippage effects. Yield values were also observed in the cone and plate and capillary data of Minagawa (182) on TiO_2 filled molten plastics by Chapman and Lee (55) for a talc filled polypropylene.

The yielding values observed by Vinogradov are not evident in the capillary viscosity data of White and Crowder (321) or in the work of Nakajima and Collins (198) because the experiments in these later works were carried out at higher shear rates (1 to 10 sec^{-1}).

The extrudate appearance in capillary experiments is affected by filler loading. The onset of "elastic turbulence" or "melt rupture" is retarded with the higher loadings of carbon black. Increasing the shear rate from about 1 sec^{-1} first appears dull then as a "fish scale"

then as a periodic screw-like distortion and finally as a grossly distorted extrudate (300,306).

Decreasing the shear rate (or corresponding shear stress) from 1 sec^{-1} Vinogradov also observed a transition from smooth extrudate to a pronouncedly rough surface. This is associated with the yielding stress limit being approached near the capillary wall. This phenomena was also observed by Huang (118).

The capillary experiments of White and Crowder also show the effect of carbon black surface area and structure which increase the viscosity. This effect is greater at low shear rates than at high shear rates.

The "extrudate shrinkage" or "die swell" of filled systems decreases with increasing filler loadings (65,182,198,321). The extrusion shrinkage decreases with increasing length to diameter ratio of the capillary but increases with increasing extrusion rate. Increasing carbon black surface area and structure decreases the extrusion shrinkage. The extrusion shrinkage increases with increasing material relaxation times. Nakajima and Collins (198) show the extrudate shrinkage (die swell) is very low for L/D ratios in the range of 5 to 40. Cotton (65) uses a Monsanto laser die swell detector for quickly and accurately measuring the extrudate diameters.

Normal stresses have been measured for TiO_2 filled systems (182) and for calcium carbonate (107). There have been no reports of normal stress data for carbon black filled systems. While White and Minagawa observed an increase in normal stress with increased filler loading

measured in a Weissenberg cone and plate rheometer, Han (108) observes a decrease in normal stress with increased filler loading in the Han slit rheometer.

3. Extensional Viscosity Measurements

Ballman (16) first reported experimental evaluations of extensional viscosities obtained at constant true strain rate in 1965. Goldberg, Bernstein and Lianis (92) in 1969 and Vinogradov (301) in 1970 used a similar technique which involved exponentially increasing the rate of separation of material clamps. Meissner (171), 1969, achieved this constant strain rate using two sets of rotational clamps which rotate at a constant velocity. Macosko and Lorntsen (152), 1972, and, independently, Ide (119) used a simpler wind-up device and force transducer to measure the same type of deformation. These rheometers and a later design by Ide (122) have been used to obtain extensional viscosity data for unfilled elastomers and polymer melts (81,92,119,120, 129,147,171,172,174,297,301,322,323).

The deformations of these rheometers are at a constant elongation rate. The transient response of the extensional viscosity increases to a level of approximately three times the shear viscosity for very low extension rates. At high deformation rates the stress or extensional viscosity increases apparently without limit and the sample breaks. When a steady state extensional viscosity is obtained, the viscosity is seen to increase with increasing deformation rate (in contrast to steady shear viscosity which decreases).

There have been very few studies of extensional viscosity of filled systems (51,204). The "tubeless syphon" of Nicodemo et al. was used to obtain data that showed an increase in elongational viscosity with increasing glass bead filler loading. The glass (cylinder) fiber data of Chan (51) from the Ide rheometer showed an increase in steady state extensional viscosity with increasing glass filler loading. Another interesting observation of Chan was that the unbounded extensional stress flow regime was not obtainable for the glass fiber systems. All samples at all extension rates showed the steady state plateau.

In the extension to break data of Nakajima and Collins (194) show a large random scatter when carbon black is compounded with the polymer and very uniform results in the unfilled polymers. They suggest that the incorporation of carbon black introduced a large number of sample defects which lead to random breakage of the extending filaments. The higher loading did lead to higher stresses to break and strain hardening in the tensile strain experiments.

CHAPTER III

EXPERIMENTAL METHODS

A. MATERIALS

The polymers used in this study are commercially available and important to various parts of the polymer industry. The polystyrene is a high molecular weight plastic. The polybutadiene (BR) is a soft, low modulus, elastomer. The characteristics of these polymers are tabulated in Table III-1.

These polymers were each compounded with various loadings of carbon black. The carbon black N 110, supplied by Phillips Petroleum, has a high surface area and high structure relative to those carbon blacks commonly used in the rubber industry. Its properties are tabulated in Table III-2.

B. SAMPLE PREPARATION

The carbon black and polystyrene were preblended in a 3/4" Brabender extruder using an extruder barrel temperature of 160°C. The extrudate was then further mixed on a 3" Farrel roll mill. The relative roll speed was 14:10 and roll temperatures were 160°C. The ASTM milling procedure ASTM D3182 was followed as closely as possible. Nip spacings of 60, 40, and 30 mils were used as suggested in the procedure. A total mil time of one hour was used to insure complete mixing and a good dispersion.

TABLE III-1
POLYMER PROPERTIES

Item/Polymer	Polystyrene	Polybutadiene
Molecular Weight		
M_w	214,000 (54)	398,000 (130)
M_n	83,400 (54)	118,500 (130)
Molecular Dispersity		
MWD	2.57	3.36
Polymerization Method	Free Radical	Titanium Based Ziegler Catalyst
Density @ 20C		
ρ (gm/cm ³)	1.0525	
Thermal Expansivity		
β	5.55×10^{-4}	

TABLE III-2
CARBON BLACK N110 PROPERTIES

Carbon Black	Phillips N110	Reference
Surface Area	140 m ² /gm (130-160) (140)	CTAB-SA (134) (248)
DBP Absorption	cc/100 gm (109) (110-119)	24M4-DBP (134) (298)
Density	1.95 gm/cc	(248)
Mean Particle Diameter	190 Å	(248)

Samples were then compression molded into 10 cm × 10 cm × .3 cm sheets under a pressure of 10^8 dyne/cm² or extruded at 170°C into filaments of about .4 cm diameter. The filaments were annealed at 170°C for 10 minutes in hot silicone oil before further testing.

Similar procedures were used in compounding the carbon black with the BR elastomer. The elastomers and carbon black were compounded directly on the roll mill which was preheated to 50°C. The ASTM milling and sheet forming procedures were again followed as closely as possible.

The extrusion and compression mold temperatures for the elastomeric samples was 100°C.

C. SMALL STRAIN EXPERIMENTS

1. Stress Relaxation Experiments

A small step strain is imposed using a constant elongation rate rheometer (119). The samples were thermally equilibrated in silicone oil at 170°C before deformation. The samples were then stretched at constant elongation rates, between a roll rotating at linear velocity V and a clamp. This deformation was continued at a high rate until extension λ of 1.2 to 1.5 were obtained and the stresses were then allowed to relax.

The relaxing force is monitored as a function of time using a standard Instron load cell and recording chart. The relaxation modulus $E(t)$ was determined from

$$E(t) = \frac{P_{11}}{e_{11} - e_{22}} = \frac{F(t) \lambda}{A_0(e_{11} - e_{22})} \quad (\text{III-1})$$

where $F(t)$ is the force, A_0 the original cross sectional area, λ the extension ratio (A_0/λ is the deformed area) p_{11} is the tensile stress and $e_{11} - e_{22}$ is the nonlinear tensile strain. We have used the Finger deformation measure (284)

$$e_{11} - e_{22} = \lambda^2 - \frac{1}{\lambda} \quad (\text{III-2})$$

In a constant elongation rate experiment

$$\frac{dL}{dt} = \dot{E} L \quad \lambda = \frac{L(t)}{L(o)} = e^{\dot{E}t} \quad (\text{III-3})$$

where $\dot{E}$ is v/L and v is the linear velocity of the roll.

A second method of determining the extensional stress relaxation modulus, used for elastomeric materials, is the simple extension experiment. A strip specimen of rubber is suddenly extended a small amount ($\lambda \approx 1.2$ to 1.5) and the relaxing forces are monitored as a function of time. In this experiment the stretch ratio is simply

$$\lambda = \frac{L(t)}{L(o)} \quad (\text{III-4})$$

These stress relaxation experiments for the elastomeric materials were conducted at 25° and 100°C .

The stress relaxation experiment was also done using a parallel plate shear testing device (89). In this "sandwich shear device" the relaxation modulus is determined in shear flow. The sample is rapidly

sheared a small amount (20-50% strain) and the relaxing force is monitored as a function of time. While this experiment is suitable for elastomeric samples at moderate temperatures it is not suitable for the shear relaxation of melts at temperatures greatly exceeding the glass transition temperature T_g . The modulus, for small strains, is given by

$$G(t) = \frac{P_{12}}{e_{12}} = \frac{F(t)}{A_0 e_{12}} \quad (\text{III-5})$$

Here e_{12} is the shearing strain $\dot{\gamma}t$. This experiment, used for the elastomer materials, was done at 25° and 100°C.

2. Dynamic Experiments

The orthogonal rheometer or eccentric rotating disk experiment (103,165,305,336) was used to determine the dynamic moduli of the materials. The Mechanical Spectrometer (153) was used for this experiment. The measurement temperature was maintained at 170°C for the polystyrene melts and at 100°C for the elastomers.

In this type of flow the material is contained between two parallel plates. The upper plate is axially displaced a small distance with respect to the lower plate. The upper plate is driven at a constant rotational frequency and the lower plate turns freely at that frequency. The forces F_y in the direction of the axial displacement and F_x in a direction orthogonal to the plane of axial displacement are measured.

The measured forces and geometry of the configuration give the dynamic moduli directly.

$$\eta' = \frac{F_x h}{\omega \pi R_a^2} = \frac{P_{xy}}{\omega \gamma} \quad (\text{III-6})$$

$$G' = \frac{F_y h}{\pi R_a^2} = \frac{P_{yz}}{\gamma} \quad (\text{III-7})$$

The frequency ω is given by

$$\omega = \frac{\Omega}{2\pi} \quad (\text{III-8})$$

D. LARGE STRAIN EXPERIMENTS

1. Capillary Measurements

Measurements of viscosity, extrudate swell and end pressure losses were made in an Instron capillary rheometer. Three dies of length-diameter ratio L/D of 9.5, 18.2 and 27.8 with diameter D of 0.053 inches were used.

The total pressure required to extrude a polymer fluid is the sum of a capillary die pressure loss plus entrance and exit losses. This is

$$P_t = \Delta P_{\text{die}} + \Delta P_{\text{entrance}} + \Delta P_{\text{exit}} = \Delta P_{\text{die}} + \Delta P_{\text{ends}} \quad (\text{III-9})$$

By a force balance ΔP_{die} may be related to the shear stress at the wall of the die $(P_{12})_w$ and ΔP_{ends} . This leads to

$$P_t = 4(P_{12})_w L/D + \Delta P_{\text{ends}} \quad (\text{III-10})$$

Equation III-10 suggests the "Bagley plot" (13) where (P_t) is plotted versus L/D and $(P_{12})_w$ determined from the slope. ΔP_{ends} is then the intercept.

The shear rate at the die wall $\dot{\gamma}_w$ was obtained using the Weissenberg's equation (80,180,187)

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'} \right) \frac{32Q}{\pi D^3} \quad (\text{III-11})$$

where Q is the volumetric extrusion rate and n' is

$$n' = \frac{d \log (P_{12})_w}{d \log \left(\frac{32Q}{\pi D^3} \right)} \quad (\text{III-12})$$

The parameter n' is determined from the slope of the doubly logarithmic plot of wall shear stress $(P_{12})_w$ against the flow parameter $\left(\frac{32Q}{\pi D^3} \right)$.

The extrudate swell measurements were obtained on the solidified extrudates. This was represented in terms of

$$B = \frac{d}{D} \quad (\text{III-13})$$

where d is the extrudate diameter. The extrudates were annealed in hot silicone oil at 170°C and the value of B again determined.

The temperature of the reservoir and die for all capillary experiments was maintained at 170°C for polystyrene samples and 100°C for the elastomers.

2. Cone and Plate Measurements

Measurements of steady state and transient shear stresses and steady state normal stresses were obtained in a cone-plate geometry in both a Weissenberg Rheogoniometer and a Mechanical Spectrometer for the polystyrene compounds. Various cone angles (5.73 and 4.0 degrees) and diameters (2.5 and 5.0 cm) were used. For cone angle α and radius R the shear rate is given by (189)

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad (\text{III-14})$$

where Ω is the rotation rate of the moving member. The shear stress σ_{12} is determined from the torque M by (80, 189)

$$P_{12} = \frac{3M}{2\pi R^3} \quad (\text{III-15})$$

and the normal stress from the measured normal force F using

$$P_{11} - P_{22} = \frac{2F}{\pi R^2} \quad (\text{III-16})$$

The data are taken in both clockwise and counterclockwise rotation directions and the results are averaged. Generally measurements of this type are limited to low shear rates as melt instabilities arise leading to "ball up" and material exit at the gap. This occurs at values of $\dot{\gamma}$ of order 5 sec^{-1} . The normal stress measurements at high loadings are not reproducibly measurable except at the lowest shear rates ($\dot{\gamma} < 0.10 \text{ sec}^{-1}$). The transient shear stresses, also subject to the

high shear rate instabilities, are measured by observing the change in torque with time after sudden imposition of a constant speed rotation. The temperature of these experiments is 170°C.

3. Sandwich Shear Device: Transient Shear Experiment

In addition to the shear relaxation experiment, the sandwich shear device is also used in the determination of the transient stress response to the onset of a steady shearing deformation for elastomeric samples (1,89,94,181). The device consists of a flat plate, which is attached to the fixed jaws of the Instron tensile tester and two outer plates which are attached to the jaws of the moving cross head and load cell of the tensile tester (Figure III-1). The outer plates symmetrically sandwich in two identical slabs of sample material on either side of the stationary flat plate. All plate surfaces are serrated to preclude slip at the surface.

The stress is given by

$$P_{12}(t) = \frac{F(t)}{2A} \quad ; \quad \dot{\gamma}(t) = \frac{P_{12}(t)}{(v/h)} \quad (\text{III-17})$$

where h is the thickness of a single sample slab. The shear rate is

$$\dot{\gamma} = \frac{v}{h} . \quad (\text{III-18})$$

4. Constant Extension Rate Rheometer

The constant extension rate rheometer apparatus and procedure are described in detail by Ide (119,122). This apparatus was also used in

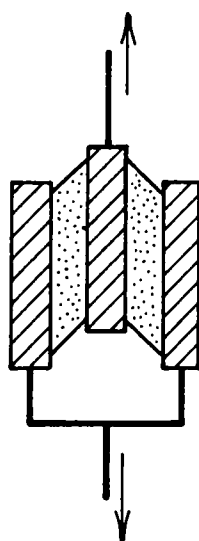


Figure III-1. Sandwich shear testing device.

the stress relaxation experiment. The apparatus illustrated in Figure III-2 consists of a horizontally positioned load cell and constant velocity take up spool. A silicone oil bath maintains constant temperature and supports the deforming rod. A set of three continuously variable synchronous drive motors provide constant extension rates from .01 to 10 sec⁻¹.

The sample, an extruded and thermally equilibrated filament, is clamped on one end to a fixed stationary clamp and taken up on roll at a linear velocity V at the other end of the bath. The constant elongation rate is given by

$$\dot{E} = \frac{V}{L} \quad (\text{III-19})$$

where L is the filament length being stretched (distance between clamp and roll). The tensile stress is given by

$$P_{11}(\dot{E}, t) = \frac{F(t)}{(A_0/\lambda)} = \frac{F(t)}{A_0} e^{\dot{E}t} \quad (\text{III-20})$$

The elongational viscosity is

$$\chi(\dot{E}, t) = \frac{F(t) \lambda}{A_0(V/L_0)} = \frac{P_{11}(t)}{\dot{E}} \quad (\text{III-21})$$

The take up spool provides continuous gripping and no slip especially in the case of polymer melts. The melted polymer rapidly cools when withdrawn from the hot oil by the spool. The cooled filament freezes and no slip is possible.

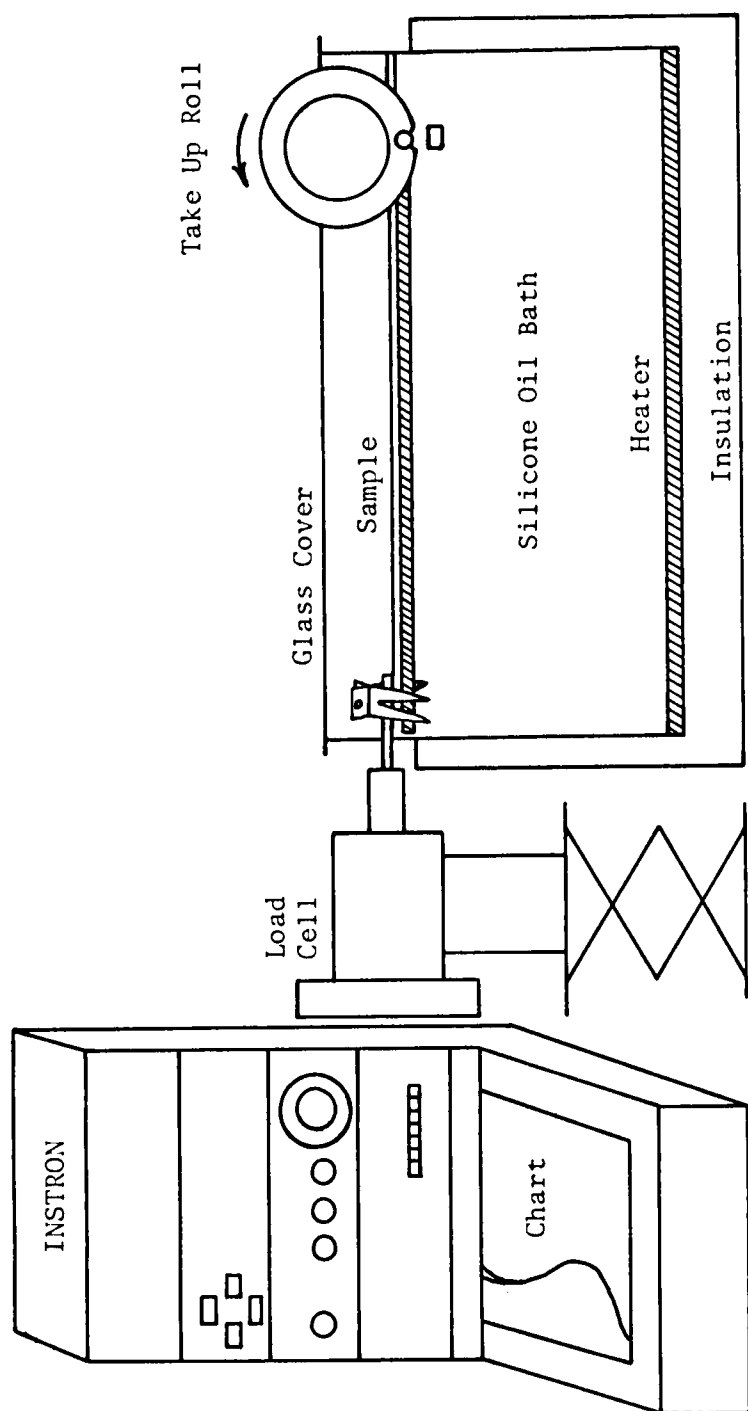


Figure III-2. Schematic diagram of the experimental apparatus.

The clamp at the load cell end must apply sufficient force to hold the sample without slipping yet not enough to deform or damage the sample. One system used involved taping the end of the sample with masking tape, inserting the taped end into a spring steel clip and attaching the clip to the alligator clamp. If the clamp is not operating properly the filament will break at the clamp. With proper operation of the clamping system the filament is observed to draw out continuously to an ever decreasing thread-like diameter or to break at random along the length depending on sample composition and deformation rates.

The polystyrene samples were measured at 170°C and the elastomer samples at 100°C.

CHAPTER IV

EXPERIMENTAL RESULTS

A. DYNAMIC EXPERIMENTS

Classical dynamic experiments were carried out using an eccentric rotating disk apparatus. The dynamic experiments were carried out at small (5%) strains at 170°C for the polystyrene systems and at 2% and 100°C for the polybutadiene systems.

While we cannot be certain of the linearity of the highly filled results we present the experimental data in terms of a modulus (defined as the dynamic stress divided by the strain) for purposes of comparison. In general the dynamic moduli (Figures IV-1 through IV-6) increase in magnitude from low frequencies to high frequencies with the loss modulus $G''(\omega)$ being greater than the storage modulus $G'(\omega)$ at the low frequencies and the storage modulus $G'(\omega)$ larger at higher frequencies. The modulus-frequency curves near a frequency of one reciprocal second.

For the polystyrene systems the low concentrations of carbon black filler (0, 5, 10%) exhibit ever diminishing moduli with decreasing frequencies while the higher concentration curves (20, 25%) show a low frequency plateau region. The low frequency plateau region was not evident in the range of loadings (0, 2.3, 12%) used in the polybutadiene systems. In the highly filled polystyrene systems the low frequency dynamic viscosity $\eta'(\omega)$ appears ever increasing with decreasing frequency with slope of -1. This corresponds to the low frequency plateau in loss modulus $G''(\omega)$. The dynamic viscosity of the

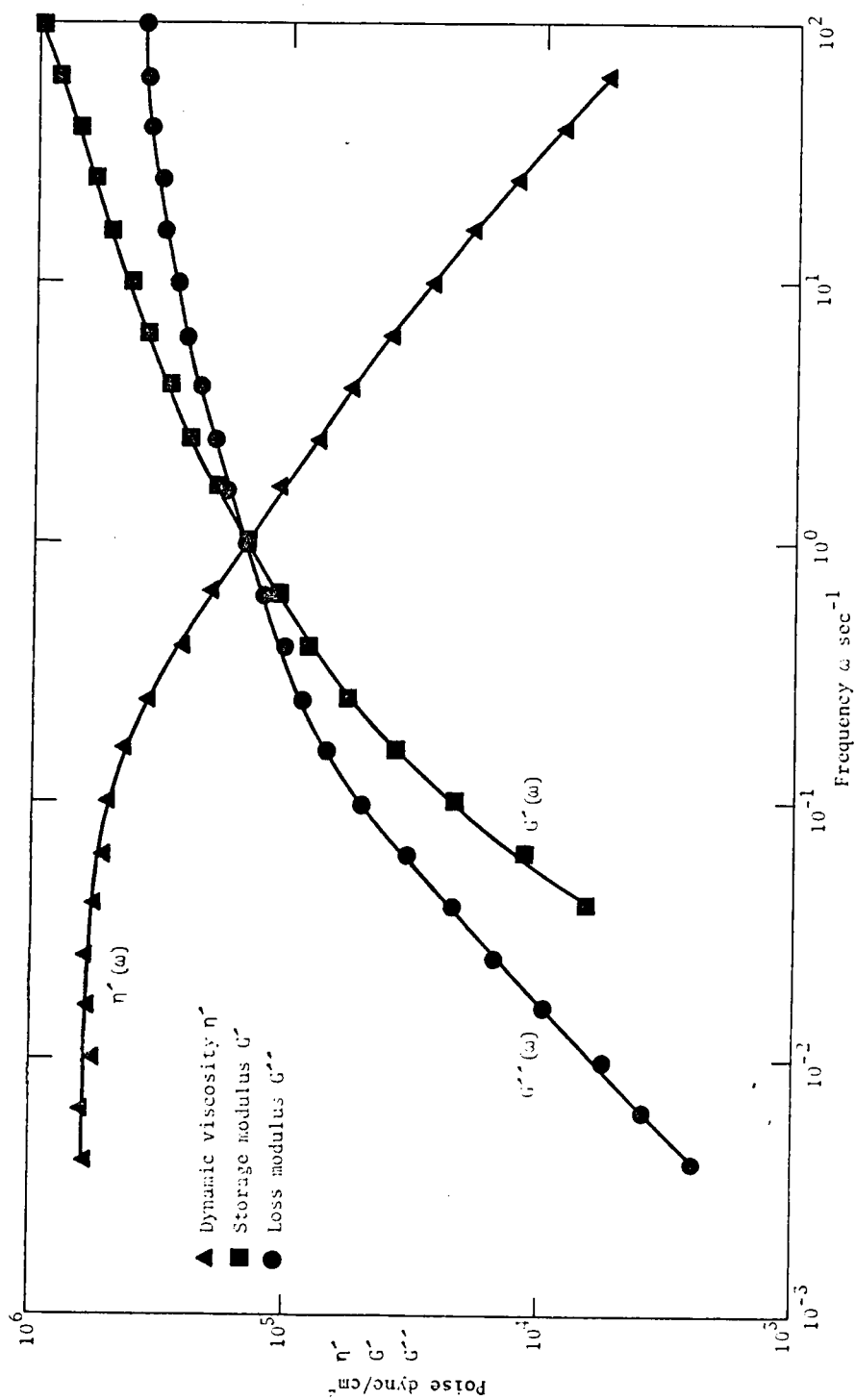


Figure IV-1. Dynamic viscosity and moduli of polystyrene 678u at 170°C.

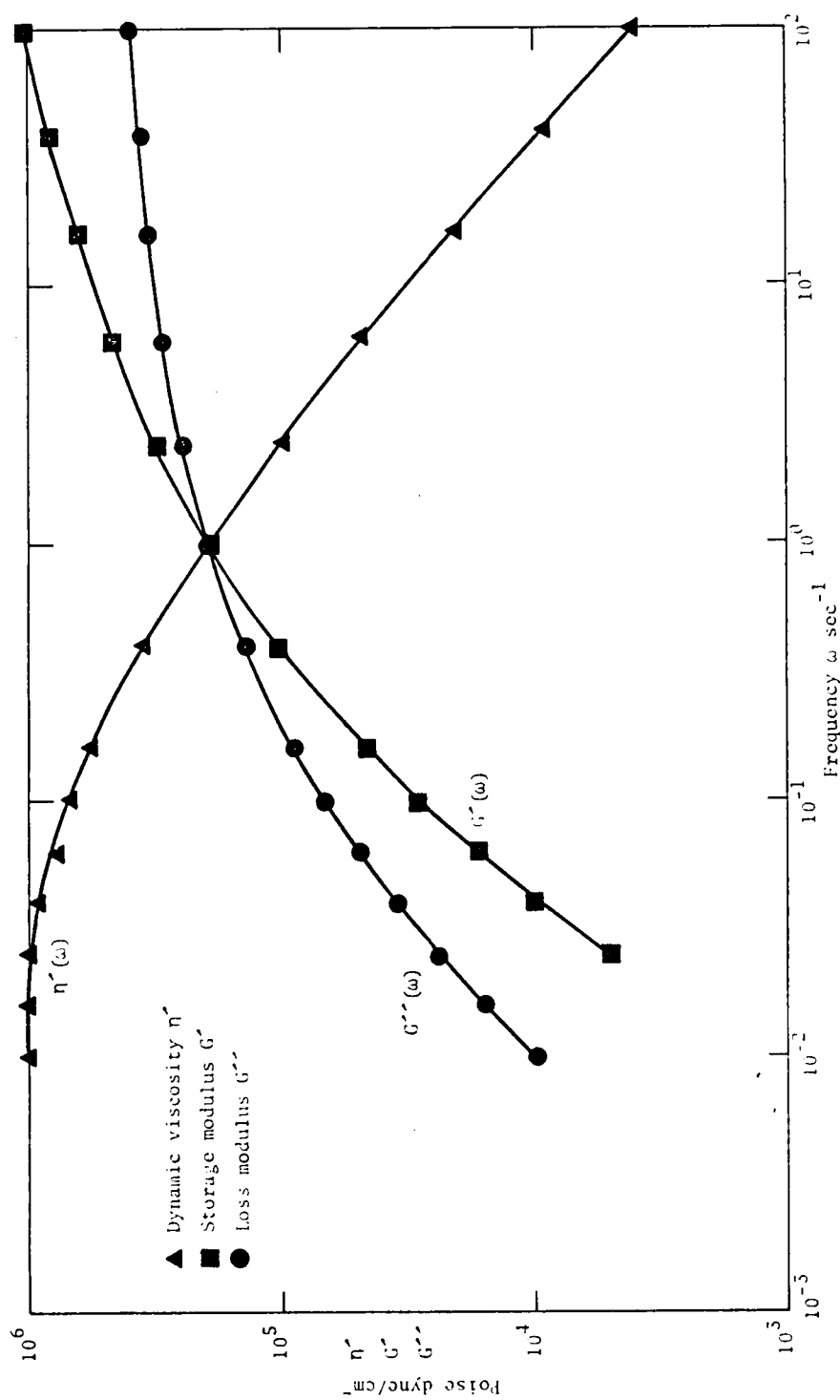


Figure IV-2. Dynamic viscosity and moduli of 5% NI10/PS678u at 170°C.

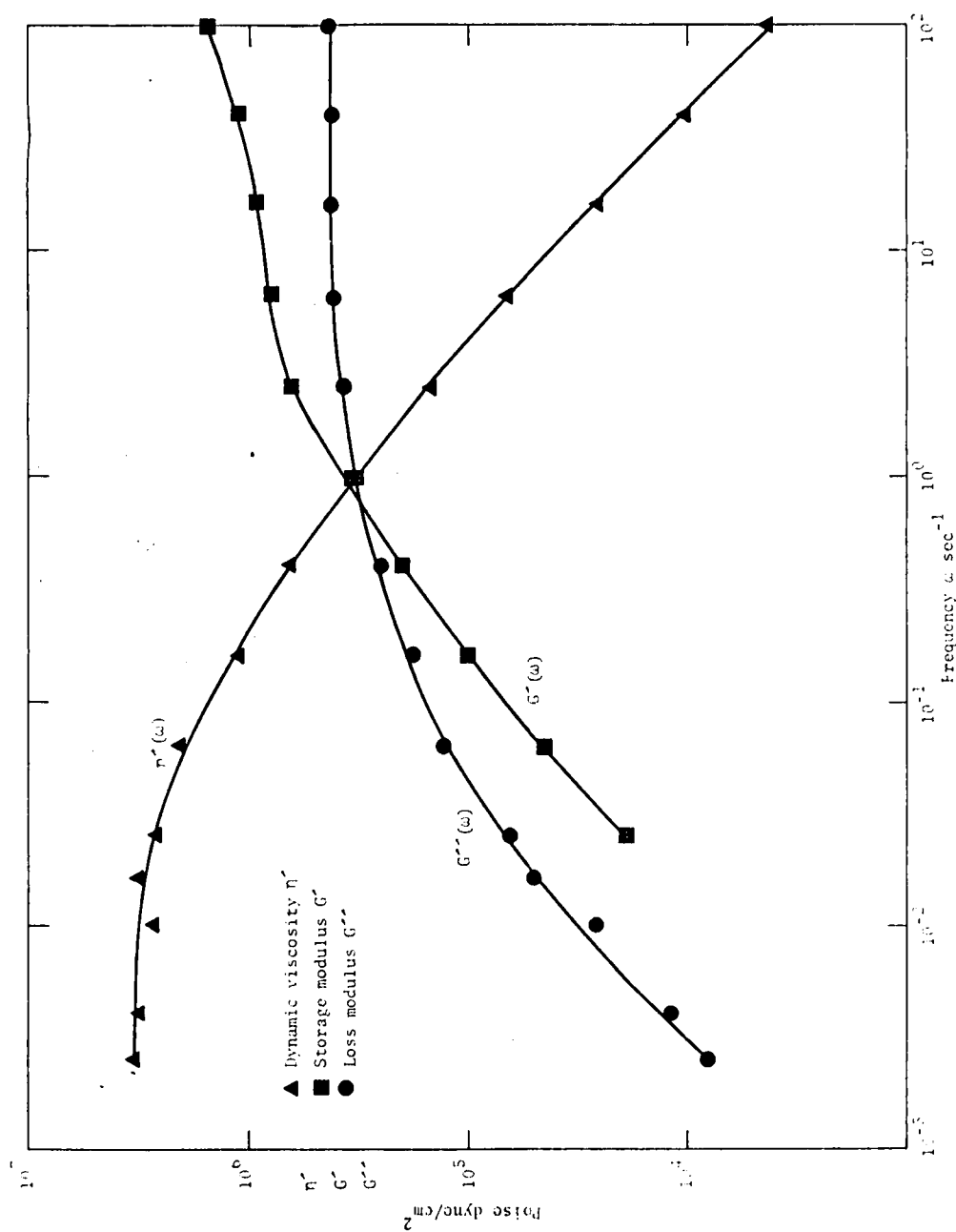


Figure IV-3. Dynamic viscosity and moduli of 10% NI10/PS678u at 170°C.

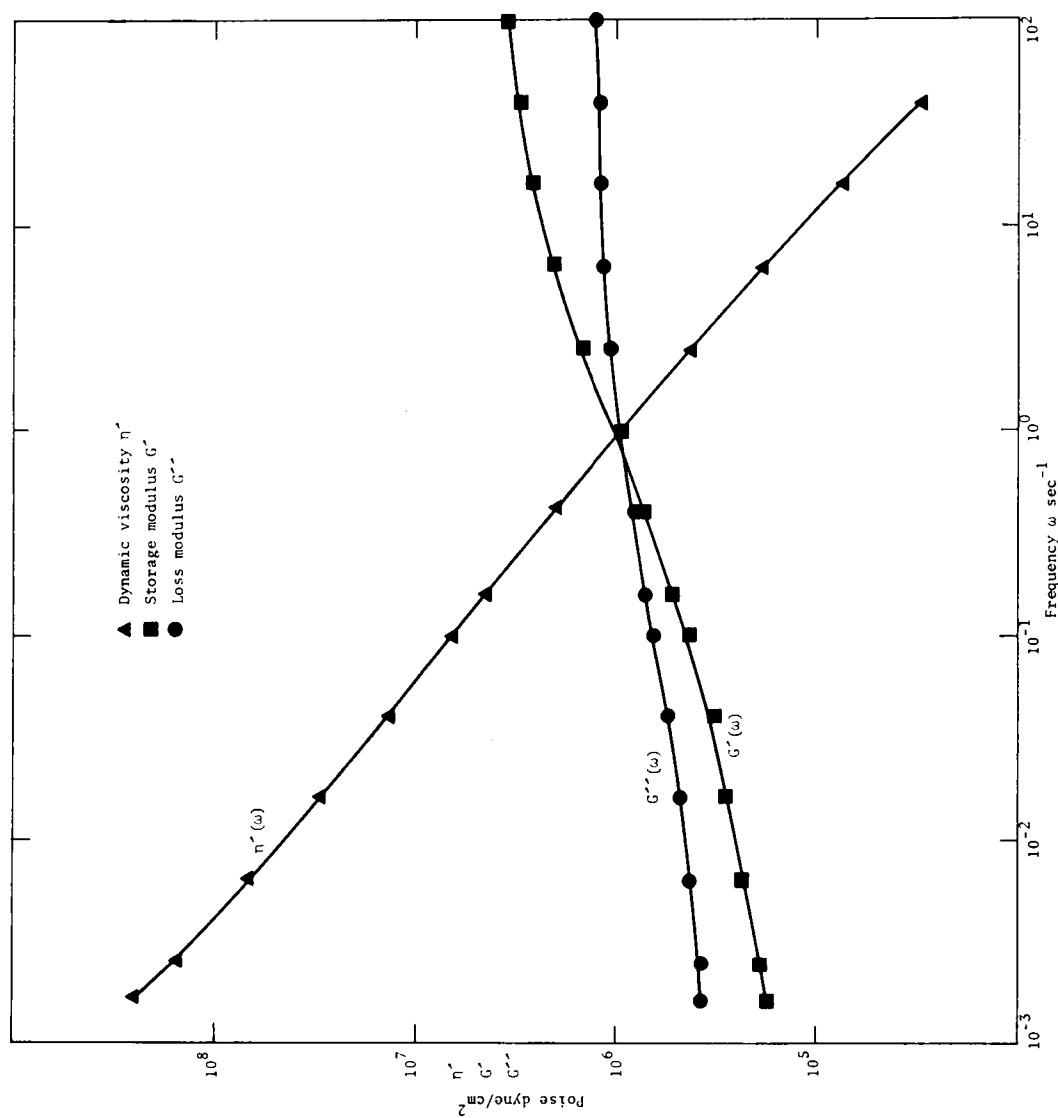


Figure IV-4. Dynamic viscosity and moduli of 20% N110/PS678u at 170°C.

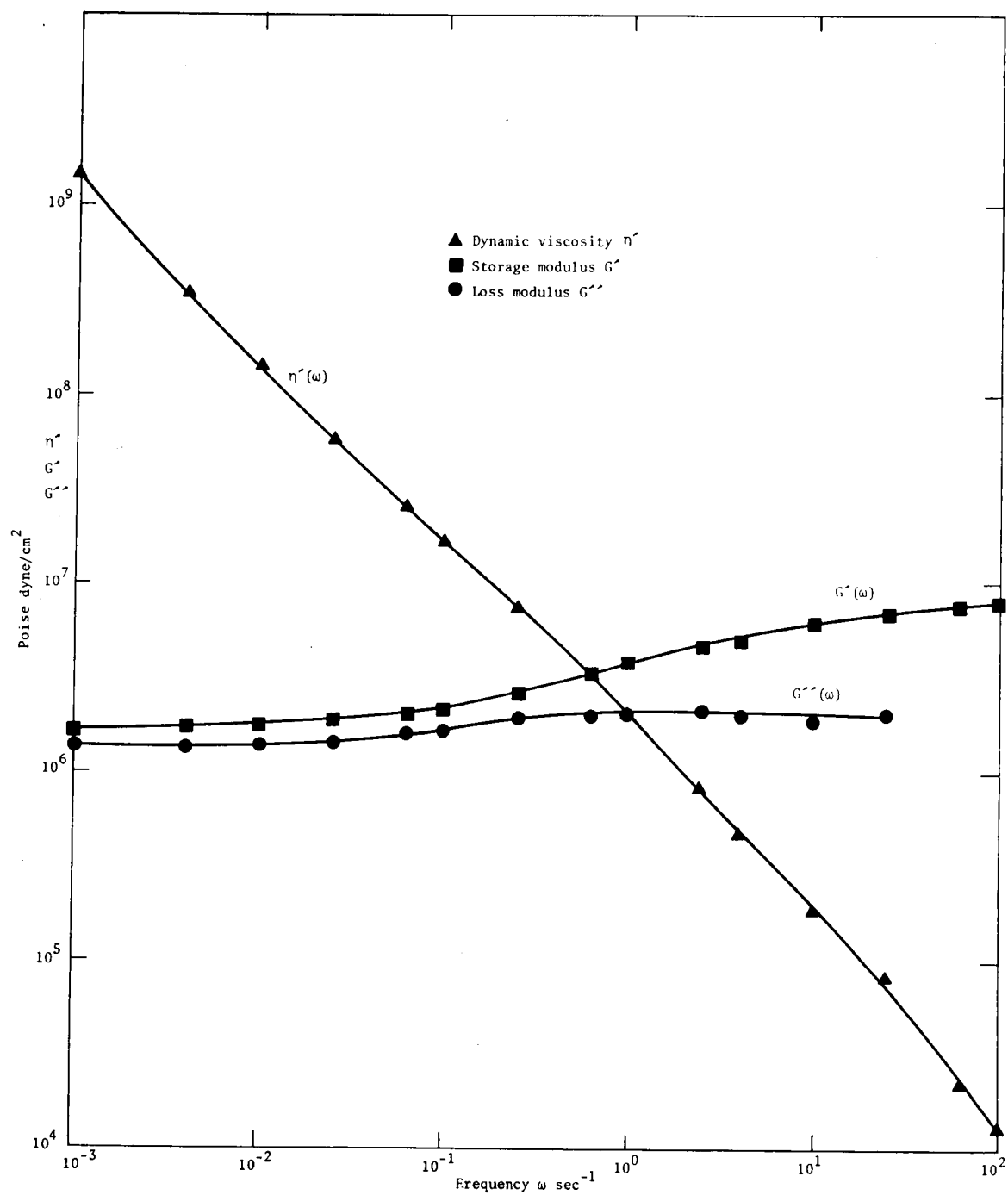


Figure IV-5. Dynamic viscosity and moduli of 25% N110/PS678u at 170°C.

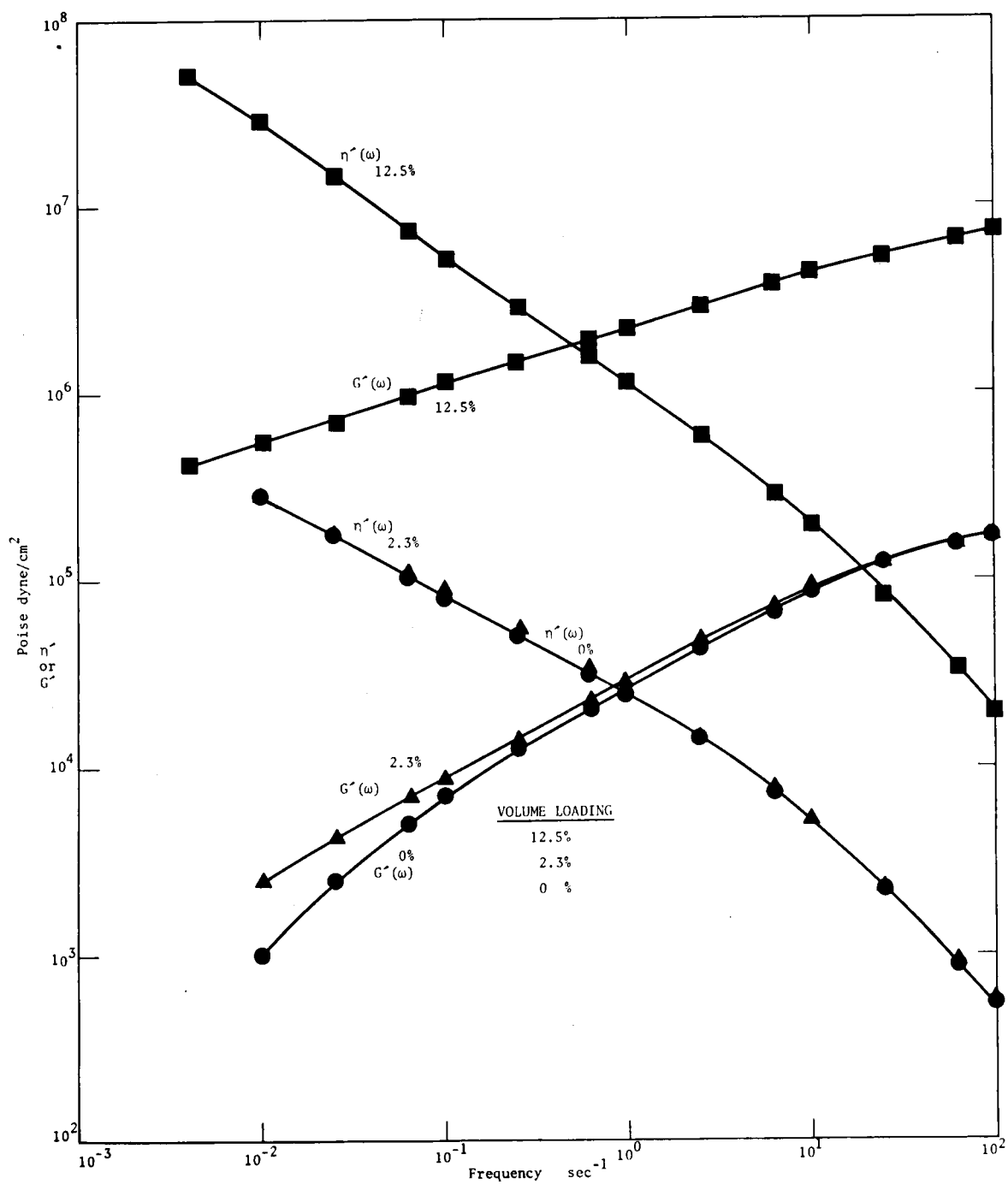


Figure IV-6. Dynamic viscosity and storage modulus N110 C.B. in polybutadiene #1203 at 100°C.

lower loading polystyrene systems appear to approach a Newtonian plateau limit (Figure IV-7) while that of the polybutadiene systems appear ever increasing (Figure IV-6).

B. STRESS RELAXATION

The static stress relaxation experiments were carried out in the Ide extensional rheometer. Using a high extension rate (0.24 sec^{-1}) for a short duration (0.9-1.8 sec) various extension ratios ($1.08 < \lambda < 1.34$) were obtained. The resulting shear relaxation modulus $G(t)$ is shown for the polystyrene systems in Figure IV-8 and the tensile relaxation modulus $E(t)$ is shown for the polybutadiene systems in Figure IV-9.

In general the higher loading systems have a larger relaxation modulus and longer apparent characteristic relaxation time. The modulus of the low loading polystyrene systems and the polybutadiene systems appear ever decreasing in time. The highly filled polystyrene systems, however, show a plateau in the long time relaxation modulus.

The low loading polystyrene systems (5% and 10%) appear to relax more rapidly than the unfilled polystyrene melt. This problem and the analysis of the stress relaxation experiment are discussed in Chapter V.

C. STEADY SHEAR FLOW MEASUREMENTS

The steady state shear viscosities were measured in the Instron capillary rheometer. The range of shear rates is from 10^{-1} to 10^3 reciprocal seconds. The viscosities increase with increasing carbon black loading and decrease with increasing shear rate. The difference

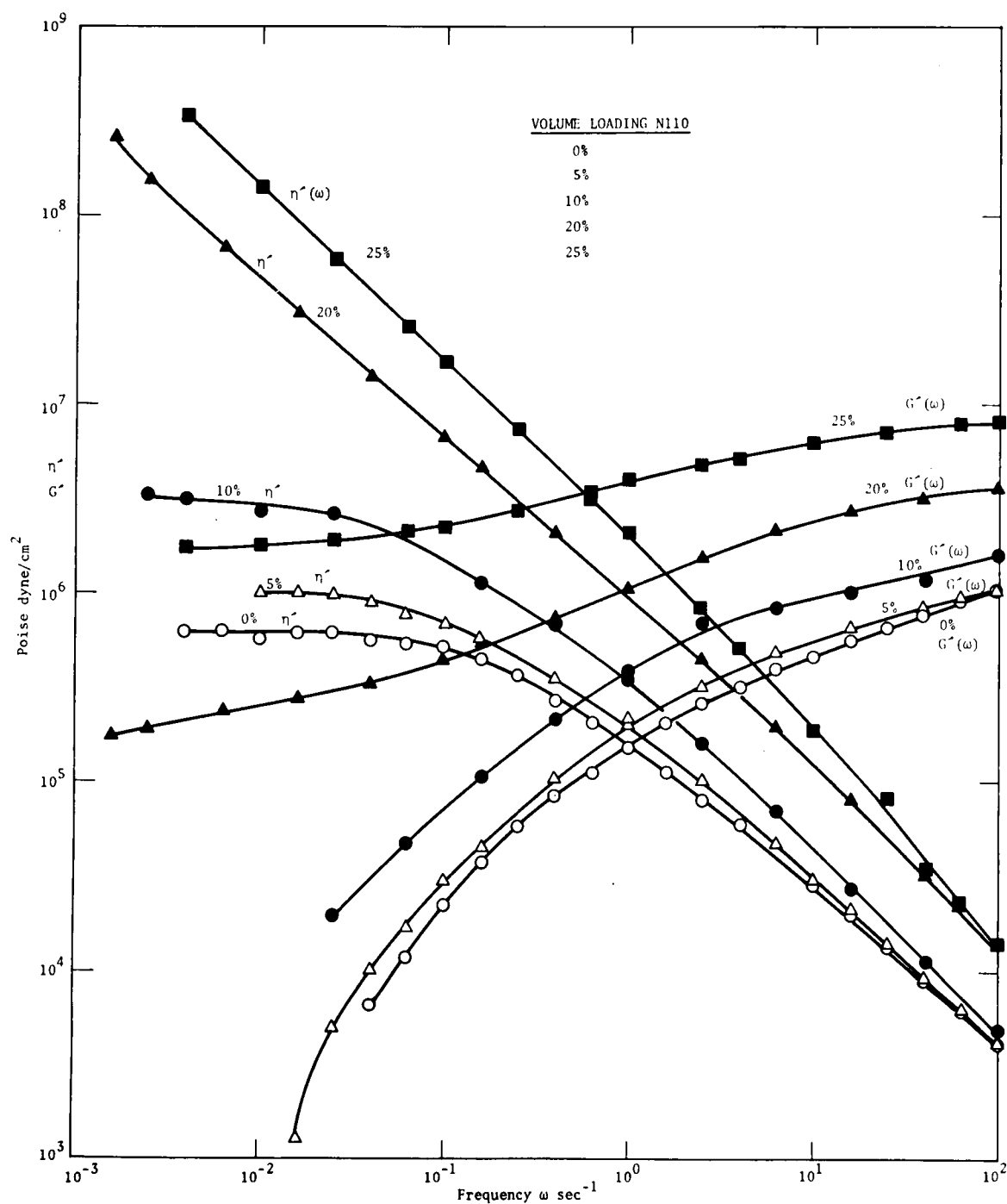


Figure IV-7. Dynamic viscosity and storage modulus of carbon black filled polystyrene melts at 170°C.

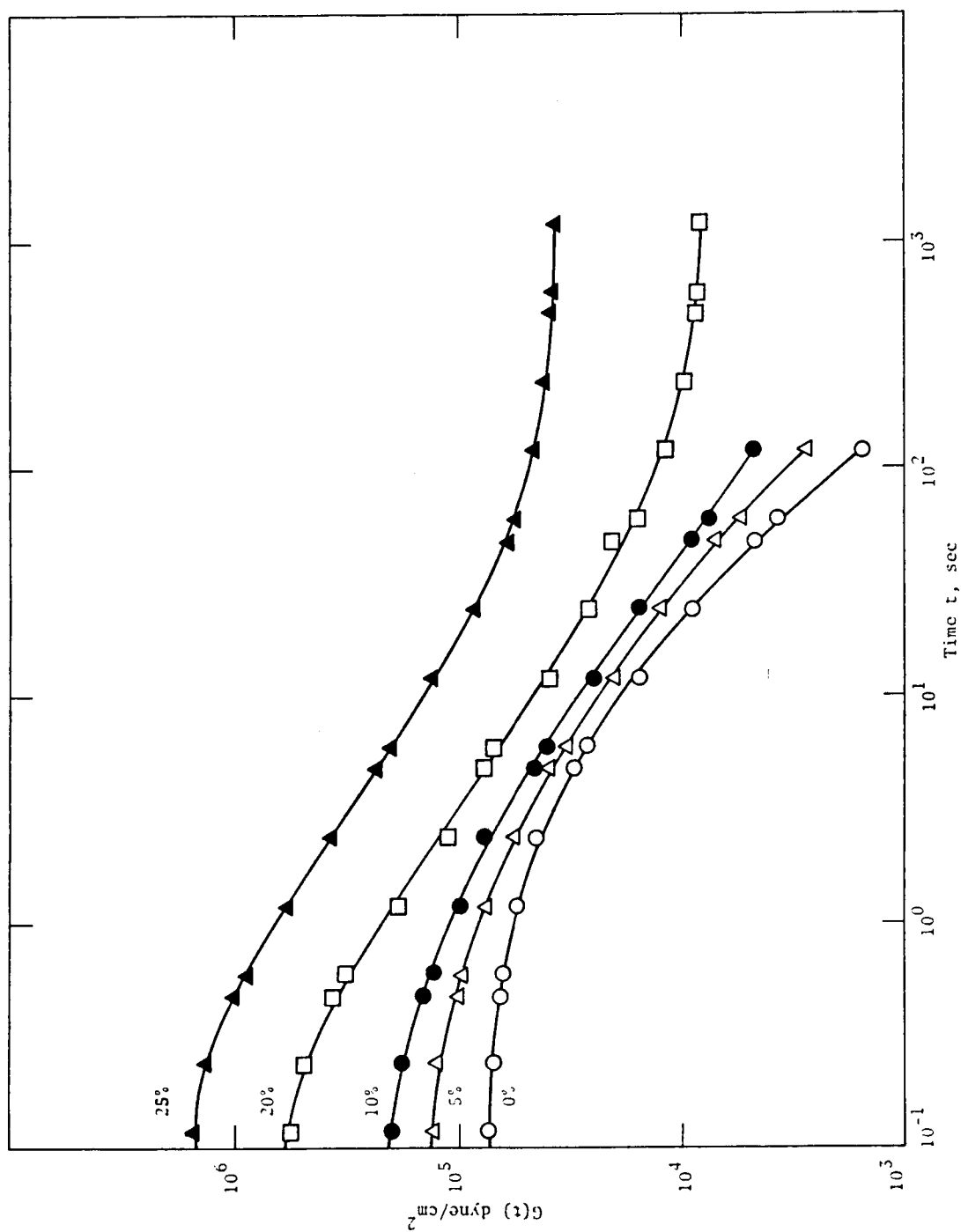


Figure IV-8. Shear relaxation modulus $G(t)$ for N110/PS678u from extension relaxation experiments at 170°C .

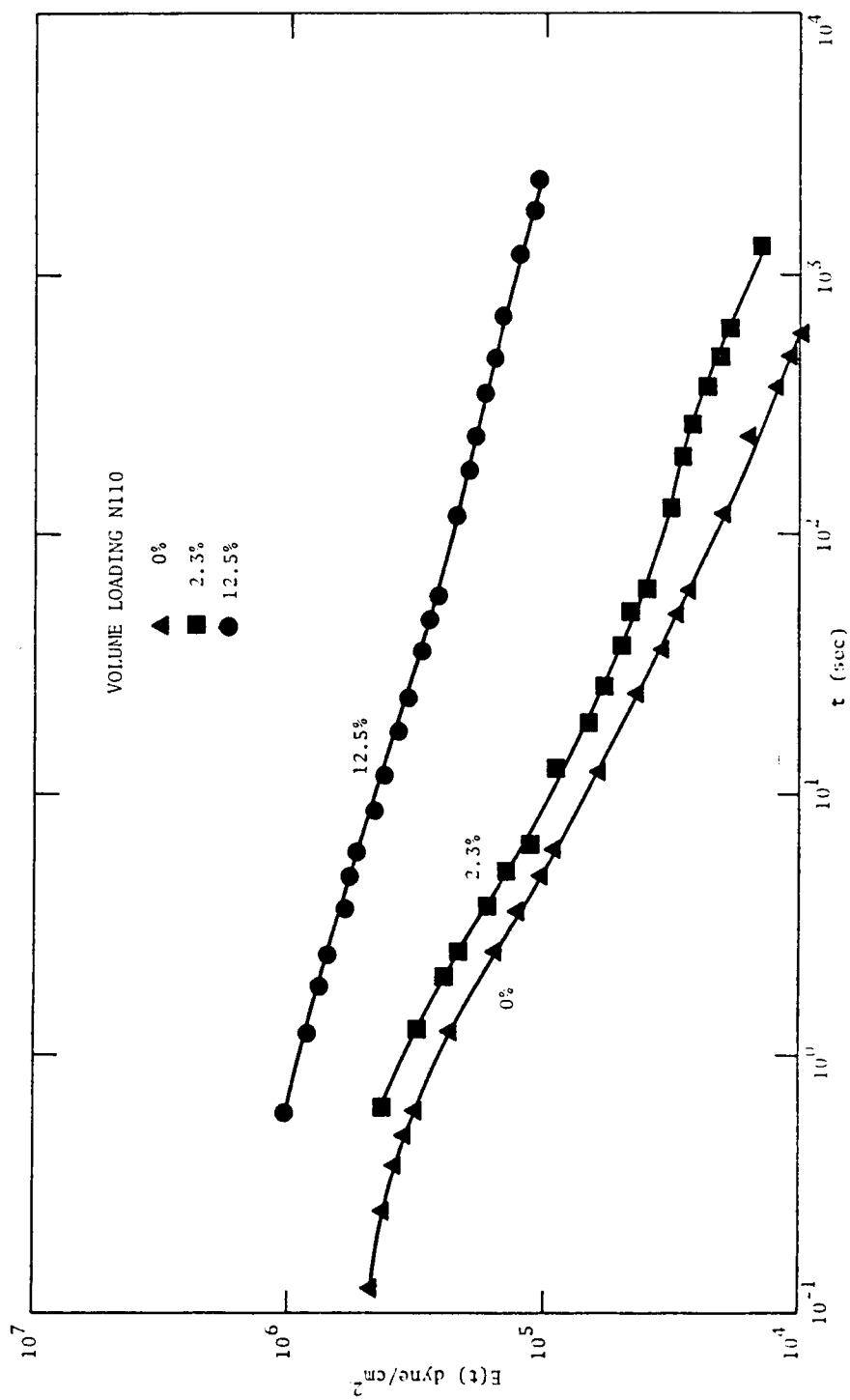


Figure IV-9. Extension relaxation modulus $E(t)$ for N110/polybutadiene from constant extension rate/relaxation experiments at 100°C.

in viscosities with loading is most pronounced at low shear rates. The viscosity-shear rate curves for the polystyrene systems are shown in Figure IV-10 and for polybutadiene systems in Figure IV-11.

The viscosity of the polystyrene melts was also measured in the cone and plate configuration of the Rheometrics Mechanical Spectrometer and Weissenberg Rheogoniometer. The cone and plate measurements range in shear rate from 10^{-2} to 10^0 reciprocal seconds. The data from the capillary and cone and plate rheometers appear consistent in the common range of shear rates (10^{-1} to 10^0 sec^{-1}). The low loading polystyrene systems (0, 5%) appear to reach a Newtonian plateau in the low shear rate region while the highly filled systems appear ever increasing in viscosity with decreasing shear rate. The highest loading systems (20, 25%) have limiting low shear rate slopes of -1 on the doubly logarithmic plot.

A plot of the same steady shear data as viscosity versus shear stress indicates an apparent yield stress for both systems in the case of higher loadings. The polystyrene systems show definite yielding values at $\sigma_y = 1.49 \times 10^5$ and $6.78 \times 10^5 \text{ dynes/cm}^2$ for the 20 and 25% loaded systems (Figure IV-12) while the suggested values of 3×10^5 and $2 \times 10^6 \text{ dynes/cm}^2$ for the 2.3 and 12.5% loaded polybutadiene systems are not very distinct (Figure IV-13).

D. PRIMARY NORMAL STRESS

The primary normal stress difference ($N_1 = P_{11} - P_{22}$) was measured in the steady shear cone and plate experiments. Figure IV-14 shows the

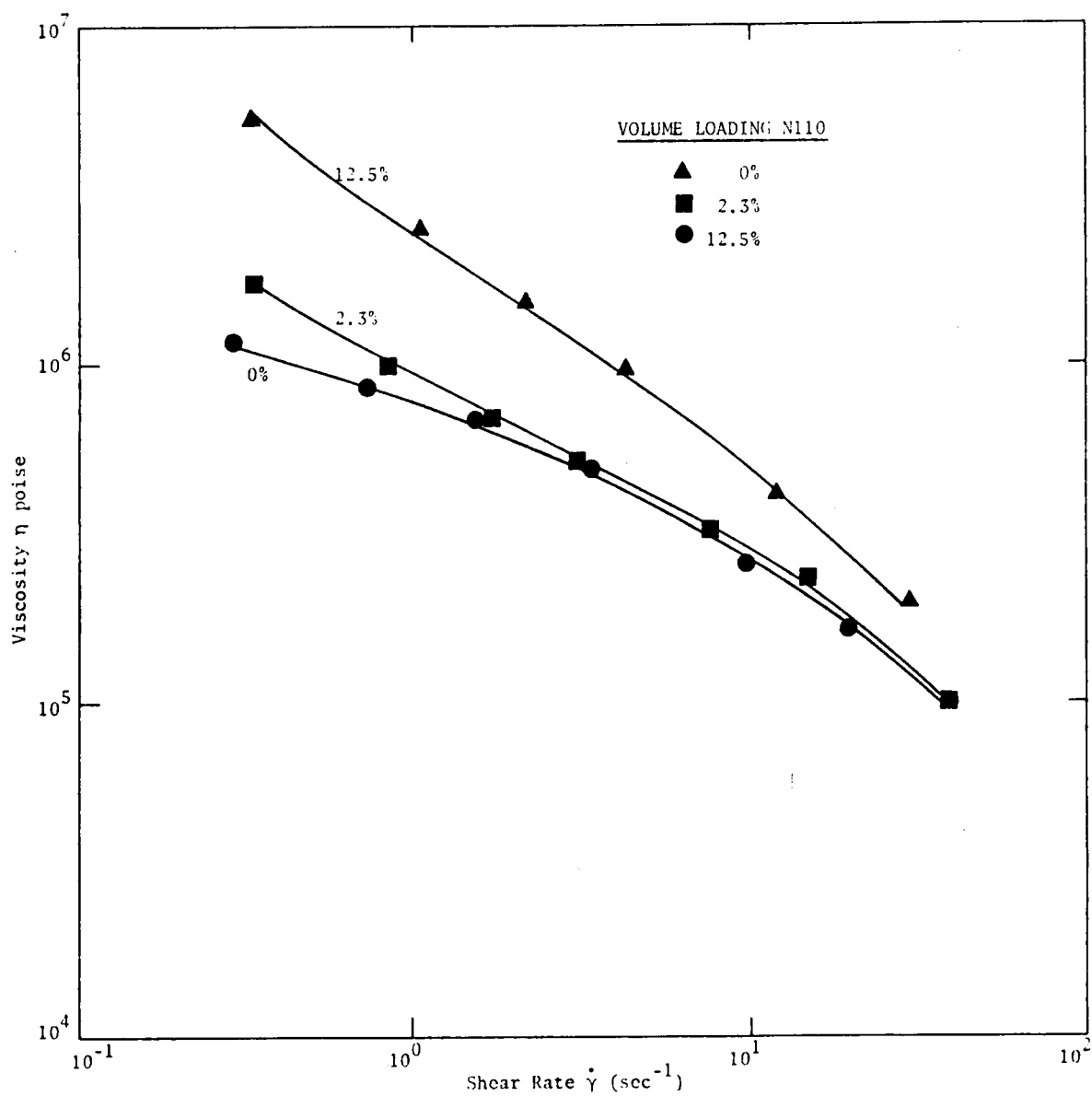


Figure IV-10. Steady state shear viscosity N110/polybutadiene from capillary experiment at 100°C .

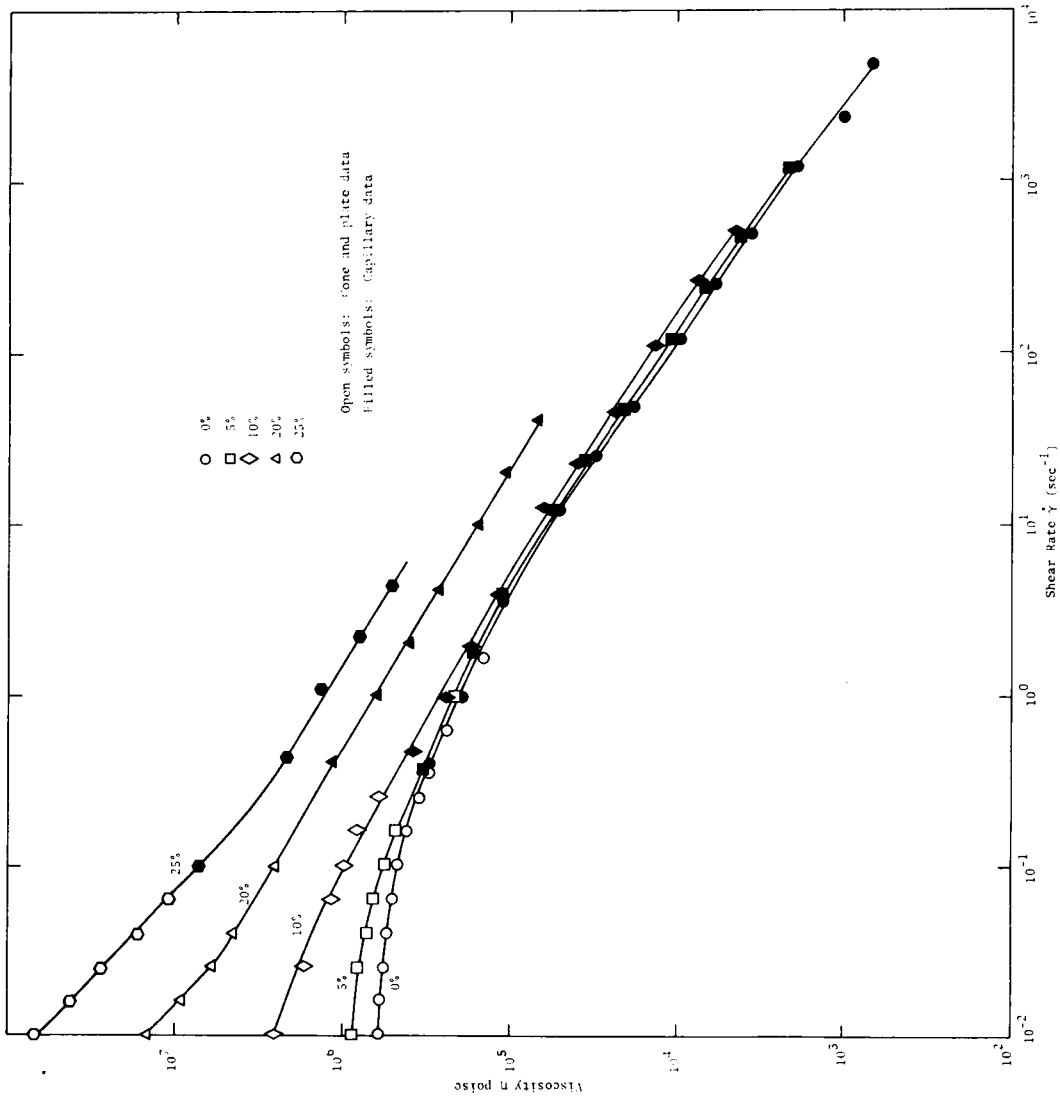


Figure IV-11. Steady state shear viscosity vs. shear rate N110/PS678u at 170°C.

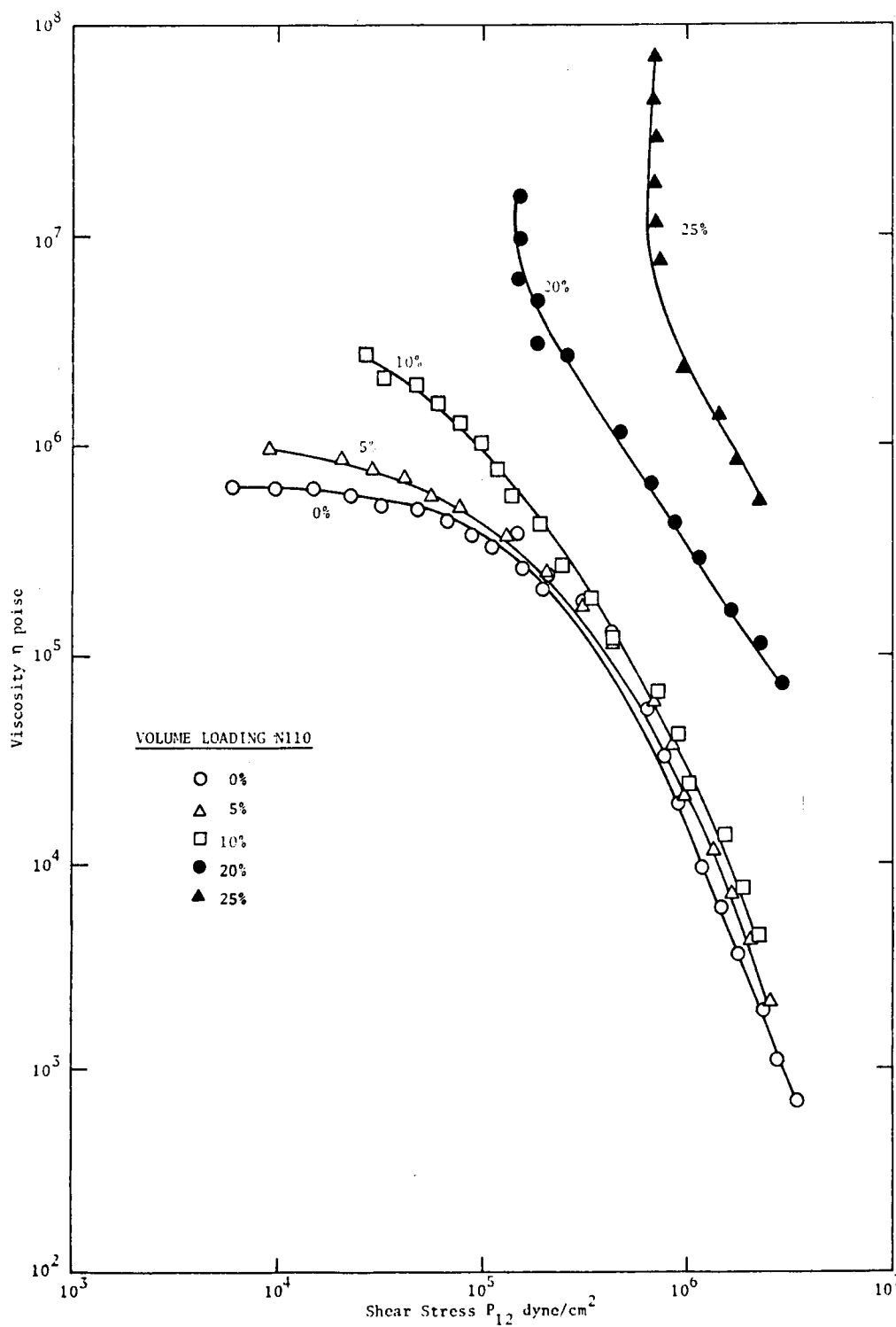


Figure IV-12. Steady state shear viscosity vs. shear stress N110/PS678u at 170°C.

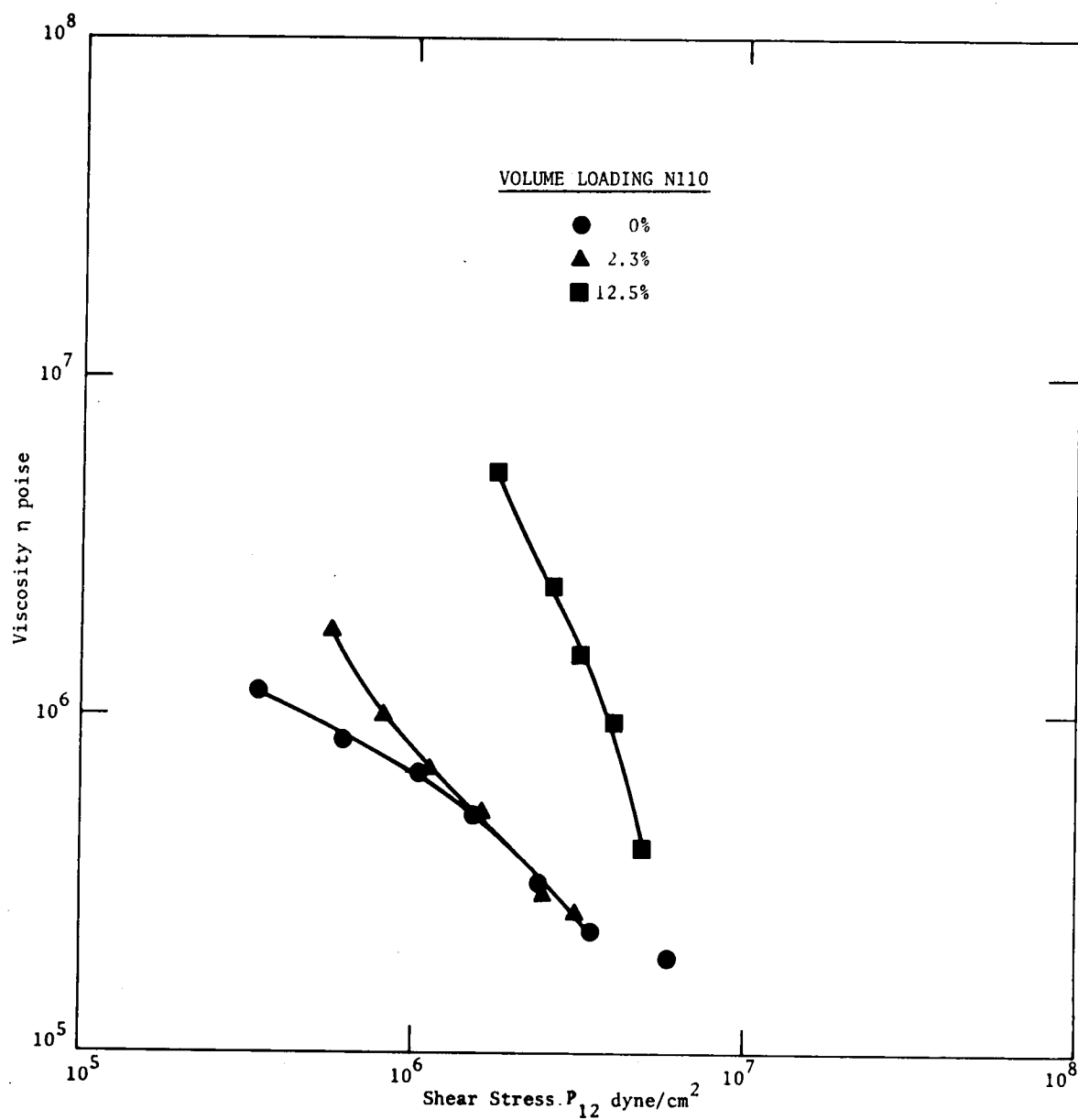


Figure IV-13. Steady state shear viscosity vs. shear stress N110 polybutadiene at 100°C.

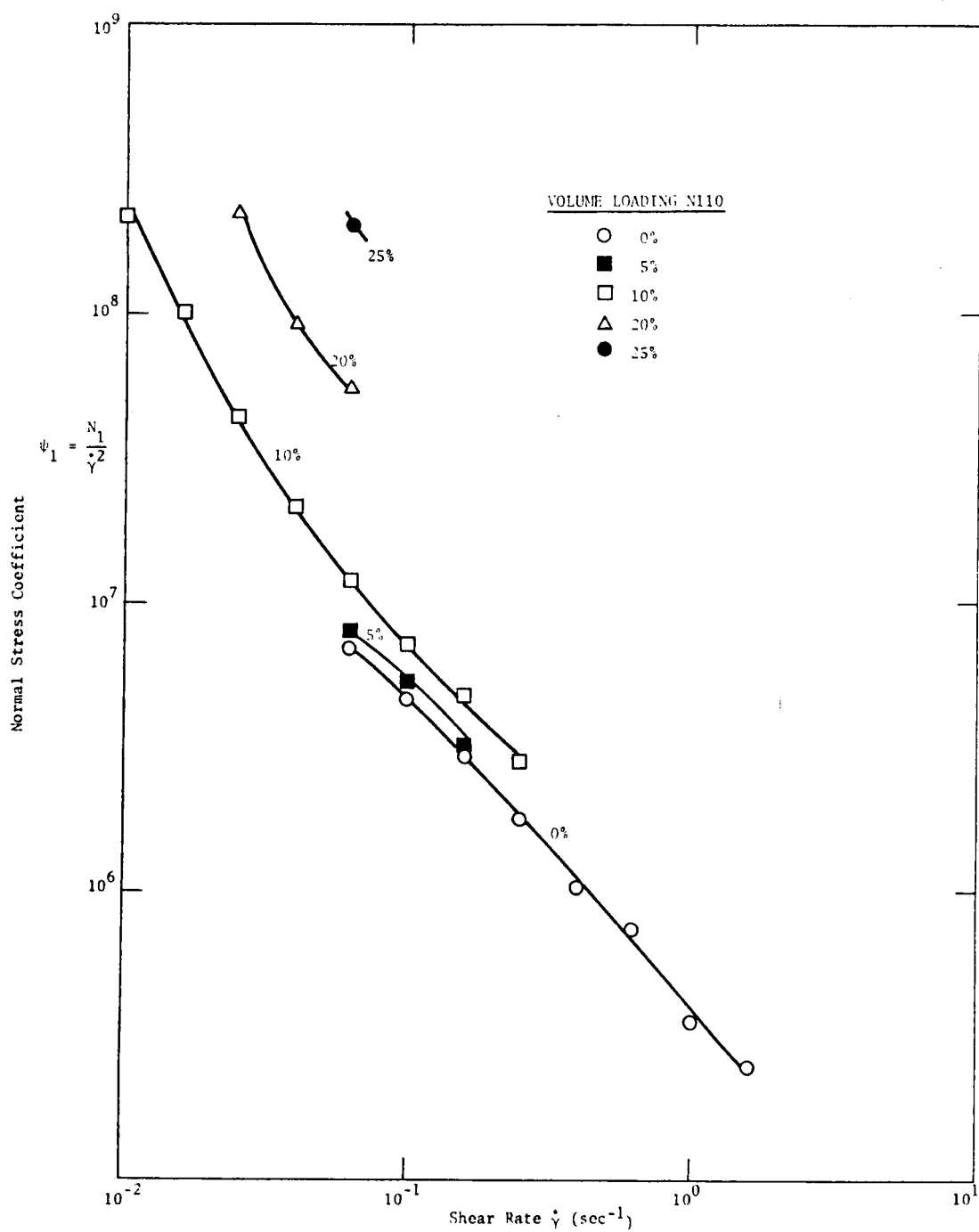


Figure IV-14. Normal stress coefficient ψ vs. shear rate N110/PS678u at 170°C.

normal stress coefficient ($\psi_1 = \frac{N_1}{\dot{\gamma}}$) plotted against shear rate. The normal stress coefficient increases with increasing carbon black loading, decreases with increasing shear rate and appears ever increasing with decreasing shear rate.

Figure IV-15 shows the almost straight line character of the log normal stress-log shear stress plot suggesting a power law type of dependence of N_1 on P_{12} . The normal stress is seen to decrease with increasing carbon black loading at a constant shear stress.

The normal stress data appear rather incomplete because of the very limited range in which it is possible to obtain reproducible measurements. The highly filled materials, which were demonstrated to exhibit apparent yield values in other experiments, are subjected to large normal stresses during the loading of the sample. This large residual stress does not completely decay with time. Stresses then increase with continued deformation until the sample is grossly distorted at high strains or increase to a maximum plateau region then decrease. Values of the maximum plateau region, when reproducible, are recorded here as data points.

No measure of the polybutadiene systems was possible in the cone and plate systems because the samples appeared to become distorted ("ball up") in the gap before a steady state plateau region was achieved. The sample also slips on the cone and plate surface.

E. EXTRUDATE SWELL

The die swell of the frozen extrudates from the capillary viscosity experiment was measured. The capillary die used had a length to diameter

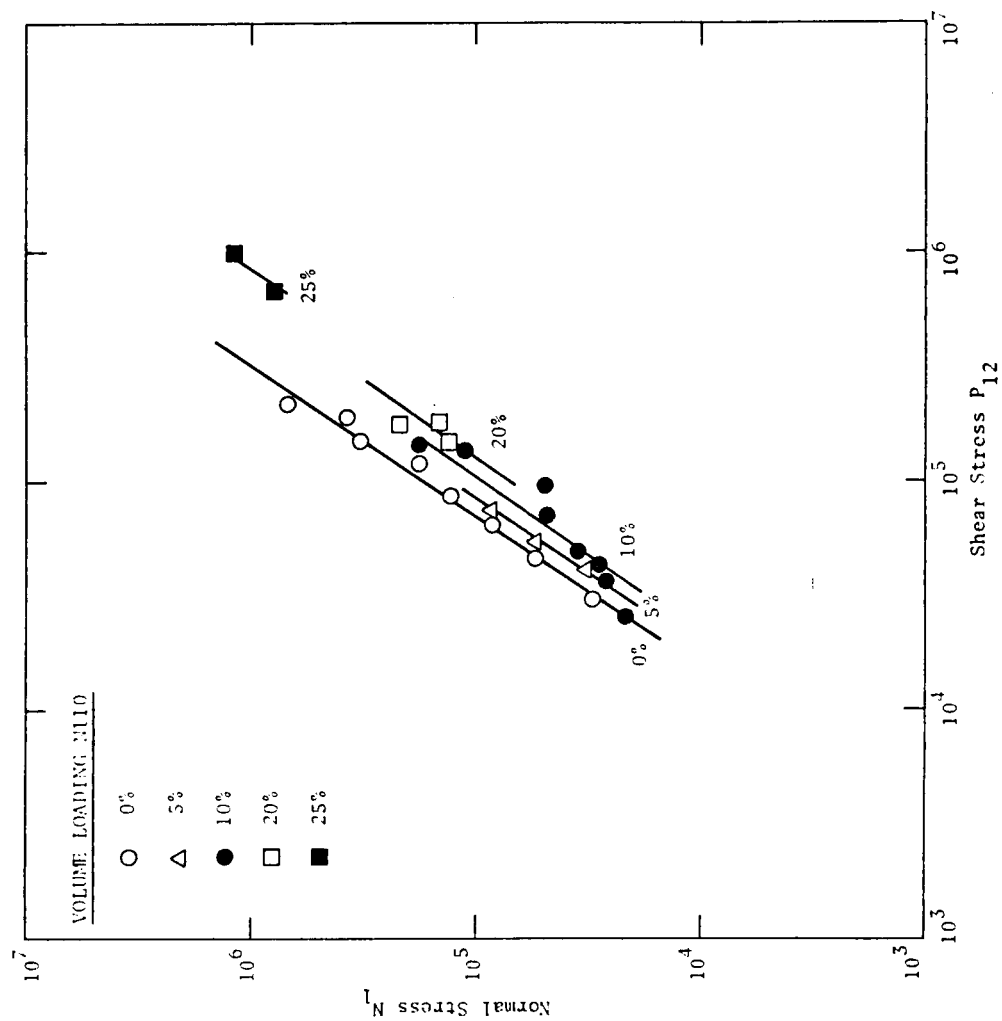


Figure IV-15. Primary normal stress difference vs. shear stress N110/PS678u at 170°C.

ratio of 10 and a 45° die entry angle. The melt in the capillary rheometer reservoir and in the die was maintained at 170°C and extruded vertically into ambient air. All extrudates were cut to a length of 2" and the diameters were measured after the material cooled to room temperature.

The die swell ratio B_F is defined as the ratio of the diameter of the frozen extrudate to the diameter of the die. The die swell ratio B_F is plotted in Figure IV-16 as a function of shear rate at the capillary wall. The figure shows that the die swell increases with increasing carbon black loadings. The shear rate at the wall was obtained from the capillary viscosity experiment results.

The die swell ratio B_A is defined as the ratio of the annealed extrudate diameter to the diameter of the die. A 3-centimeter length of extrudate was placed in a silicone oil bath at 170° for 5 minutes. The bath was cooled to 100° in 7 minutes using an air fan. The "annealing" procedure relaxes the frozen residual stresses and the extrudate swells in diameter and shrinks in length. The extrudate swell ratio, $\frac{D_2}{D_1}$, and the extrudate shrinkage ratio, $\sqrt{\frac{L_1}{L_2}}$, were found to agree within 2% for all samples measured. The effect of the annealing procedure is greatest for the unfilled samples 4 to 14% increasing with increasing shear rate.(Figure IV-17).

F. TRANSIENT SHEAR VISCOSITY

The transient shear viscosity of polybutadiene systems was measured in the parallel plate "sandwich shear" testing device at 100°C. The

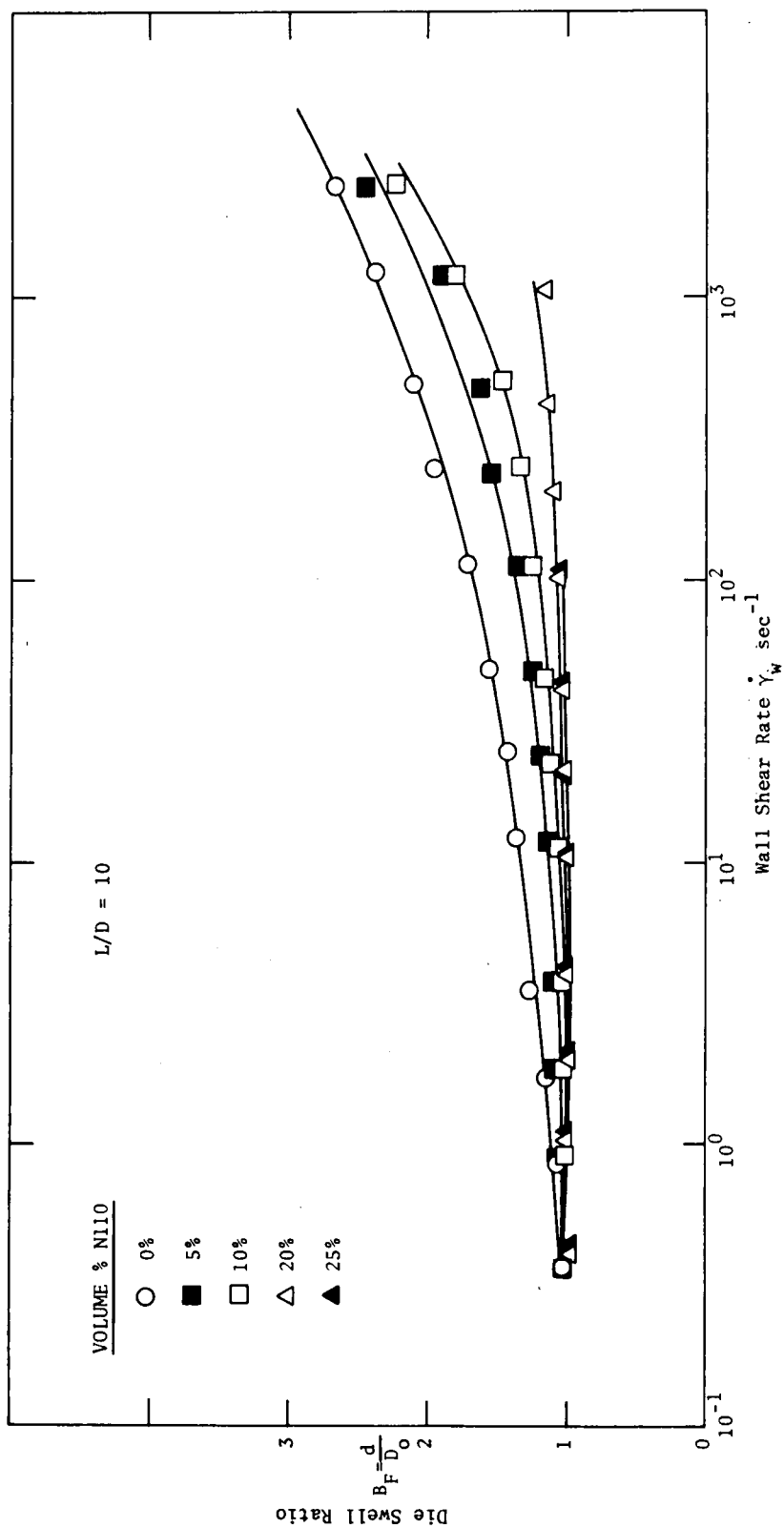


Figure IV-16. Die swell of frozen extrudate for N110/PS678u compounds at 170°C.

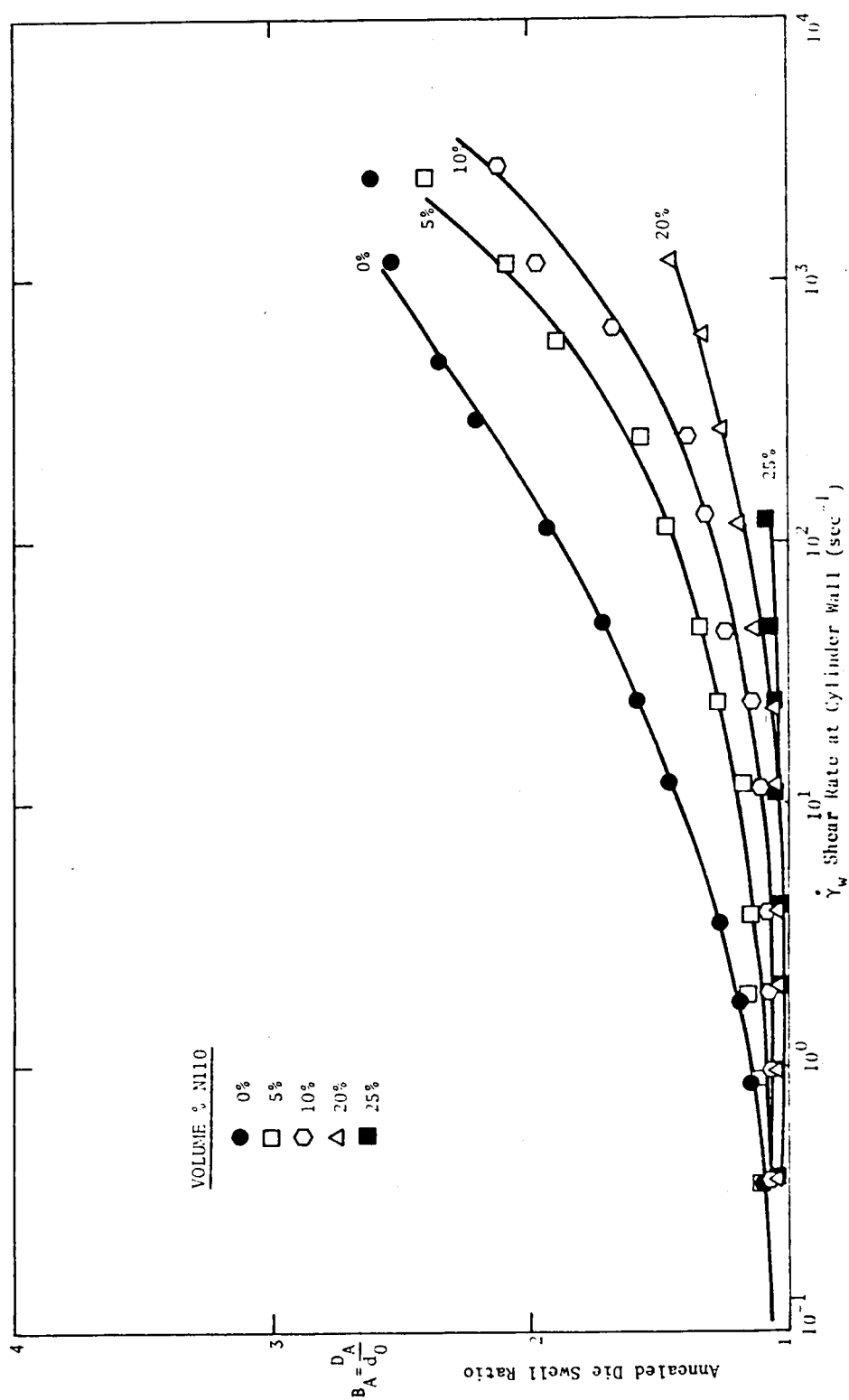


Figure IV-17. Die swell of annealed extrudate for N110/PS678u compounds at 170°C.

range of shear rates was from .00055 to .055 reciprocal seconds (Figures IV-18 through IV-21).

The low shear rate data approached the highest asymptotic limit with ultimate viscosities decreasing with increasing shear rate. The steady state values were difficult to determine because of the experimental problems. The sample tears away from the plates at the large strains required for the determination of the steady state values. The stress overshoot values are readily apparent in the data. The overshoot is most pronounced in the low loading systems (0, 2.3%) and is less evident in the highest loading case (12.5%).

The viscosities of the more highly filled systems are higher than the lower loading systems under equivalent conditions. This can be seen in Figure IV-21 where the transient shear viscosity at a shear rate of $\dot{\gamma} = 0.005 \text{ sec}^{-1}$ is plotted for three levels of carbon black loading.

G. EXTENSIONAL VISCOSITY

The Ide rheometer was used in measuring the extensional viscosity of 1/8" diameter filament samples. Constant extension rate deformations ranged from .0063 to 0.2 sec^{-1} . Figures IV-22 through IV-26 show the transient extensional viscosities of the polystyrene melts. The polybutadiene systems are shown in Figures IV-27 through IV-29.

In the range of extension rates used the low loading (0, 5 and 10%) polystyrene systems do not clearly illustrate steady state extensional viscosity plateau regions, even at the lowest measured rates. The highly filled polystyrene systems (20, 25%) clearly indicate steady state extensional viscosity plateau regions at each of the rates used.

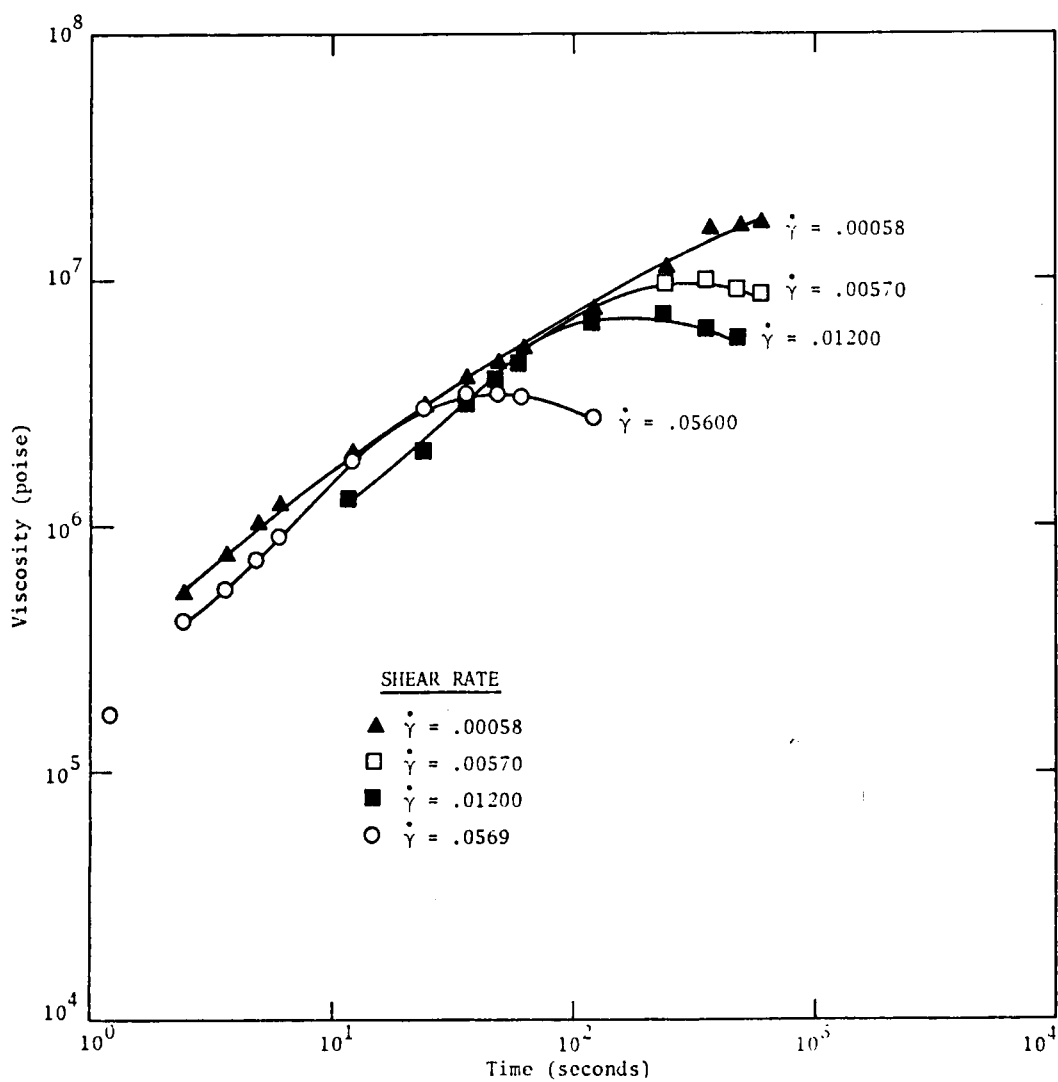


Figure IV-18. Transient shear viscosity for polybutadiene at 100°C.

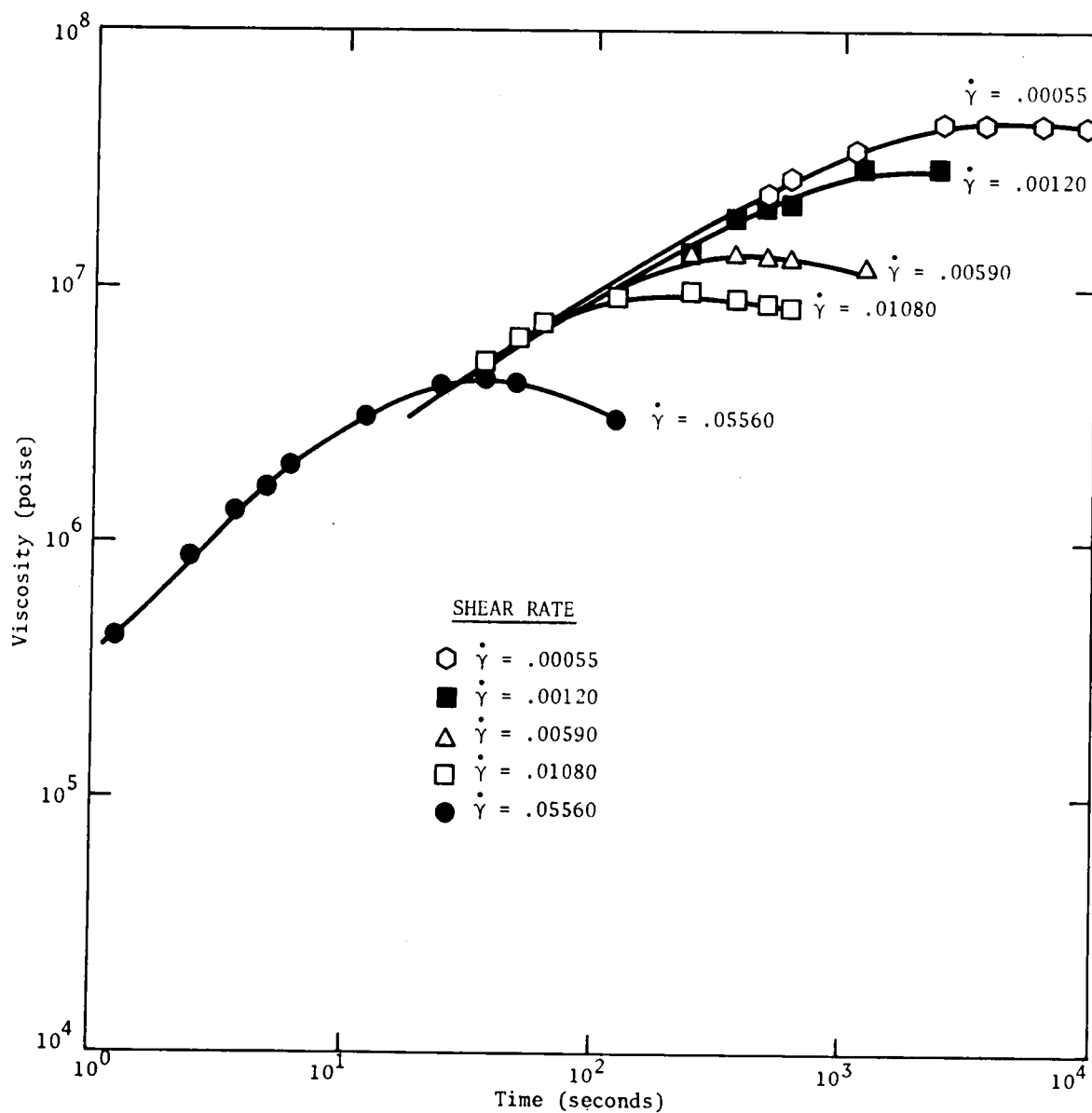


Figure IV-19. Transient shear viscosity for 2.3% N110 in polybutadiene at 100°C.

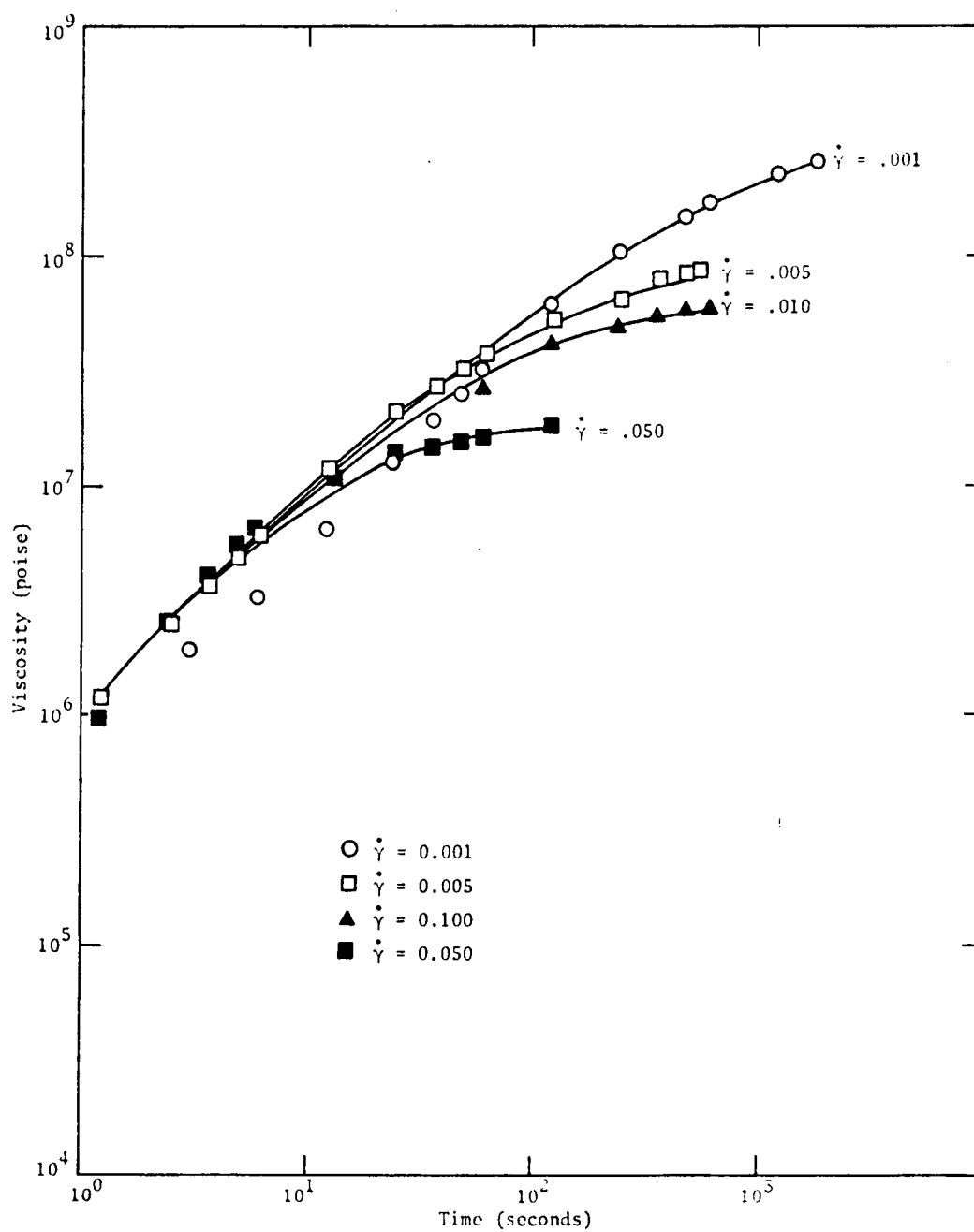


Figure IV-20. Transient shear viscosity for 12.8% N110 in polybutadiene at 100°C.

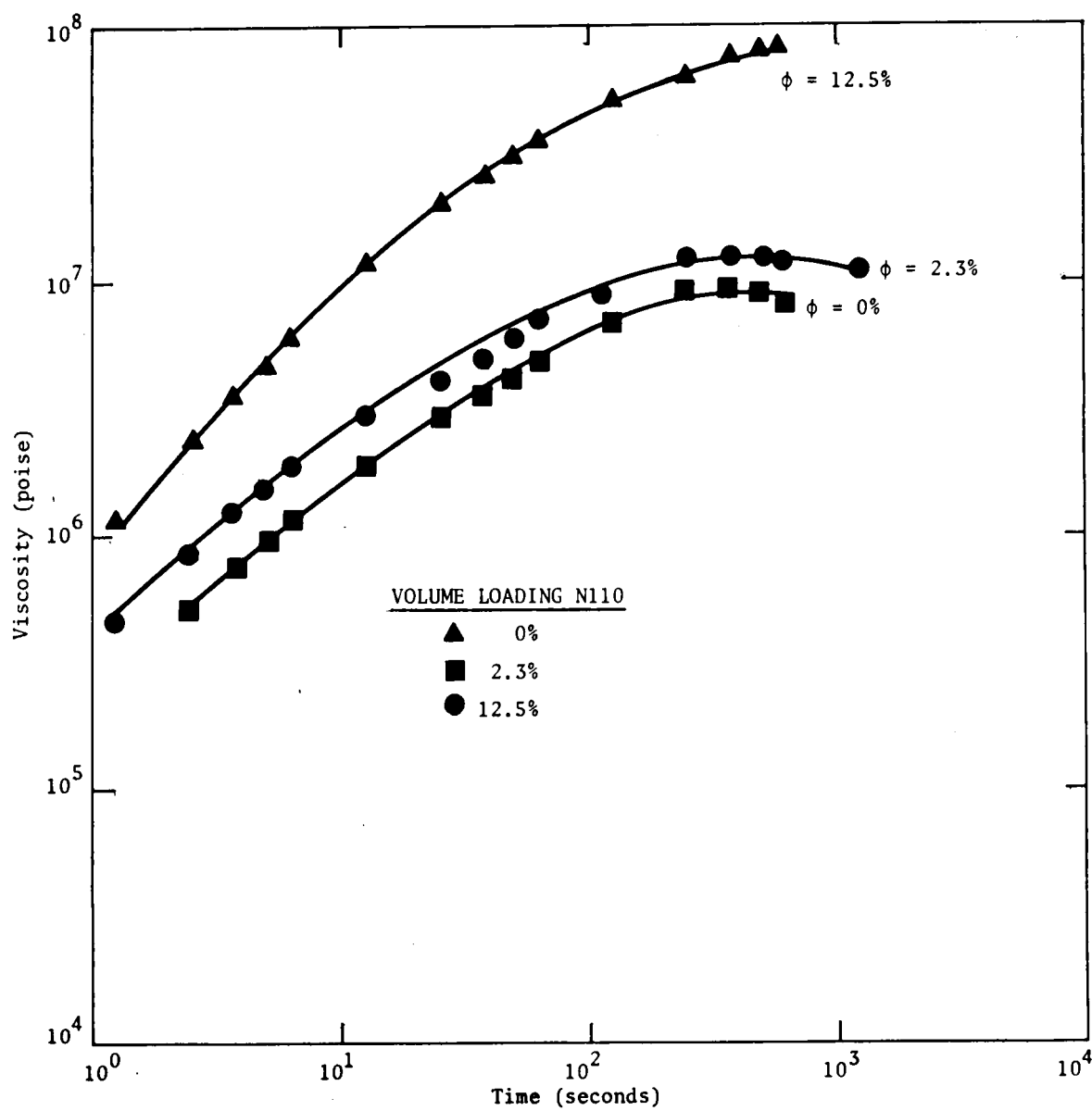


Figure IV-21. Transient shear viscosity for N110/polybutadiene compounds at 100°C for .005 sec⁻¹ shear rate.

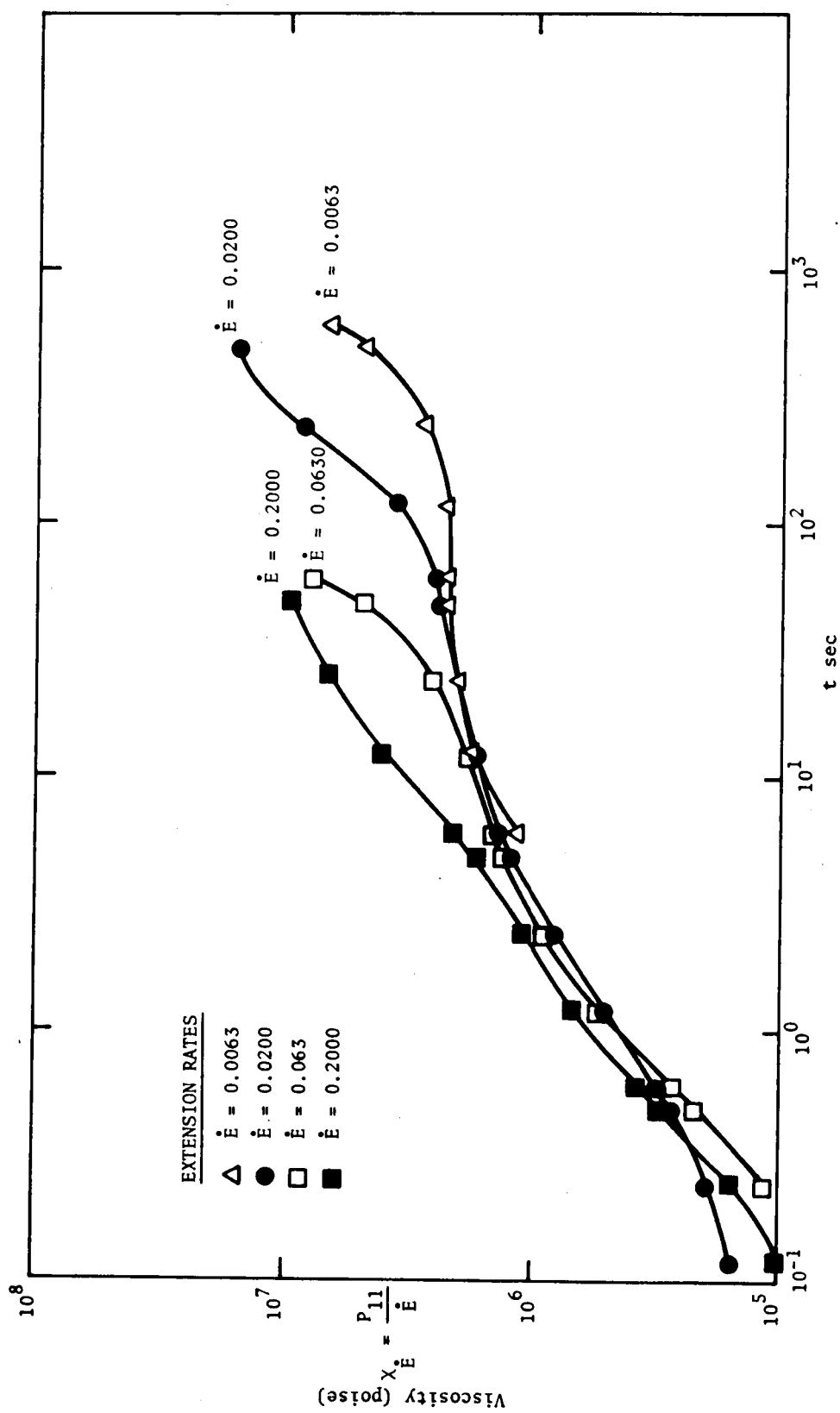


Figure IV-22. Transient extensional viscosity for PS678u at 170°C.

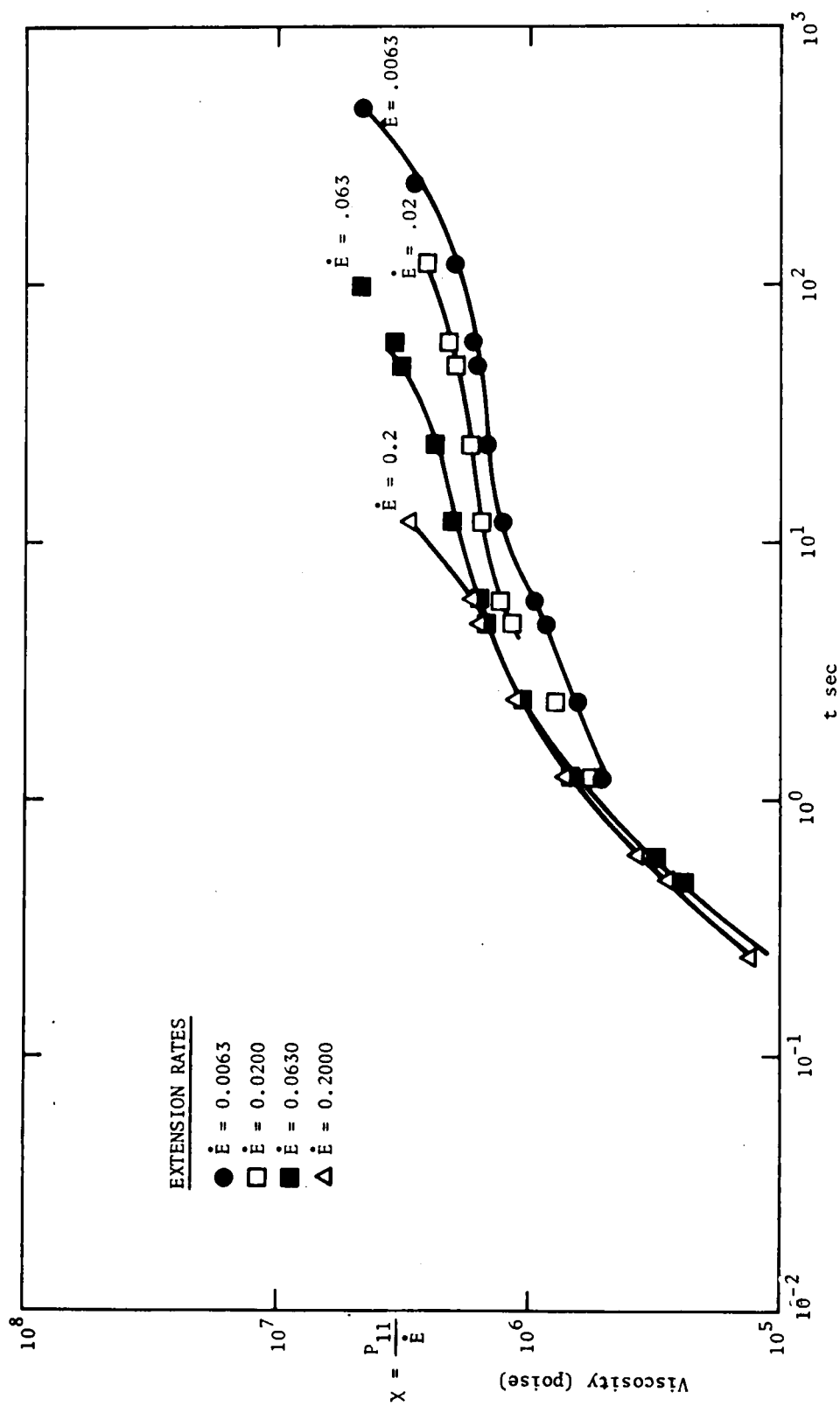


Figure IV-23. Transient extensional viscosity for 5% N110 in PS678u at 170°C.

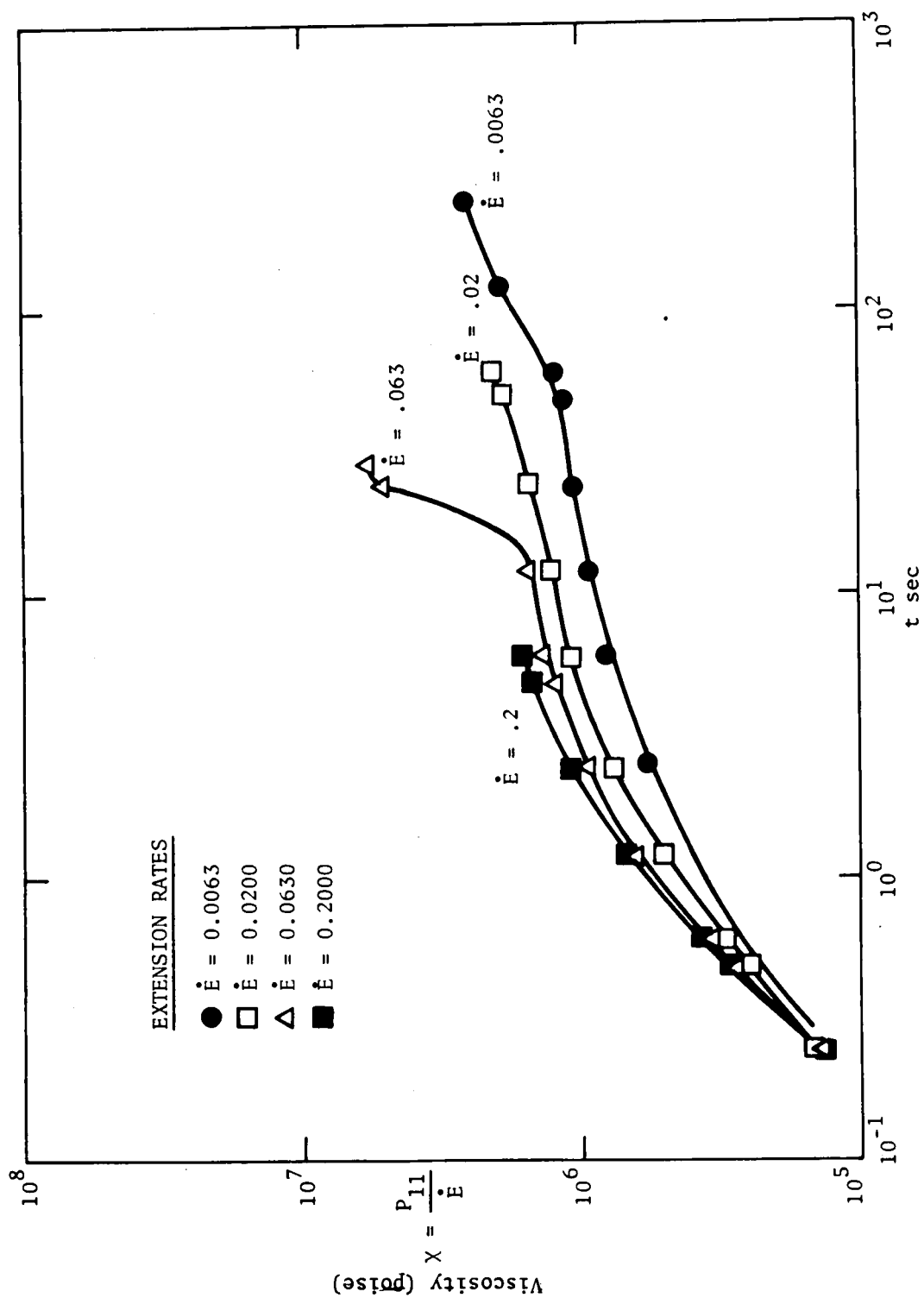


Figure IV-24. Transient extensional viscosity for 10% N110 in PS678u at 170°C.

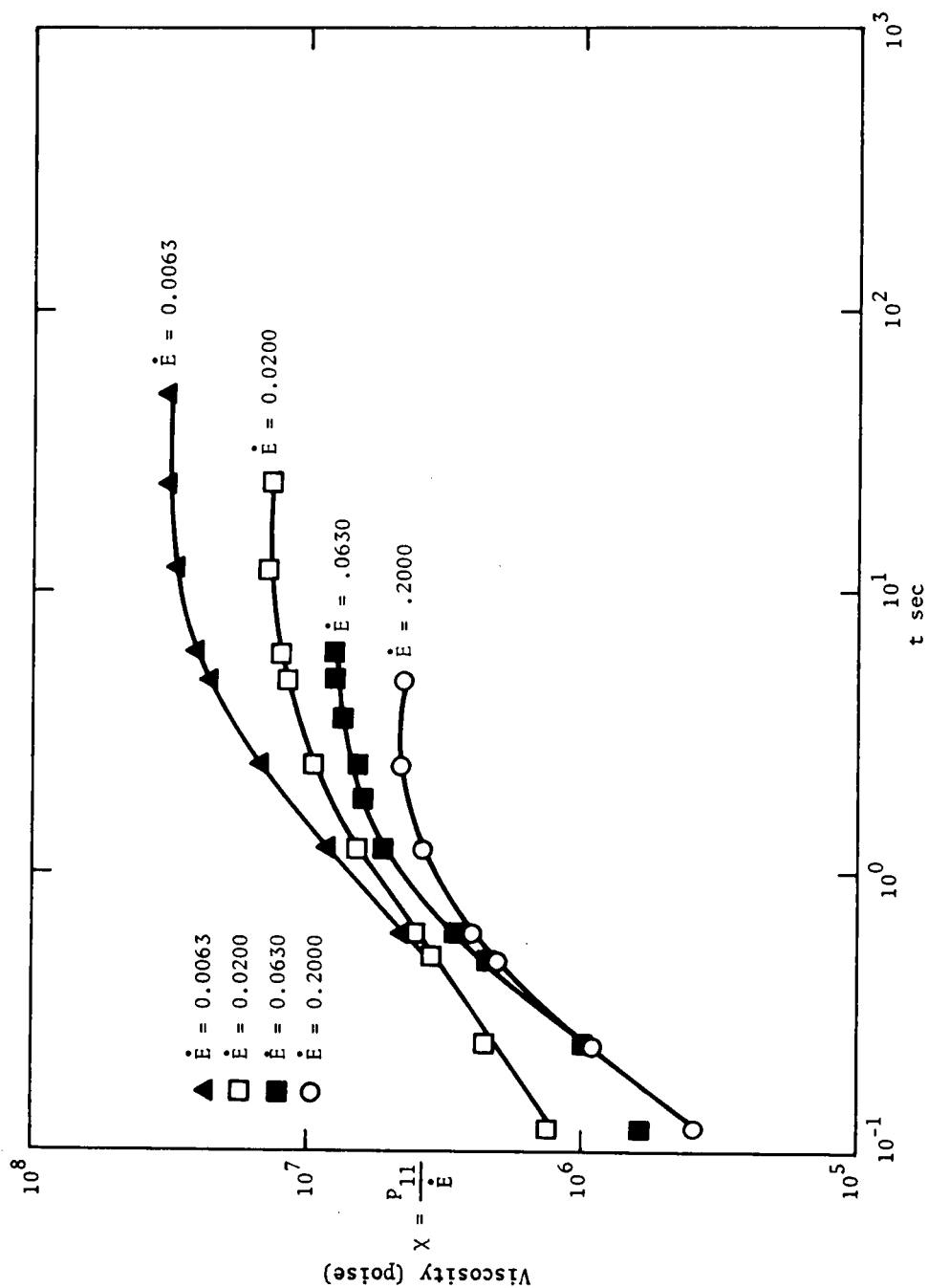


Figure IV-25. Transient extensional viscosity for 20% N110 in PS678u at 170°C.

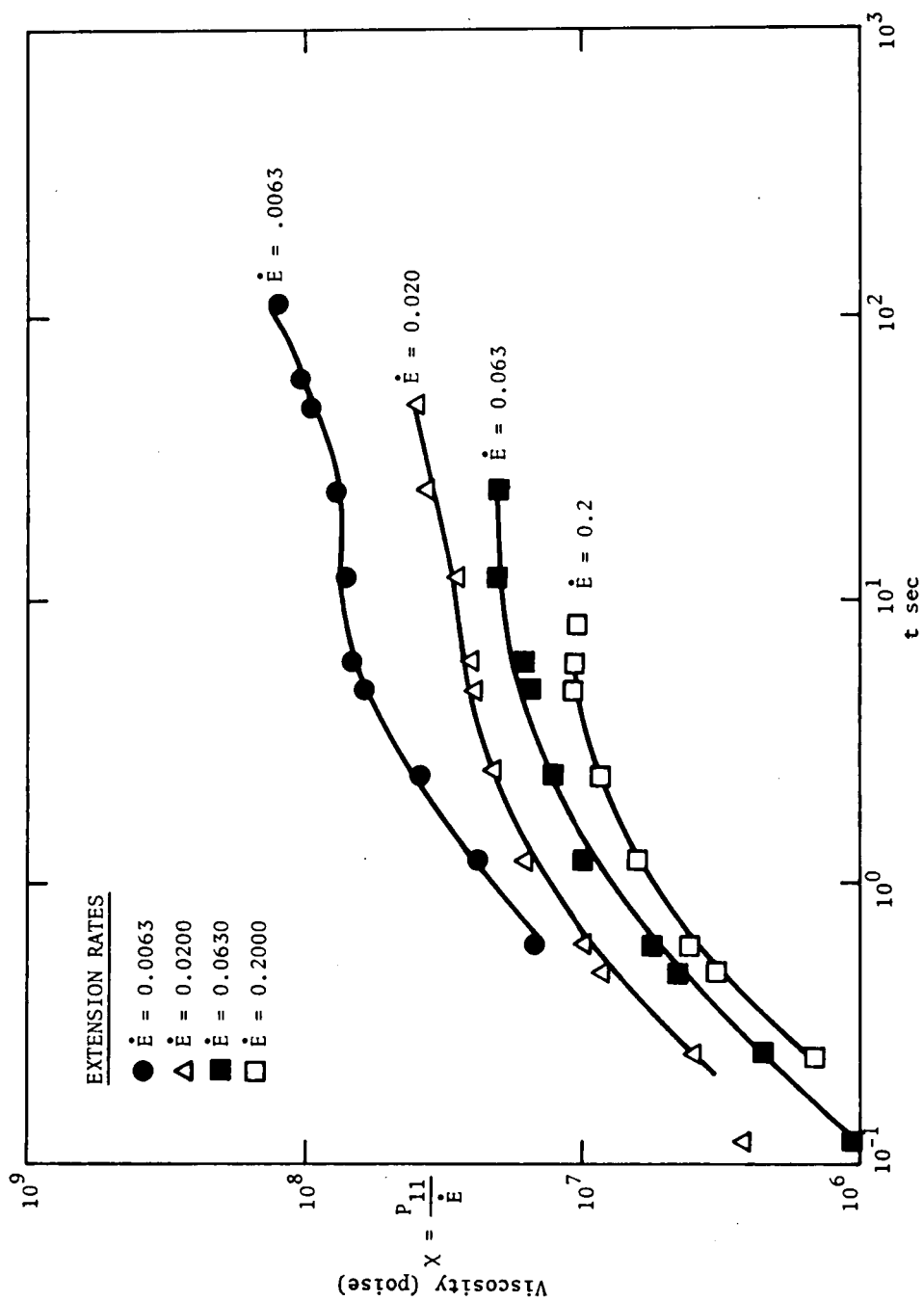


Figure IV-26. Transient extensional viscosity for 25% NI10 in PS678u at 170°C.

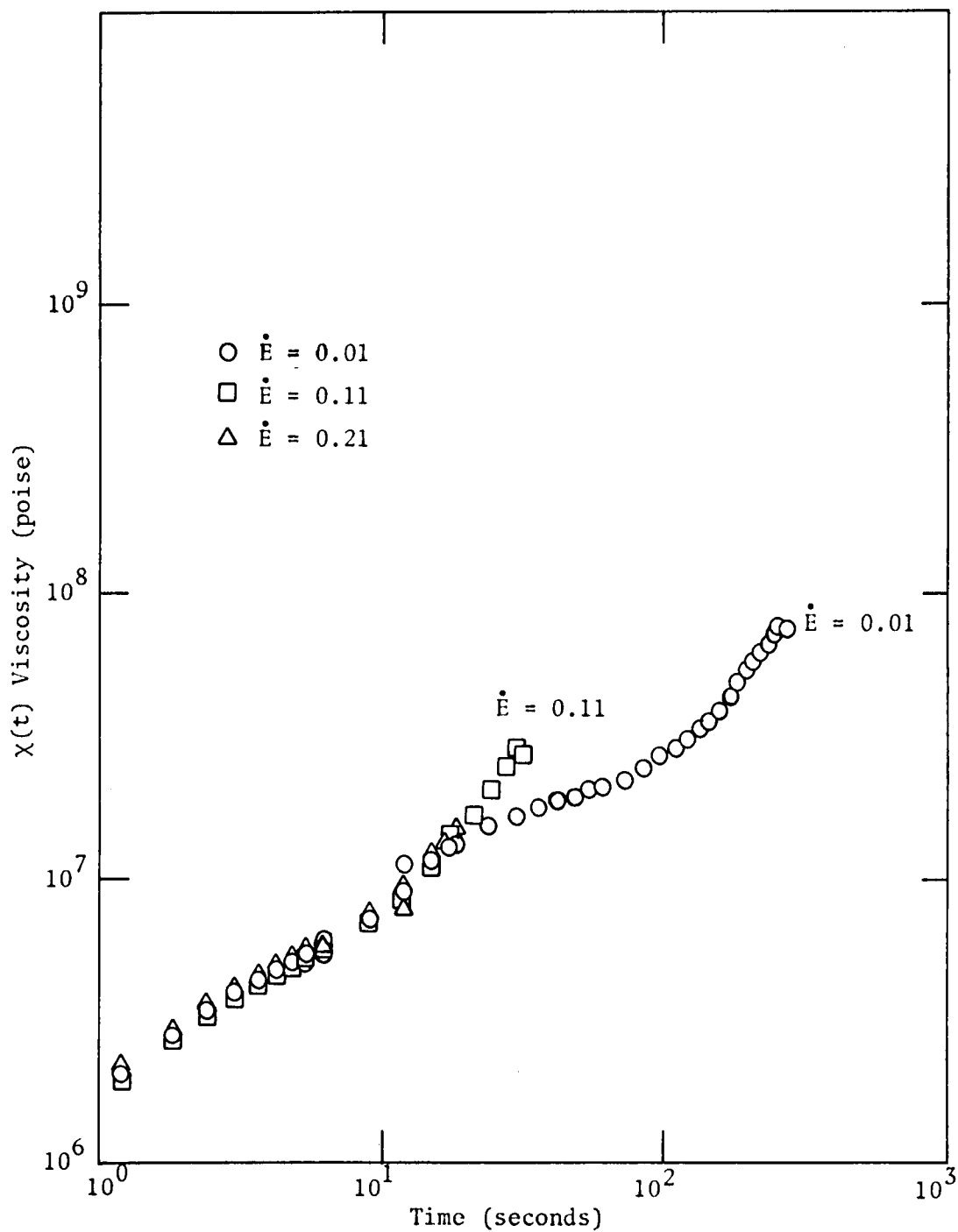


Figure IV-27. Transient extensional viscosity for polybutadiene at 100°C.

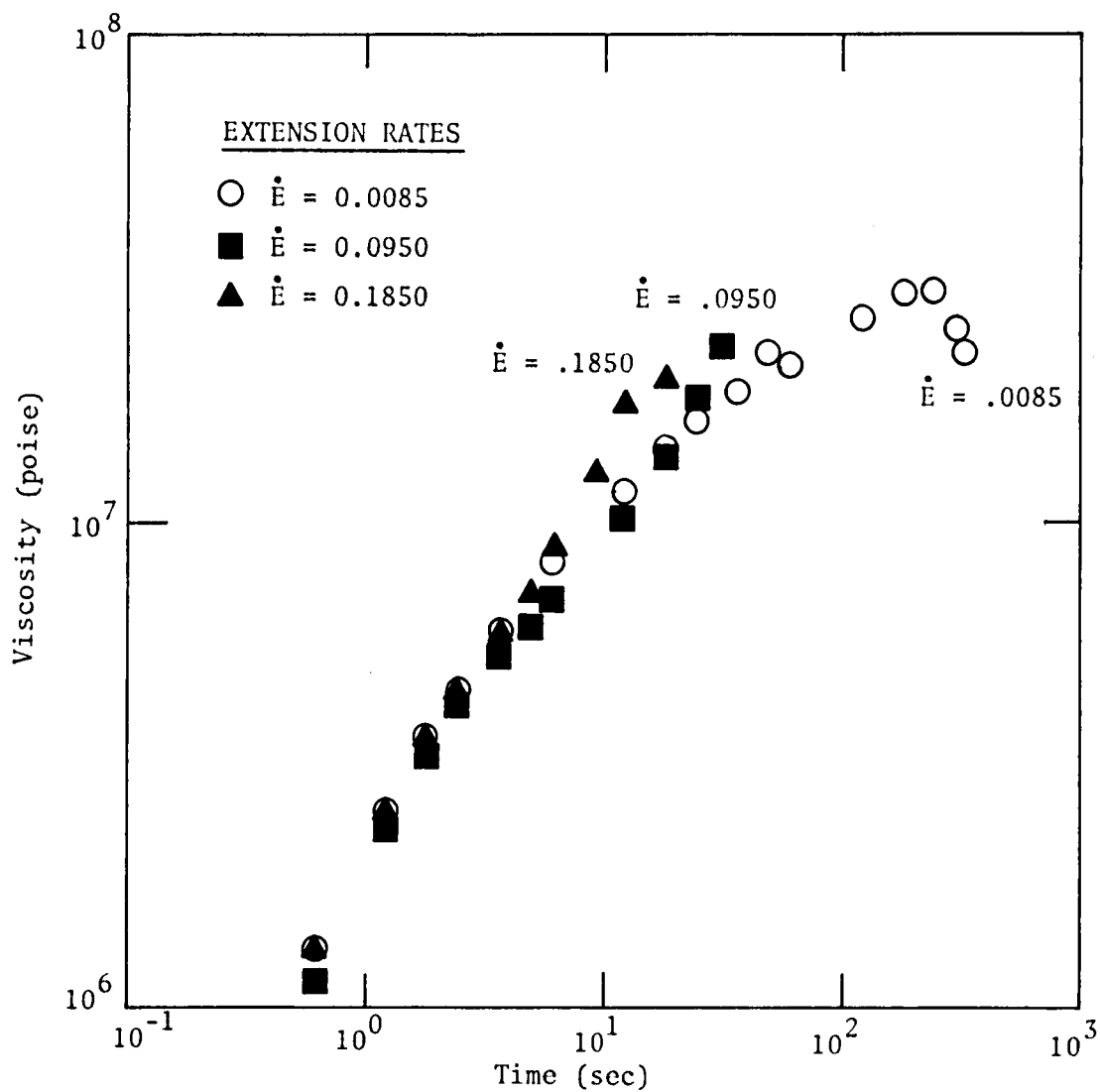


Figure IV-28. Transient extensional viscosity for 2.3% N110 in polybutadiene at 100°C.

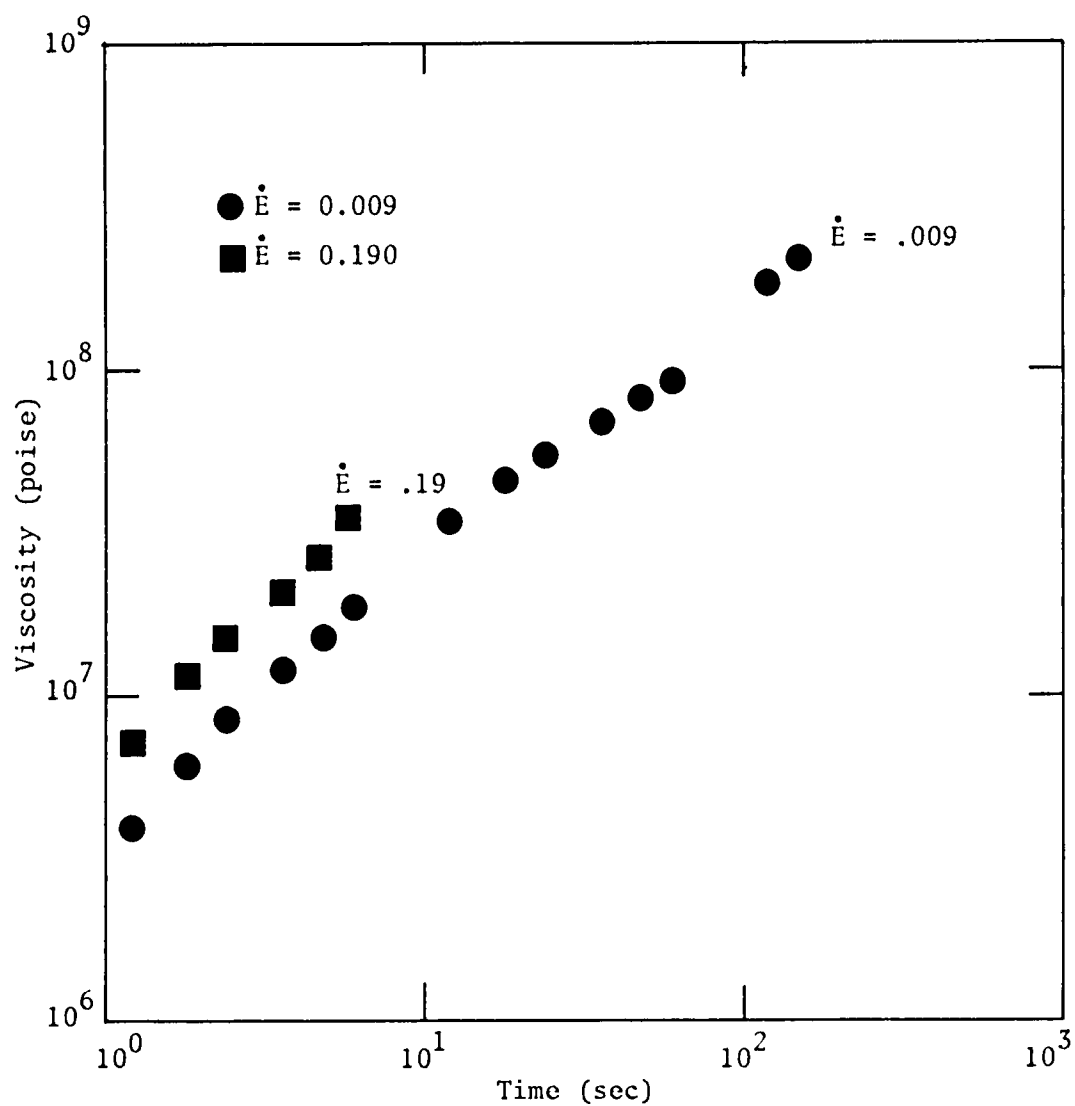


Figure IV-29. Transient extensional viscosity for 12.8% N110 in polybutadiene at 100°C.

The steady state extensional viscosity for these systems decreases with increasing extension rate (Figure IV-30). Figure IV-31 shows the steady state extensional viscosity as a function of tensile stress. The data appear to approach a limiting or yielding stress of 1.5×10^5 and 5×10^5 dynes/cm².

The transient extension rate data of the polybutadiene systems do not indicate a steady state extensional viscosity plateau for the rates and loadings used.

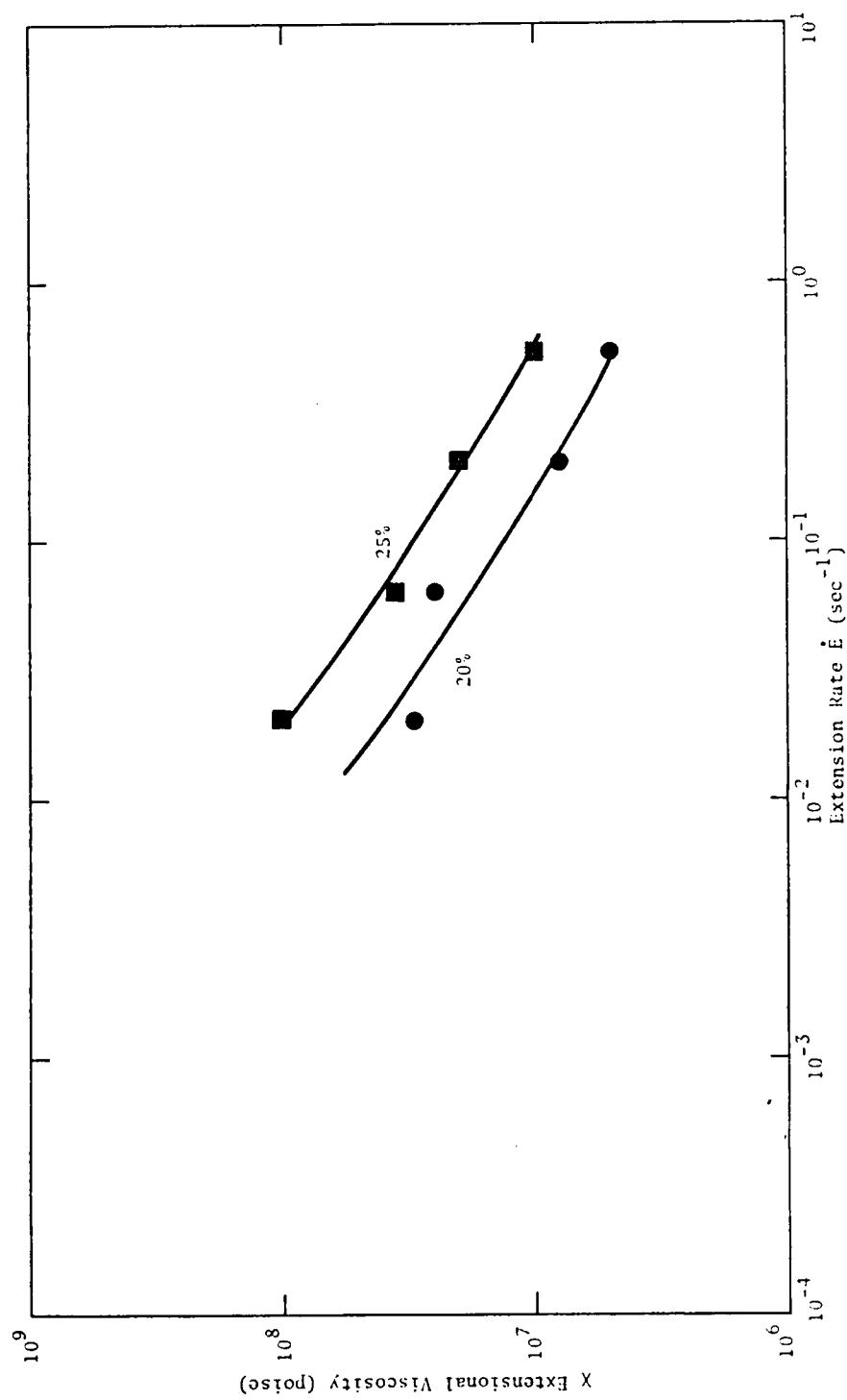


Figure IV-30. Steady state extensional viscosity vs. extension rate for PS678u/N110 C.B. at 170°C.

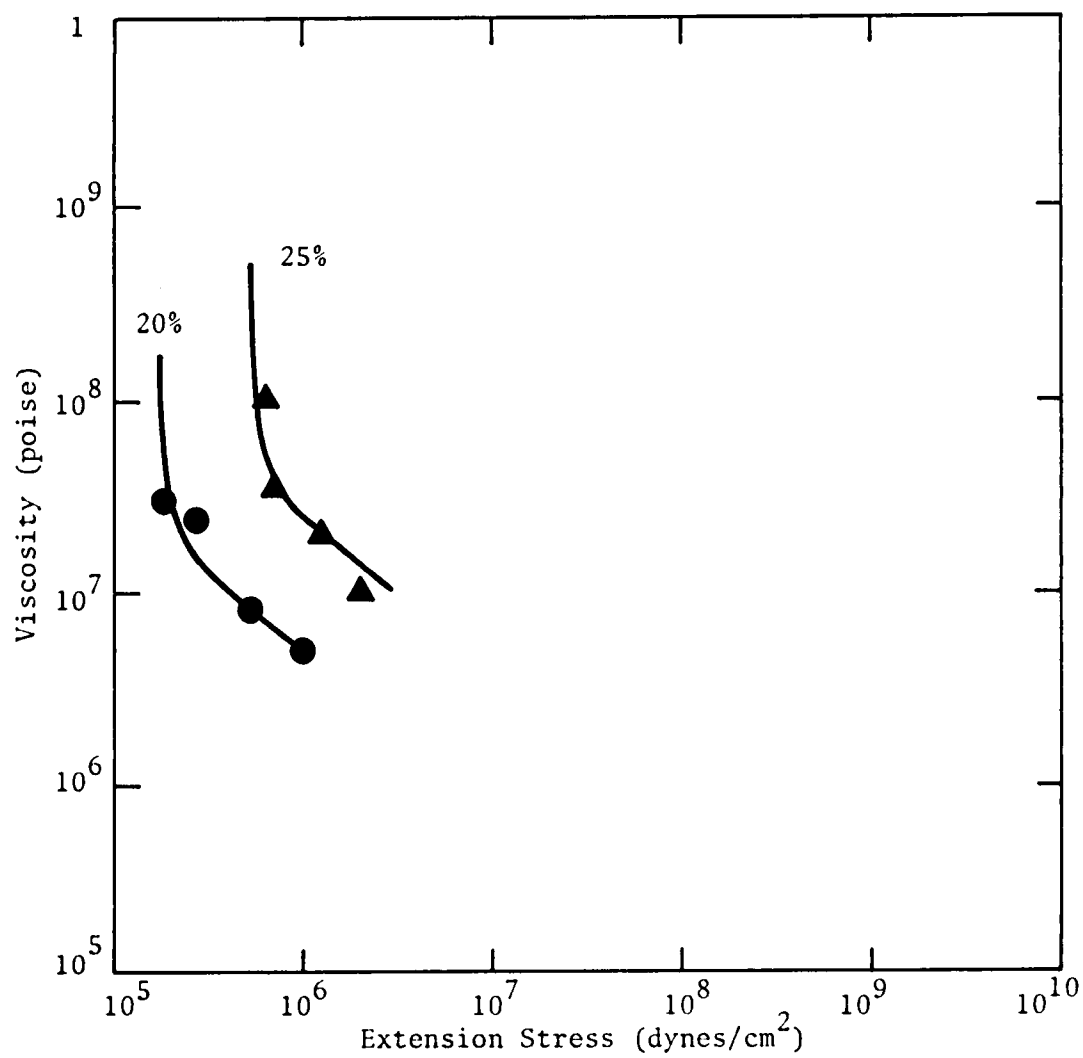


Figure IV-31. Extensional viscosity vs. tensile stress for polystyrene 678u/N110 C.B. at 170°C.

CHAPTER V

INTERPRETATION OF THE LINEAR EXPERIMENTAL RESULTS FOR THE UNFILLED POLYSTYRENE MELT

A. OVERVIEW OF ANALYSIS

In order to obtain a linear viscoelastic response over a broad time spectrum one can make use of dynamic experimental data and, using linear viscoelastic theory, transform the dynamic modulus in the frequency domain to a relaxation modulus in the time domain. In this chapter we show how the linear results are interpreted using the shear relaxation modulus $G(t)$, provide a comparison of various methods of evaluating the spectral distribution function $H(\tau)$ from dynamic modulus data, and integrate the spectral distribution function to obtain the shear relaxation modulus $G(t)$.

This linear analysis is important to the interpretation of filled polymer melts because it is the small strain, zero loading case. We build on this linear response in interpreting the large strain unfilled experimental results and finally the filled nonlinear experimental results.

B. REPRESENTATION OF THE LINEAR VISCOELASTIC RESPONSE USING THE SHEAR RELAXATION SPECTRUM $G(t)$

In Chapter II the Boltzmann superposition integral was presented [Equations (II-1)-(II-3)]. This can be written

$$P_{12} = \sum_{i=1}^n G(t-\tau_i) \gamma_i = \int_{-\infty}^t G(t-s) d\gamma(s) \quad (V-1)$$

The shear relaxation modulus can be represented in terms of discrete or continuous functions by

$$G(t) = \sum G_i e^{-t/\tau_i} = \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad (V-2)$$

The relaxation spectrum $H(\tau)$ is defined as in Equation (V-2) because of the experimental observation of the logarithmic dependence of the relaxation modulus on time (83,319). These distribution functions are common in linear analysis. They were first introduced by Wiechert (319) and were later used by Alfrey (8), Tobolsky (299) and others.

In general one observes a response to an applied stress whose time dependence is determined by the manner in which it was applied. The step strain function, for example, has a corresponding kernel function $e^{-t/\tau}$ [in Equation (V-2)]. The distribution function $H(\tau)$, however, is independent of the time function at the stress development [i.e., step, impulse, sinusoidal (291,292)]. We use this function $H(\tau)$ to translate the dynamic modulus from the frequency domain to the time domain. A direct experimental verification of this calculated relaxation spectrum $G(t)$ is then possible.

C. METHODS OF EVALUATING THE RELAXATION SPECTRUM $H(\tau)$
FROM THE DYNAMIC MODULUS $G''(\omega)$

The experimental response (modulus) functions take the form of a Fredholm integral equation of the first kind (291). From Equation (V-2) we have for the step strain experiment:

$$G(t) = \int_{-\infty}^{\infty} H(\tau) [e^{-t/\tau}] d \ln \tau$$

For the sinusoidal strain (dynamic) experiment we have

$$G''(\omega) = \int_{-\infty}^{\infty} H(\tau) \left[\frac{\omega\tau}{1 + (\omega\tau)^2} \right] d \ln \tau \quad (V-3)$$

The kernel functions in brackets are associated with the type of stress development (unit step strain and sinusoidal strain). We try to obtain an explicit relation for the material function $H(\tau)$ in terms of the experimental source function $G''(\omega)$ and to integrate this relation to determine the shear relaxation modulus function $G(t)$.

Various approximation methods have been developed to invert the shear relaxation modulus $G(t)$ function to determine the relaxation spectrum $H(\tau)$ (see Appendix A). All of these methods involve only terms of the form $\frac{d^n G}{dt^n}$. The relaxation spectra $H(\tau)$ determined from these methods cannot be used to distinguish relaxation spectra containing an equilibrium modulus value ($G(t) + G_e$) from one without ($G(t)$). We therefore chose not to compare the relaxation spectrum $H(\tau)$ obtained from each source function.

A spectral distribution function $H(t)$ determined from a dynamic response function is properly defined over a time domain which depends upon the range of frequency of the dynamic function. We can integrate the spectral distribution function over this time domain to calculate a shear relaxation modulus function with a corresponding time range.

Tschoegl (291) has developed a generalized method for obtaining the different order approximations to the relaxation spectrum $H(\tau)$ from the dynamic modulus $G''(\omega)$. He uses a logarithmic differential operator $\mathcal{P}_k$ and an associated intensity function I_k to derive previously developed lower order approximations and some new higher order approximations.

$$H_k(\tau, r_0) = \mathcal{P}_k[G''(\omega)] \Big|_{\omega=\frac{1}{\tau}} \quad (V-4)$$

In this case

$$\mathcal{P}_k = a_0'' + \sum_{n=1}^k a_n'' \frac{d^n}{d \ln^n \omega} \quad (V-5)$$

The associated intensity function is

$$I_k(\omega\tau) = \mathcal{P}_k\left[\frac{\omega\tau}{1 + \omega^2\tau^2}\right] \quad (V-6)$$

This function is subject to the normalization condition and that the first (logarithmic) derivative is equal to zero and has a single

positive root. These conditions permit evaluation of the coefficients of the various κ order approximations.

$$H_0(\tau) = \frac{2}{\pi} G''(\omega) \Big|_{\omega = \frac{1}{\tau}} \quad (V-7)$$

$$H_1\left(\frac{\tau}{\sqrt{3}}\right) = \frac{2}{\pi} \left[G''(\omega) + \frac{d G''(\omega)}{d \ln \omega} \right] \Big|_{\omega = \frac{1}{\tau}} \quad (V-8)$$

$$H_1(\sqrt{3} \tau) = \frac{2}{\pi} \left[G''(\omega) - \frac{d G''(\omega)}{d \ln \omega} \right] \Big|_{\omega = \frac{1}{\tau}} \quad (V-9)$$

$$H_2\left(\frac{\tau}{\sqrt{5}}\right) = \frac{2}{\pi} \left[G''(\omega) + \frac{4}{3} \frac{d G''(\omega)}{d \ln \omega} + \frac{1}{3} \frac{d^2 G''(\omega)}{d \ln^2 \omega} \right] \Big|_{\omega = \frac{1}{\tau}} \quad (V-10)$$

$$H_2(\tau) = \frac{2}{\pi} \left[G''(\omega) - \frac{d^2 G''(\omega)}{d \ln^2 \omega} \right] \Big|_{\omega = \frac{1}{\tau}} \quad (V-11)$$

$$H_2(\sqrt{5} \tau) = \frac{2}{\pi} \left[G''(\omega) - \frac{4}{3} \frac{d G''(\omega)}{d \ln \omega} + \frac{1}{3} \frac{d^2 G''(\omega)}{d \ln^2 \omega} \right] \Big|_{\omega = \frac{1}{\tau}} \quad (V-12)$$

Four third order approximations exist but third order differentiation of experimental data is not realistic. The first (V-8, V-9) and third order approximations are due to Tschoegl (291), Schwarzl, and Staverman (252) proposed Equation (V-11). The other second order equations (V-10, V-12) were proposed in the proper form by Okano (210) and Fujita (88) but without the appropriate spectral shift

(factors involving $\sqrt{5}$) and in the case of Fujita without proper normalization of the intensity function. The forms shown here [Equations (V-10) and (V-12)] are due to Tschoegl (291).

D. COMPARISONS OF THE SPECTRAL DISTRIBUTION FUNCTIONS $H(\tau)$ OBTAINED FROM VARIOUS CALCULATION METHODS

The several "order" approximations, in theory, generally approach the limiting true value of the distribution function $H(\tau)$ as the order of the approximation increases. This is seen to be true in the discussions of Tschoegl (291,292) and is generally observed in the various carbon black loaded polystyrene melts.

These spectra were calculated using a polynomial fit of the dynamic loss modulus as in Figure V-1. This has the effect of smoothing out random noise in the data (cf. discussion of Tschoegl (291)). The dynamic data, showing a relatively large change in modulus with frequency, result in significant differences in the relaxation spectra calculated from the different order approximations as shown in Figure V-2.

In general the zeroth order approximation $H_0(\tau)$ (Eq. V-7) results in the highest prediction of $H(\tau)$. The lowest prediction of those compared here is from the approximation of Okano and Fujita $H_{20}(\tau)$ (Eqs. (V-10) (V-12)). The first approximation of Tschoegl $H_{1T}(\tau)$ (Eq. V-9) predicts a lower relaxation distribution spectrum than the second order approximation of Schwarzl and Stavermann $H_{2S}(\tau)$ (Eq. V-11). The differences among the first and second order approximations are small.

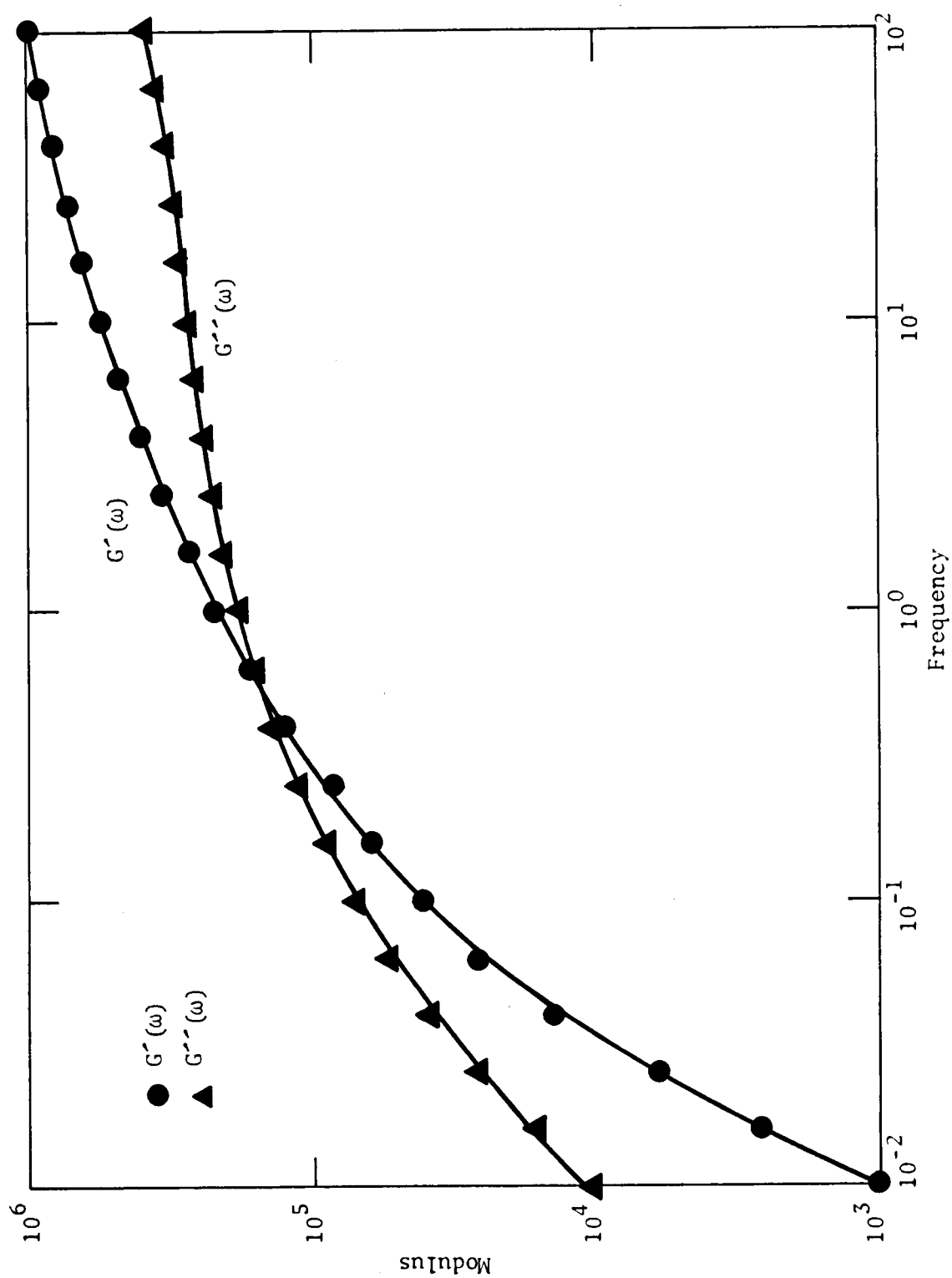


Figure V-1. Polystyrene 678u dynamic moduli at 170°C.

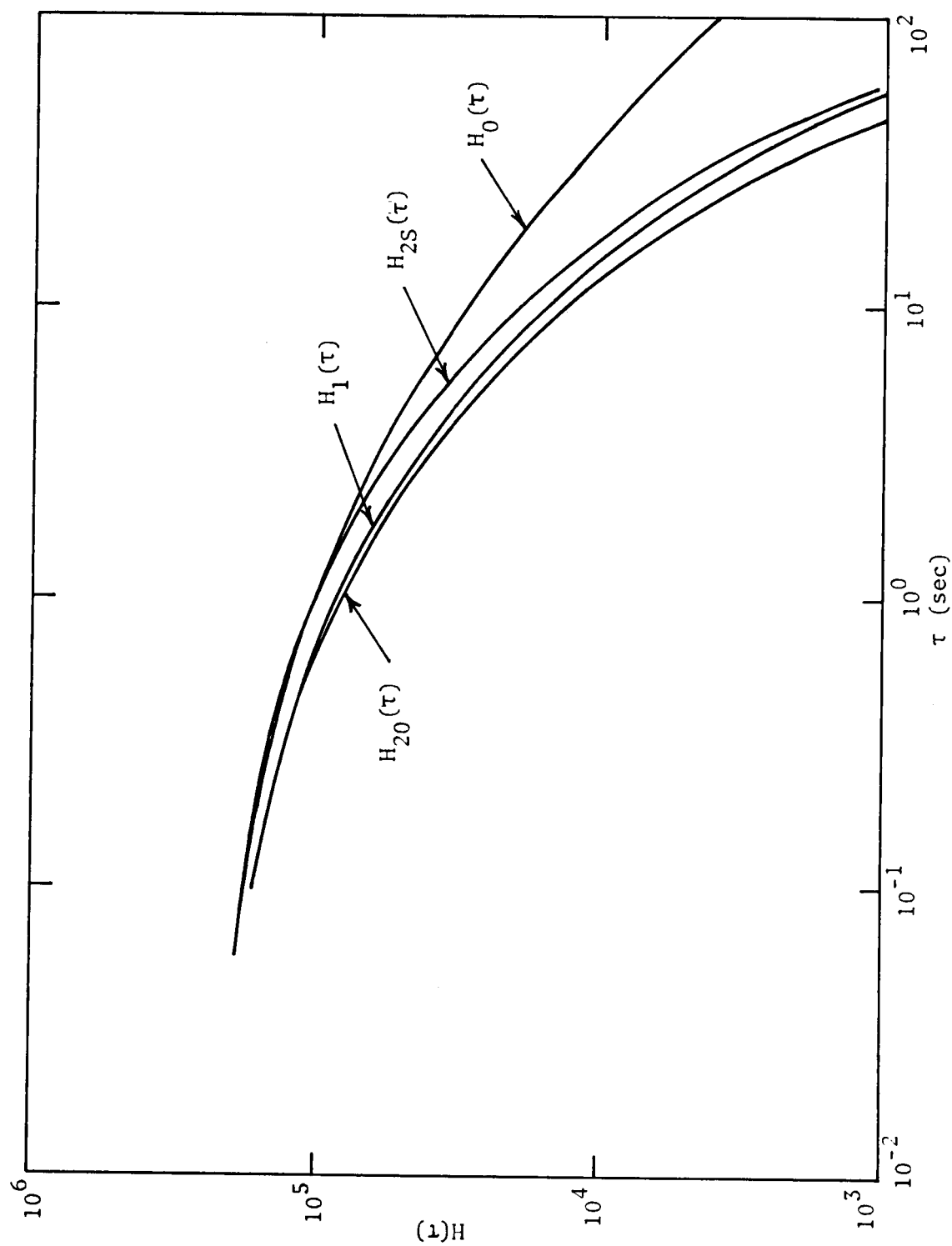


Figure V-2. Polystyrene 678u spectral distribution function at 170°C.

One test of the approximation measure is to compare the integrated spectrum prediction of the zero shear viscosity with the measured zero shear viscosity. This comparison shows that the first approximation of Tschoegl is an adequate description of the data ($\eta_0 = 6 \times 10^5$ poise for the unfilled polystyrene).

E. DETERMINATION OF THE SHEAR RELAXATION MODULUS $G(t)$ FROM THE SPECTRAL DISTRIBUTION FUNCTION $H(\tau)$

Using Equation (V-2) we integrate the spectral distribution function with the appropriate exponential kernel function to obtain the shear relaxation modulus $G(t)$. This calculation is carried out numerically by a Simpson's rule integration and the results are shown by the continuous shear relaxation curve of Figure V-3.

This continuous shear relaxation function is decomposed into the elements of a discrete relaxation spectrum using Tobolsky's "procedure X" (280). This results in the five element pairs (τ_i, G_i) listed in Table V-1. Using these elements in the discrete relaxation exponential sum of Equation (V-2) we obtain the square symbols of Figure V-3. These open symbols virtually trace the entire continuous curve demonstrating an exact representation of shear relaxation modulus by the discrete elements.

These elements contain the information of the small strain experiments. They are used in the next chapter as the small strain, zero loading limit in the interpretation of the large strain, filled system experiments.

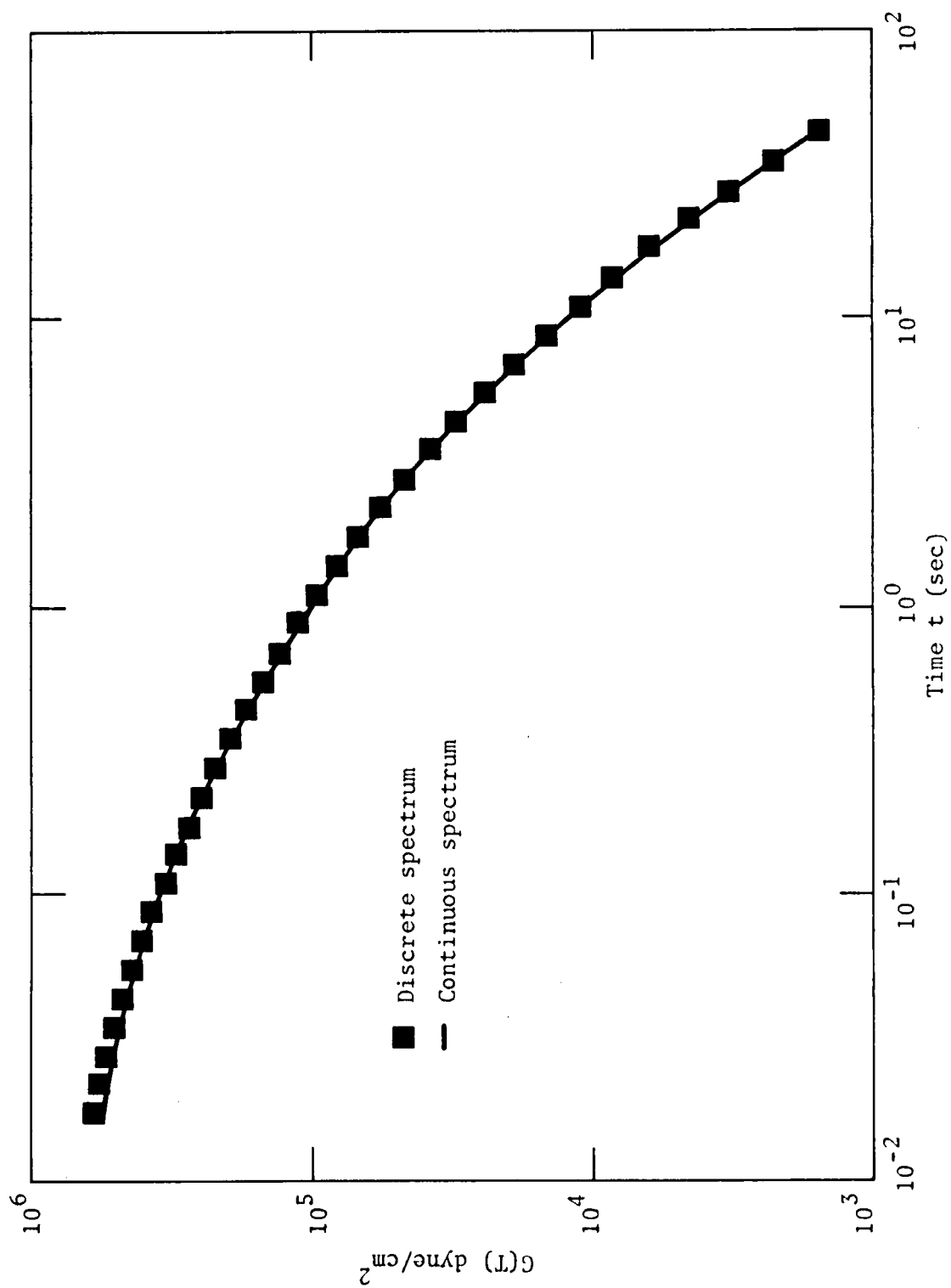


Figure V-3. Polystyrene 678u shear relaxation spectrum at 170°C.

TABLE V-1

DISCRETE RELAXATION SPECTRUM FOR UNFILLED POLYSTYRENE 678U AT 170°C

i	τ_i	G_i
1	2.318E 01	9.872E 03
2	4.587E 00	5.097E 04
3	1.057E 00	1.172E 05
4	2.635E-01	1.842E 05
5	6.286E-02	2.585E 05

CHAPTER VI

INTERPRETATION OF THE NONLINEAR EXPERIMENTAL RESULTS OF CARBON BLACK FILLED POLYSTYRENE MELTS

A. CONSTITUTIVE MODEL: A NONLINEAR THEORY FOR FILLED SYSTEMS

As we have seen in a previous chapter (Figure IV-12, p. 55) the steady state shear viscosity results illustrate apparent yielding values for the highly filled systems. This suggests a representation of the steady shear flow response in terms of a "plastic yielding" type of model. Hohenemser and Prager (238) use a formulation of this type to describe the flow of a Bingham plastic which responds as a linear fluid above the yield value. In this model there is no flow for stresses less than the yield limit $\underline{Y}$.

$$\underline{d} = 0, \text{ for } \text{tr } \underline{T}^2 < 2 \underline{Y}^2 \quad (\text{VI-1})$$

For stresses exceeding the yield threshold the material deforms with a viscous response according to

$$\underline{T} \left(1 - \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } \underline{T}^2}} \right) = 2 \eta_B \underline{d}, \text{ for } \text{tr } \underline{T}^2 \geq 2 \underline{Y}^2 \quad (\text{VI-2})$$

Here $\underline{d}$ is the symmetric rate of deformation tensor with cartesian components

$$d_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (\text{VI-3})$$

The deviatoric stress tensor $\tilde{T}$ is defined by

$$\tilde{T} = \tilde{P} + \frac{1}{3} (\text{tr } \tilde{P}) \tilde{I} \quad (\text{VI-4})$$

The symbol II_P represents the second invariant of the deviatoric stress

$$II_P = \frac{1}{2} \text{tr } \tilde{T}^2 \quad (\text{VI-5})$$

The Hohenemser-Prager equation can be rearranged into a form explicit in stress

$$\tilde{T} = \frac{2 \sqrt{II_P}}{\sqrt{2 \text{tr } \tilde{d}^2}} \tilde{d} + 2 \eta_B \tilde{d} \quad (\text{VI-6})$$

The shear stress is then given by

$$T_{12} = \sqrt{II_P} + \eta_B \dot{\gamma} \quad (\text{VI-7})$$

with apparent viscosity defined by

$$\eta_A = \frac{\sqrt{II_P}}{\dot{\gamma}} + \eta_B \quad (\text{VI-8})$$

Using this type of model we observe the stress P_{12} to have the limit $\sqrt{II_P}$ as the shear rate becomes vanishingly small. In the limit of very low shear rates the viscosity approaches

$$\lim_{\dot{\gamma} \rightarrow 0} \eta = \frac{\overline{\Psi}}{\dot{\gamma}} \quad (\text{VI-9})$$

To describe the shear flow behavior of viscoelastic melts we need to introduce an appropriate viscosity function analogous to the term $2\eta_{B\sim}^d$ in the Hohnemser-Prager form. For this "stress quantity" (denoted H) we suggest as a first approximation a single integral model.

$$H = \frac{\overline{\Psi}}{II_P^2} = \int_0^\infty [\mu_1(z) \tilde{c}^{-1} - \mu_2(z) \tilde{c}] dz \quad (\text{VI-10})$$

Here

$$\tilde{c}^{-1} = c^{-1} - \frac{1}{3} (\text{tr } c^{-1}) I \quad (\text{VI-11})$$

and (VI-11)

$$\tilde{c} = c - \frac{1}{3} (\text{tr } c) I$$

are deviatoric strain measures.

We can rearrange the defining equation (VI-10) to obtain an equation explicit in the stress P by taking the product of the equation with itself and forming the trace.

$$H^2 = \frac{\overline{\Psi}^2}{II_P^2} \left(1 - \frac{\overline{\Psi}}{II_P^2}\right)^2 \quad (\text{VI-12})$$

$$\text{tr } \tilde{H}^2 = \text{tr } \tilde{T}^2 \frac{(\text{II}_P^{\frac{1}{2}} - \tilde{Y})^2}{\text{II}_P} \quad (\text{VI-13})$$

Since $\text{II}_P \equiv \frac{1}{2} \text{tr } \tilde{T}^2$ we have

$$\frac{1}{2} \text{tr } \tilde{H}^2 = (\text{II}_P^{\frac{1}{2}} - \tilde{Y})^2 \quad (\text{VI-14})$$

or

$$\text{II}_P^{\frac{1}{2}} = \sqrt{\frac{1}{2} \text{tr } \tilde{H}^2} + \tilde{Y} \quad (\text{VI-15})$$

Hence

$$\tilde{H} = \tilde{T} \left(1 - \frac{\tilde{Y}}{\sqrt{\frac{1}{2} \text{tr } \tilde{H}^2} + \tilde{Y}} \right) \quad (\text{VI-16})$$

and

$$\tilde{T} = \left(1 + \frac{\tilde{Y}}{\sqrt{\frac{1}{2} \text{tr } \tilde{H}^2}} \right) \tilde{H} \quad (\text{VI-17})$$

This equation can be further modified to identify contributions to the stress made by the filler and by the polymer matrix. This is accomplished by examining the memory function $\mu(z)$ of Equation (VI-10).

The memory function $\mu(z)$ may, as a first approximation, be taken as

$$\mu(z) = \sum_{i=1}^n \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}}$$

$$\mu_1(z) = (1 + \frac{\epsilon}{2}) \mu(z) \quad (\text{VI-18})$$

$$\mu_2(z) = (-\frac{\epsilon}{2}) \mu(z)$$

We now come to the question as to how the $\mu_1(z)$ of the compounds relate to the $\mu_1(z)$ of the pure melt matrix. On the basis of theories of hydrodynamic interaction of modulus increase following Guth (105) we may see that G_i increases with volume loading. This is not true for the τ_i values. The filled system parameters will therefore be written

$$G_i = G_i^0 g(\phi)$$

$$\tau_i = \tau_i^0$$

where $(^0)$ denotes the parameters of the unfilled system.

The memory function $\mu(z)$ (and therefore the stress measure $\tilde{H}$) is linear in the function $g(\phi)$.

$$\begin{aligned} \tilde{H} &= \int_0^\infty \sum \frac{g(\phi) G_i^0 e^{-z/\tau_{i\text{eff}}}}{\tau_{i\text{eff}}^0} [(1 + \frac{\epsilon}{2}) \tilde{c}^{-1} - (\frac{-\epsilon}{2}) \tilde{c}] dz \\ &= g(\phi) \tilde{H}_0 \end{aligned} \quad (\text{VI-20})$$

We can therefore represent Equation (VI-17) by

$$\underline{\tau} = (g(\phi) + \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } \underline{H}_0^2}}) \underline{H}_0 \quad (\text{VI-21})$$

We use this expression as the basis for the interpretation of the nonlinear deformation experiments. The following two sections demonstrate that the constitutive model, with suitable characterization of the memory function $\mu(z)$ and yielding function $\underline{Y}(\phi)$ can be used in a unified, consistent interpretation of the experimental results presented in Chapter IV.

B. COMPARISON BETWEEN THEORY AND EXPERIMENT FOR UNFILLED MELTS IN LARGE STRAIN EXPERIMENTS

In the development of the theory for filled systems we see that the stress is determined by a "stress measure" $\underline{H}_0$ for the unfilled system, a hydrodynamic factor $g(\phi)$ and an apparent yield value $\underline{Y}(\phi)$. Before evaluating the filled system parameters $\underline{Y}$ and $g(\phi)$ we examine the ability of the unfilled constitutive model to describe data in a broad range of experiments. This involves determination of the best form of $\tau_{i\text{eff}}^0$ (II_d) in fitting the entire set of experiments. This is equivalent to examining the $\underline{H}_0$ function for the limit of $\phi = 0$ (i.e., $g(\phi) = 1$, $\underline{Y} = 0$).

Figure VI-1 shows the comparison of the theory and experiment for the unfilled polystyrene melt in a steady state shearing deformation. Here we have fit the data using the model for effective relaxation time $\tau_{i\text{eff}}$ as

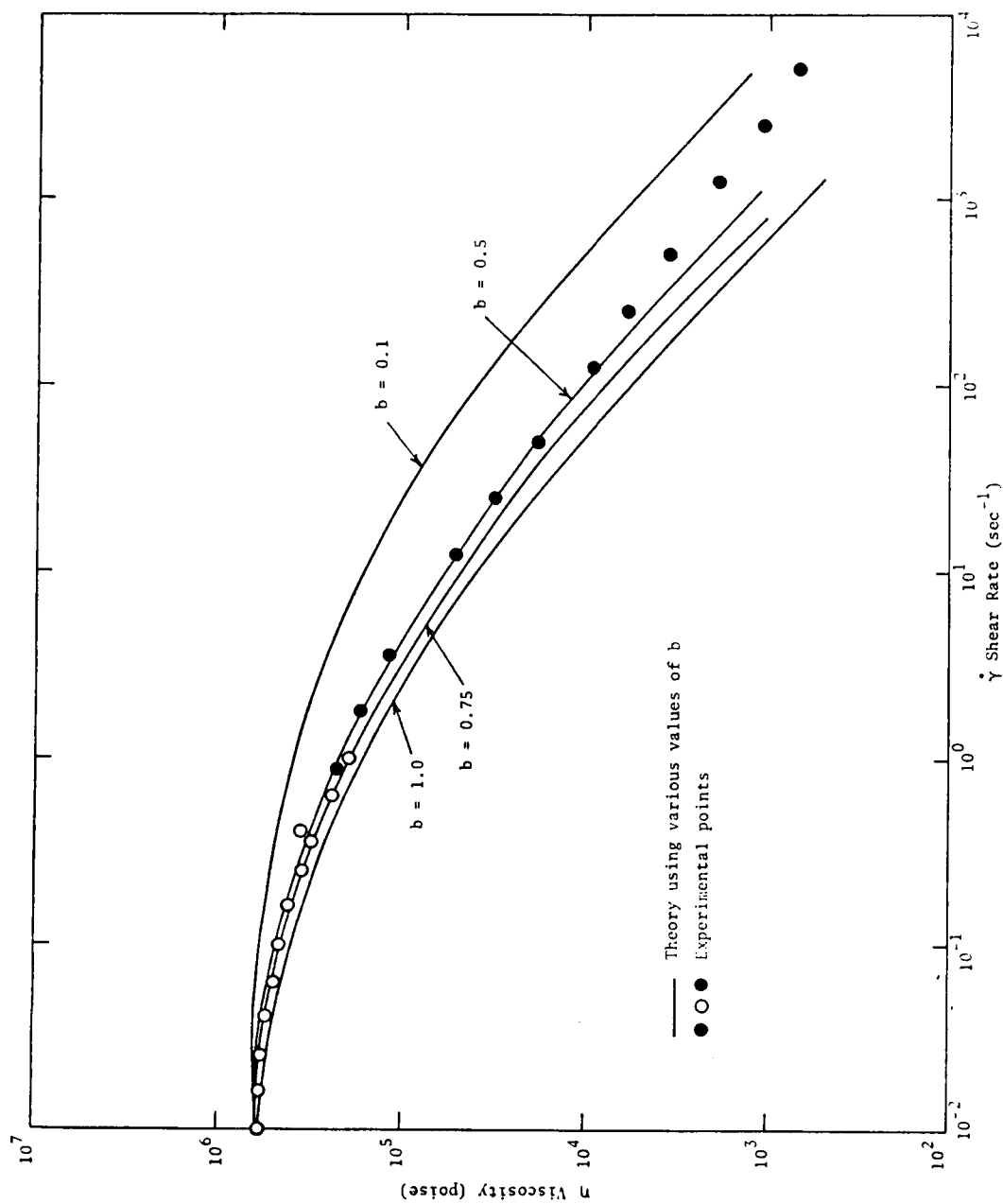


Figure VI-1-1. Theory and experiments for polystyrene 678u steady state shear viscosity at 170°C.

$$\tau_{i\text{eff}} = \frac{\tau_{i0}}{1 + b \dot{\gamma} \tau_{i0}} \quad (\text{VI-22})$$

The symbols (circles) represent experimental data from cone and plate and capillary rheometers. The continuous curve represents the theory determined using values of the b parameter of 0.5, 0.75, 1.0. The parameter b represents the stress sensitivity to deformation rate. Figure VI-1 shows that higher values of the parameter cause the viscosity function to decrease more rapidly with deformation rate. The value 0.5 is determined as the best fit parameter for this experiment.

The earlier data of Chen (56,57) shows a fit parameter of 0.99 for a similar polystyrene at 200°C. His value suggests a faster drop off of viscosity with shear rate than represented by these experiments. His data were obtained using only the cone and plate rheometer and may reflect inherent instabilities in the cone and plate experiment at higher shear rates. These difficulties are obviated by the use of capillary data which are coincident with the cone and plate data at lower rates and slightly higher at the high shear rate limit of the cone and plate data. The theory is represented in the steady state shear case by

$$\tau_{12} = \left(\sum_{i=1}^n \frac{G_i^0 \tau_i^0}{1 + b \dot{\gamma} \tau_i^0} \right) \dot{\gamma} = H_{12}^0 \quad (\text{VI-23})$$

One observes that the sensitivity of the fit of the theory to experiments is greatest for small values of the b parameter. Final determination of the best parameter to fit all experiments may result in larger values of the b parameter than 0.5 without substantial deviation in the fit.

Figure VI-2 shows the primary normal stress plotted against shear stress for steady state shearing deformations in the cone and plate geometry (open circles). The continuous lines represent the theory predictions for a range of parameter (b) values from $b = 0.5$ to $b = 1.0$ for the H_0 function

$$N_1 = H_{11}^0 - H_{22}^0 = \int 2G_i^0 \left(\frac{\tau_i^0 \dot{\gamma}}{1 + b \dot{\gamma} \tau_i^0} \right)^2 \quad (VI-24)$$

It is more difficult to access the ability of the H_0 function to fit the unfilled normal stress data since the range of deformation rates for the normal stress data is limited to only two decades in shear rate. This is because the normal stress data was only obtained using cone and plate experiments which are valid in the decades of 10^{-2} to 10^0 sec^{-1} .

As in the data of Chen (56,57) we observe values of the b parameter near 0.5 as providing the best description of the normal stress data. While slightly lower values may provide a marginally improved fit of this data, the lower values (i.e., $b = 0.1$) have a significant influence on the shear viscosity predictions which become too large at high deformation rates. In view of the shear and normal stress data we would conclude that the best value of the b parameter is 0.5.

In the case of constant extension rate experiments there may be some question as to the existence of the "steady state" extensional response. We show here the transient development of stresses in constant extension rate experiments for the purpose of establishing an

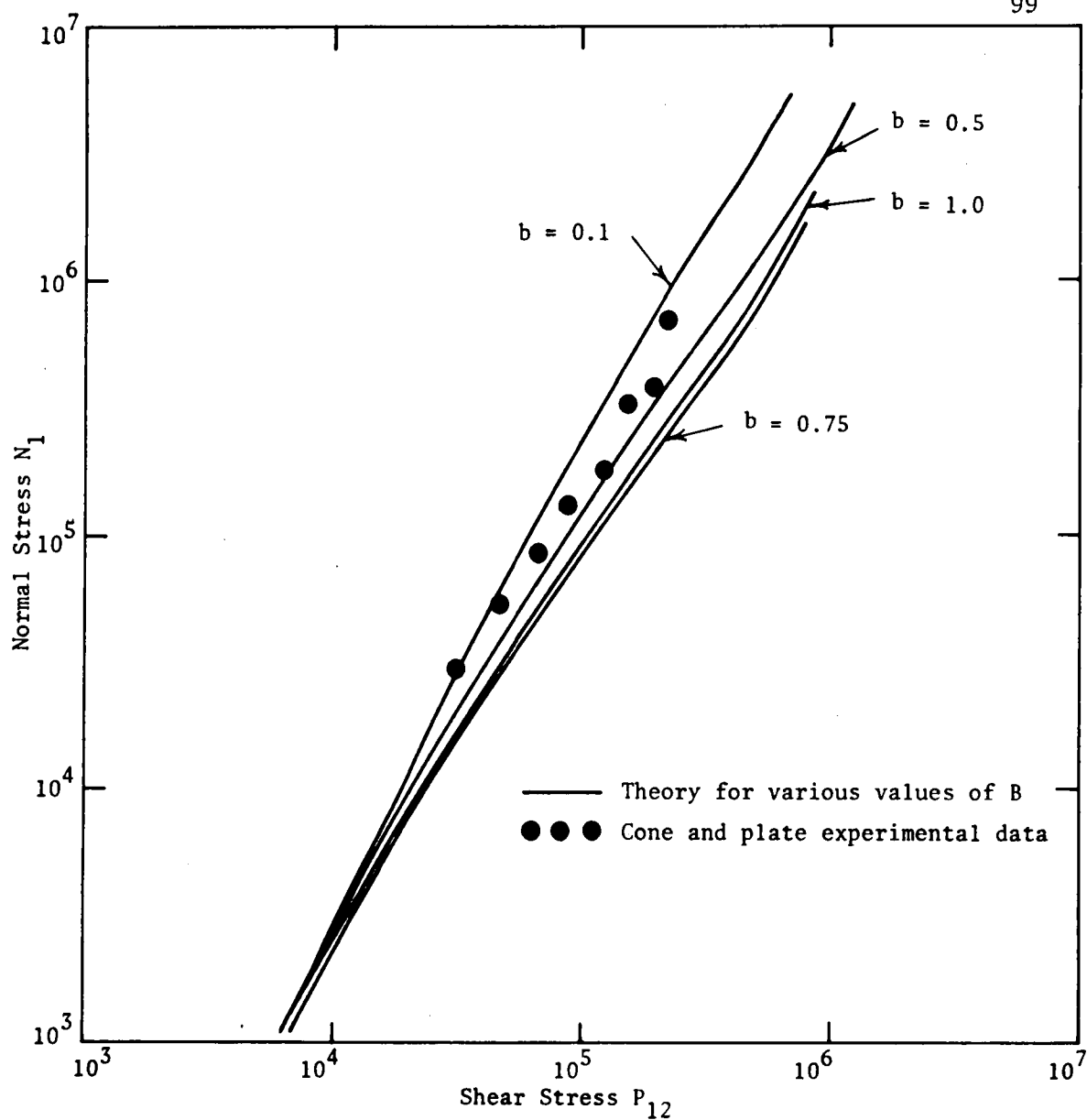


Figure VI-2. Theory and experiments for polystyrene 678u primary normal stress difference at 170°C.

optimum value of the parameter b . In later experiments with filled systems we use the more apparent steady state values of extensional viscosity. The theory shown in Figures VI-3 through VI-6 compares most favorably with the data for values of b of 0.1 (Figure VI-4).

These figures illustrate the critical nature of the response of the theory to the interaction parameter b and the maximum relaxation time τ_m . The critical value of the extension rate $\dot{E}_c$ representing the limit of steady state response is related to the interaction parameter b and the maximum relaxation time τ_m by:

$$\dot{E}_c = \frac{1}{\tau_m (2 - b\sqrt{3})} \quad (\text{VI-25})$$

The parameter b must have values between 0 and 1.15. Larger values of b in this range correspond to theory predictions of steady state extensional viscosity over a broader range of extension rates for the same τ_m . It is apparent from Equation (VI-25) that the determination of the value of τ_m is important in the determination of the value of the critical extension rate.

By examining the entire range of measured extension rates we would conclude that the best fit of both high and low rates is obtained using the value of b parameter of 0.5. This compares favorably with that obtained in shearing experiments and represents the optimum compromise for the set of experiments used to determine the function H_0 .

As shown in Figures VI-7 through VI-9 this value of b in the function represents a representation of all of the experimental data.

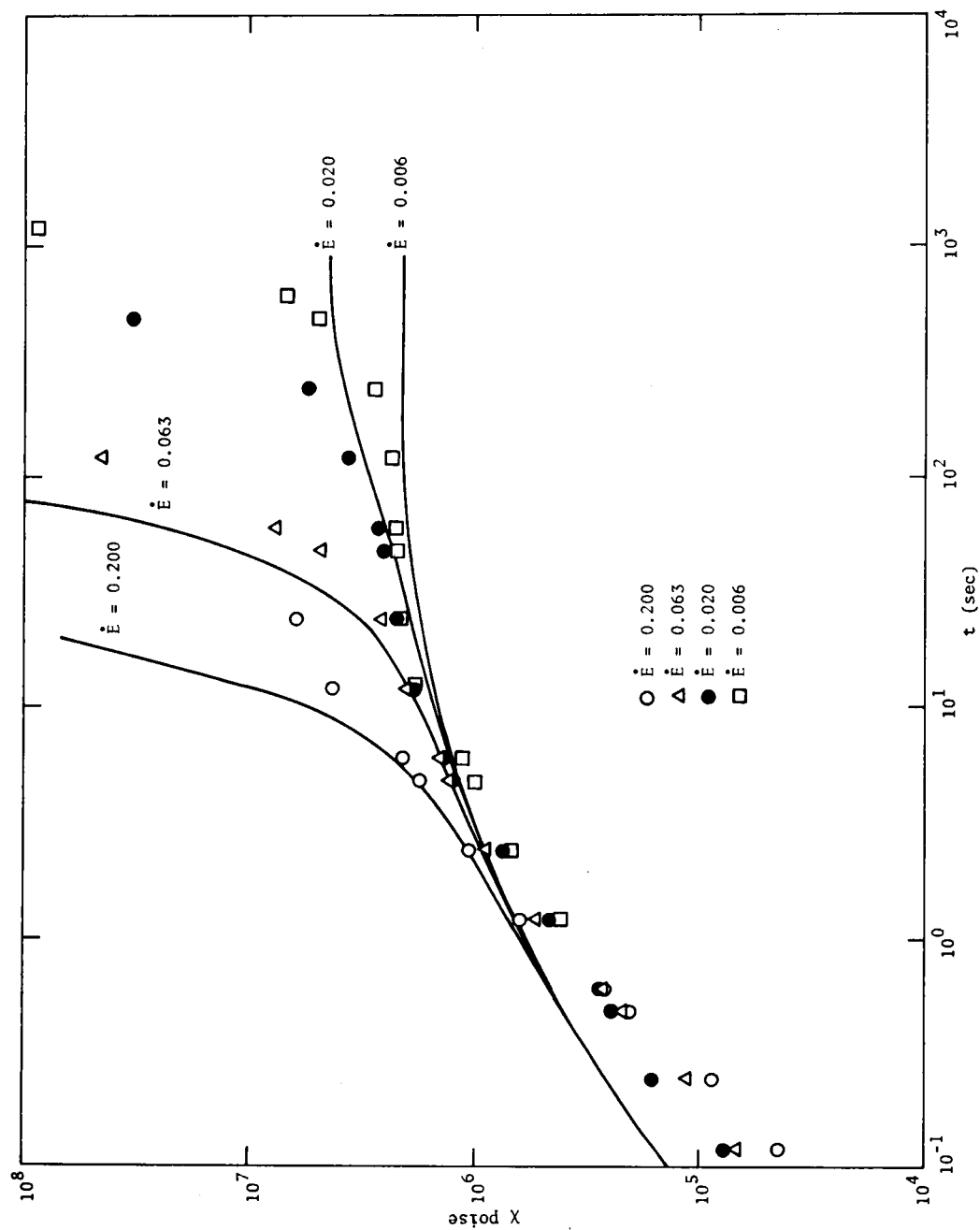


Figure VI-3. Theory parameter $b = 0.1$ and experiments for polystyrene 678u transient extensional viscosity at 170°C.

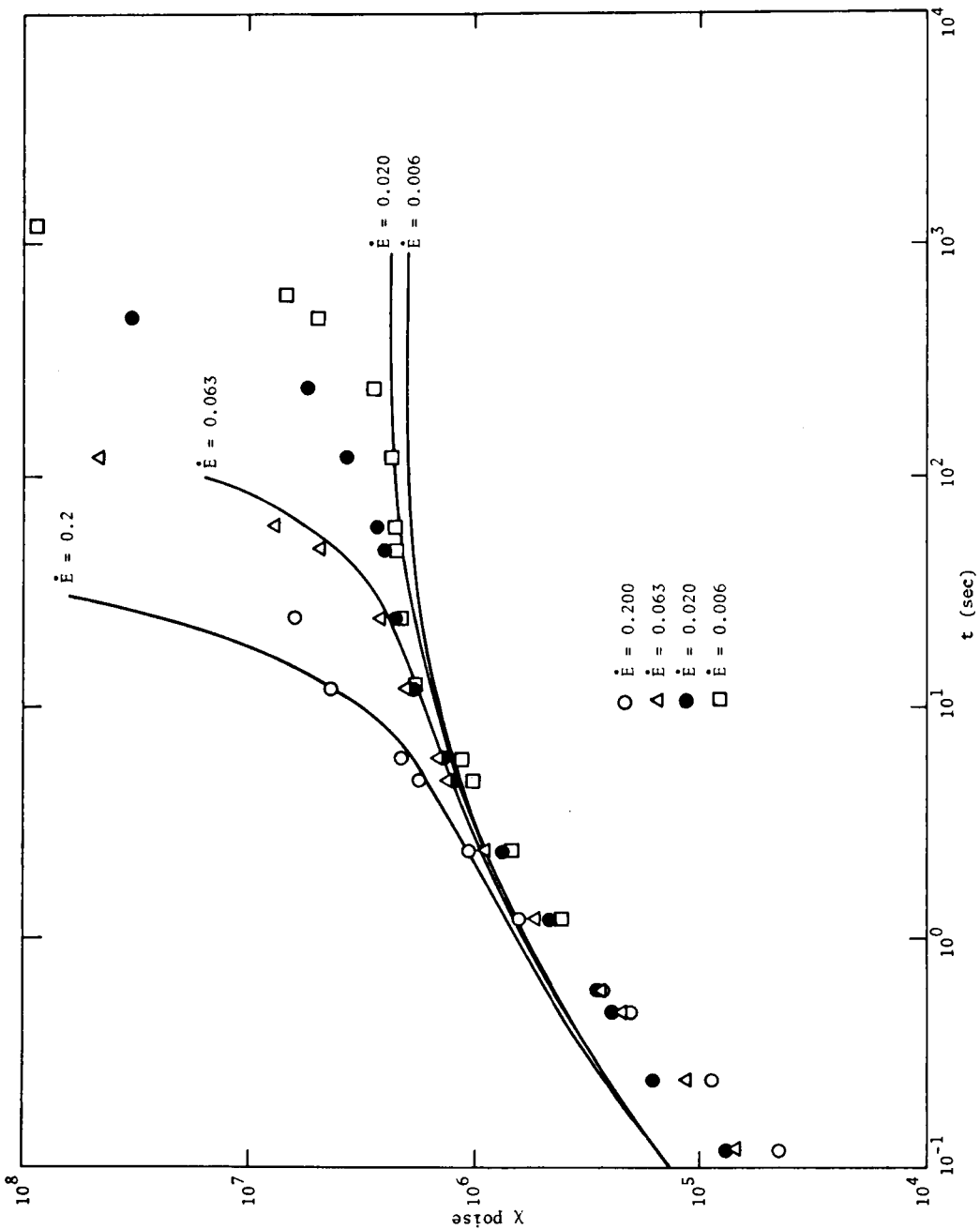


Figure VI-4. Theory parameter $b = 0.5$ and experiments for polystyrene 678u transient extensional viscosity at 170°C.

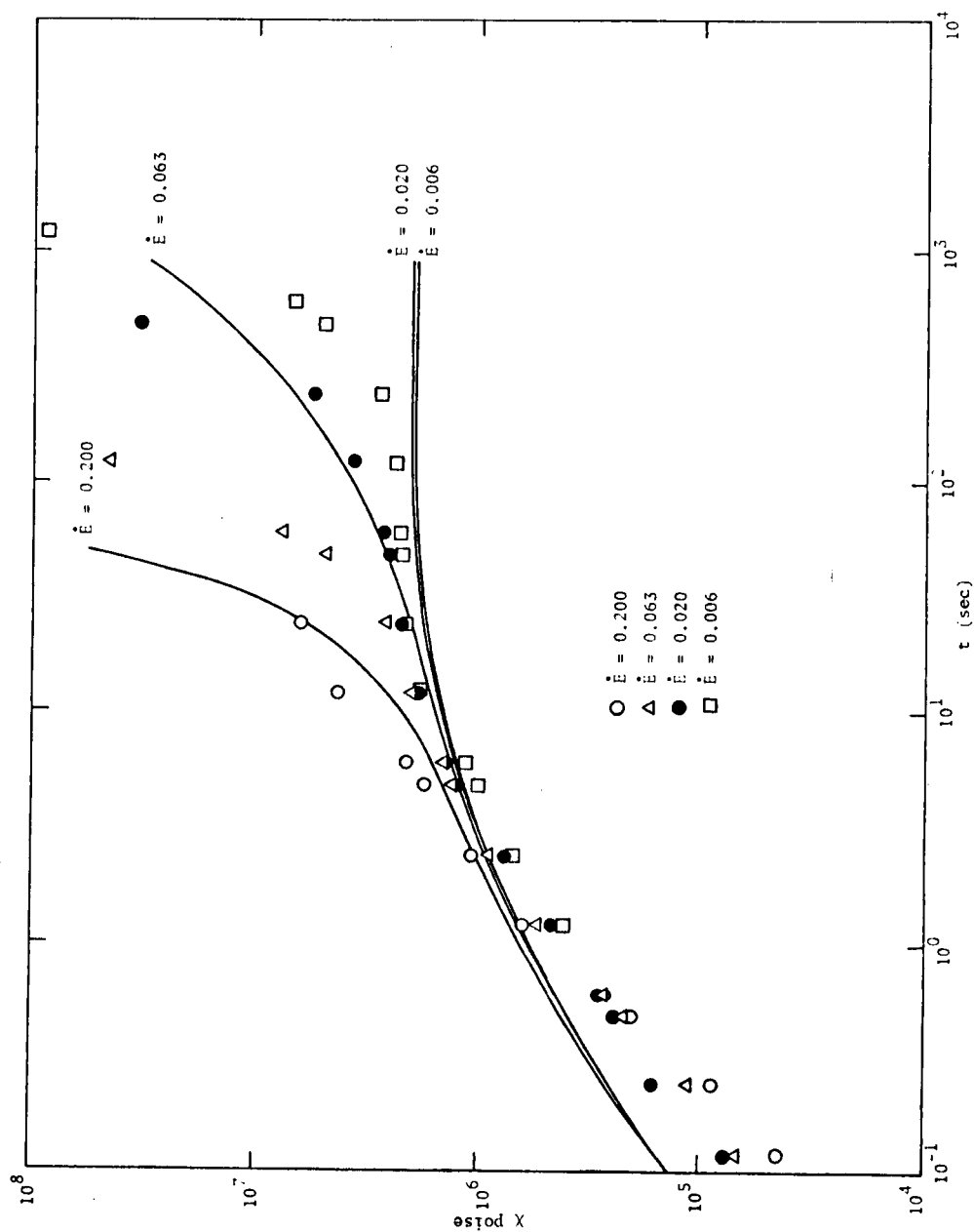


Figure VI-5. Theory parameter $b = 0.75$ and experiments for polystyrene 678u transient extensional viscosity at 170°C .

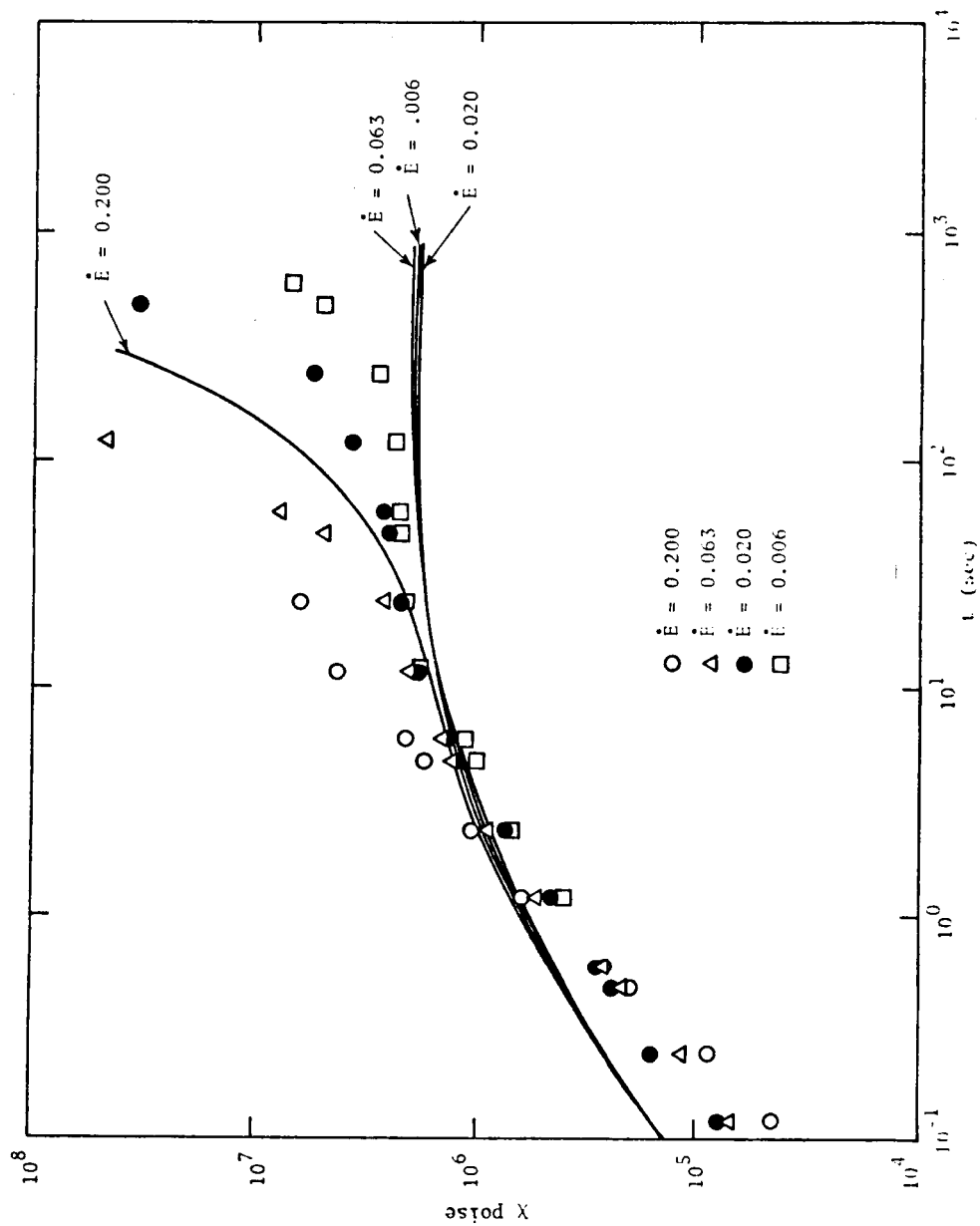


Figure VI-6. Theory parameter $b = 1.0$ and experiments for polystyrene 678u transient extensional viscosity at 170°C.

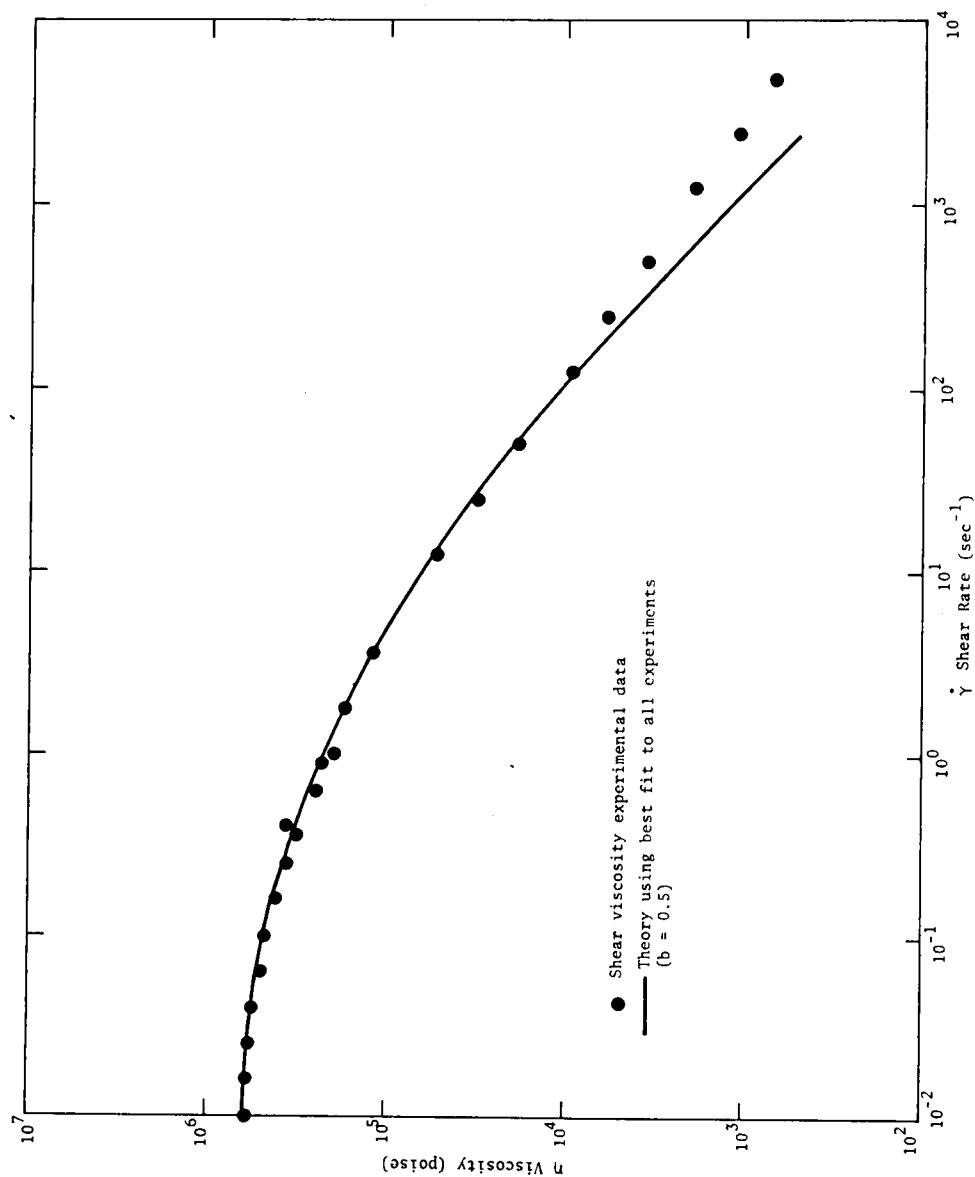


Figure VI-7. Best fit theory $b = 0.5$ and experiments for polystyrene 678u steady state shear viscosity at 170°C.

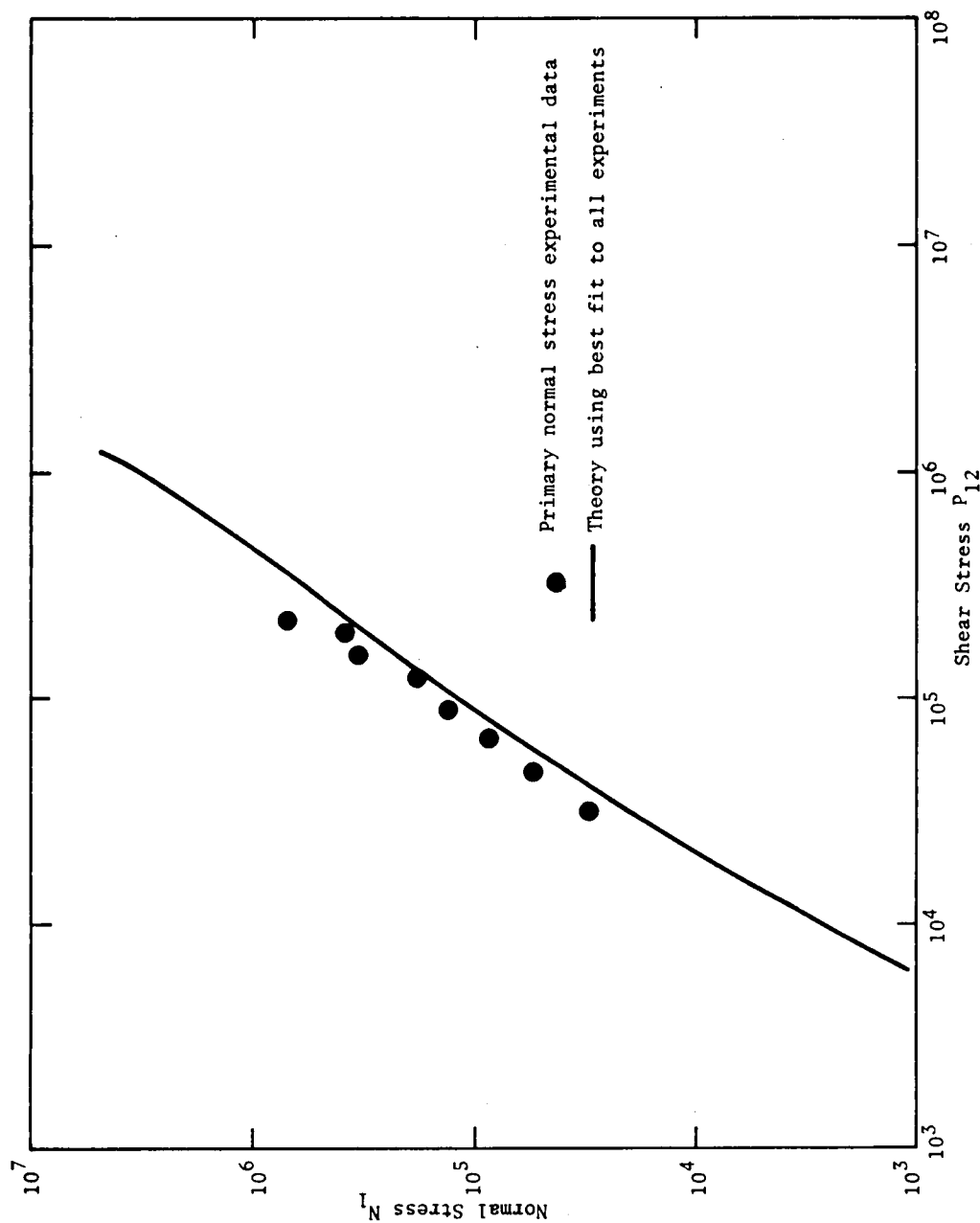


Figure VI-8. Best fit theory $b = 0.5$ and experiments for polystyrene 678u primary normal stress difference at 170°C.

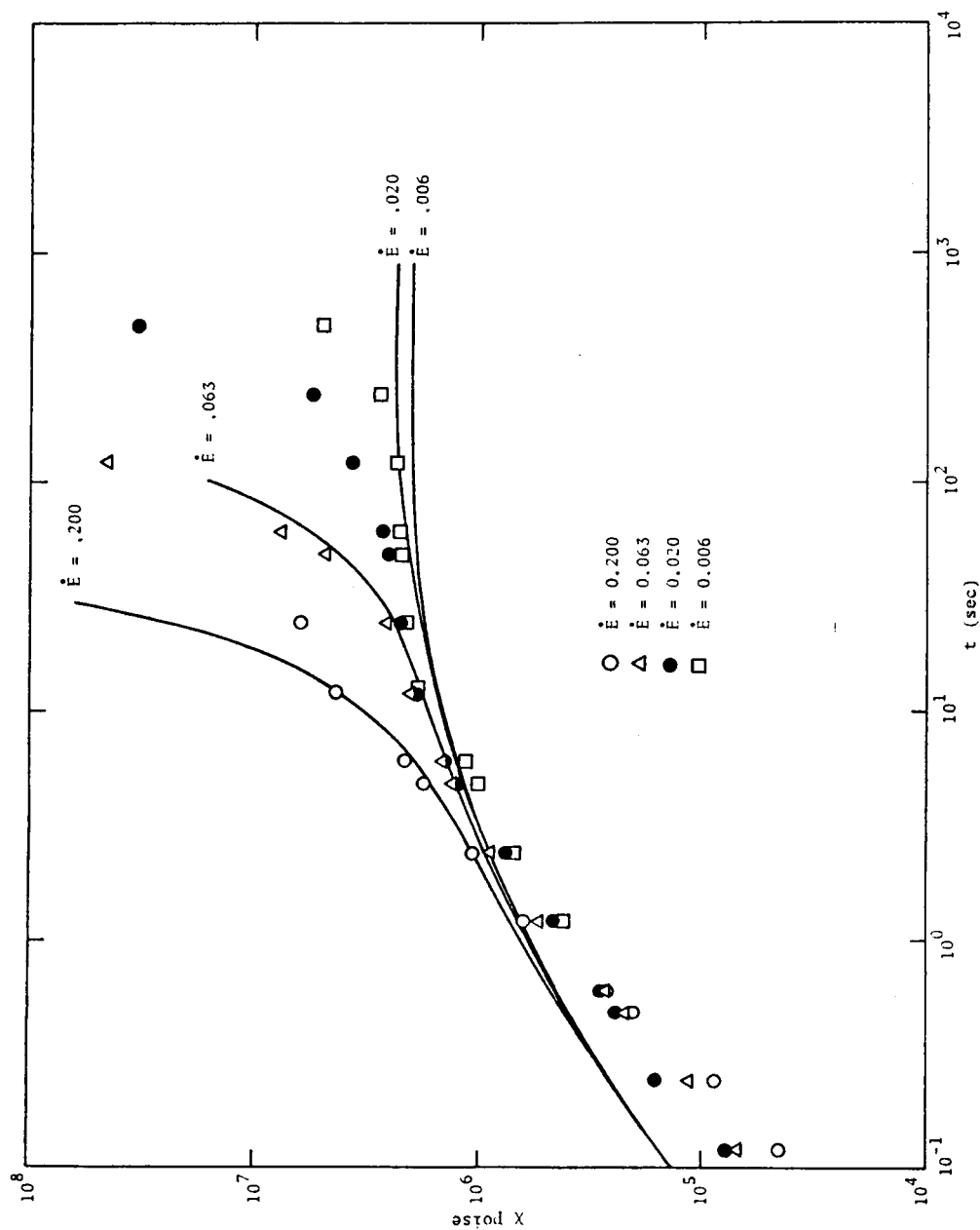


Figure VI-9. Best fit theory $b = 0.5$ and experiments for polystyrene 678u transient extensional viscosity at 170°C .

This is the best representation we could expect of data on filled systems based on the constitutive form.

C. DETERMINATION OF THE FILLED SYSTEM PARAMETERS $g(\phi)$
AND $\Upsilon(\phi)$ BY COMPARISON OF THEORY AND EXPERIMENTS
OF FILLED MELTS

Having provided a description of the linear and nonlinear response of the matrix material through evaluation of the "stress quantity" H_0 , we proceed to examine the effect of the filler particles on the nonlinear stress response. The hydrodynamic factor $g(\phi)$ is determined from theories of filled systems and the apparent yielding value $\Upsilon(\phi)$ is determined using several nonlinear deformation responses. The theory is compared with the experiments for each of the several deformation responses and best values for $\Upsilon(\phi)$ are determined.

The function $g(\phi)$ represents a noninteractive hydrodynamic factor due to the presence of filler particles. The function must have the value 1.0 in the limit of zero loading. The Mooney equation (186) has this appropriate low loading limit and was devised to also model the highly concentrated systems. The theories of Simha (256) and Frankel and Acrivos (86) were devised to explain the viscosity phenomena of high concentrations by all models but do not have the appropriate low loading limit for the function $g(\phi)$ used here. We use the Mooney equation with typical parameter value $K = 2.4$ to estimate the hydrodynamic factor $g(\phi)$ for the filled systems. This function is compared with the Frankel-Acrivos and Simha theories in Table VI and Figure VI-10. The Mooney values for $g(\phi)$ are intermediate to the other two theory values for highly filled systems.

TABLE VI-I
HYDRODYNAMIC INTERACTION TERM $g(\phi)$ CALCULATED FROM THEORIES

ϕ	Theory		
	Frankel-Acrivos	Mooney	Simha
0	0	1	0
.05	1.03	1.15	0.026
.10	1.70	1.39	0.158
.20	3.50	2.66	1.68
.25	5.00	5.00	5.00
Constant	$\phi_m = 0.46$	$K = 2.4$	$f = 1.12$
$g(\phi)$	$\frac{9}{8} \frac{\left(\frac{\phi}{\phi_m}\right)^{1/3}}{\left[1 - \left(\frac{\phi}{\phi_m}\right)^{1/3}\right]}$	$e^{\frac{2.5\phi}{1-K\phi}}$	$\frac{54}{4f^3} \frac{\phi^2}{\left(1 - \frac{\phi}{\phi_m}\right)^3}$

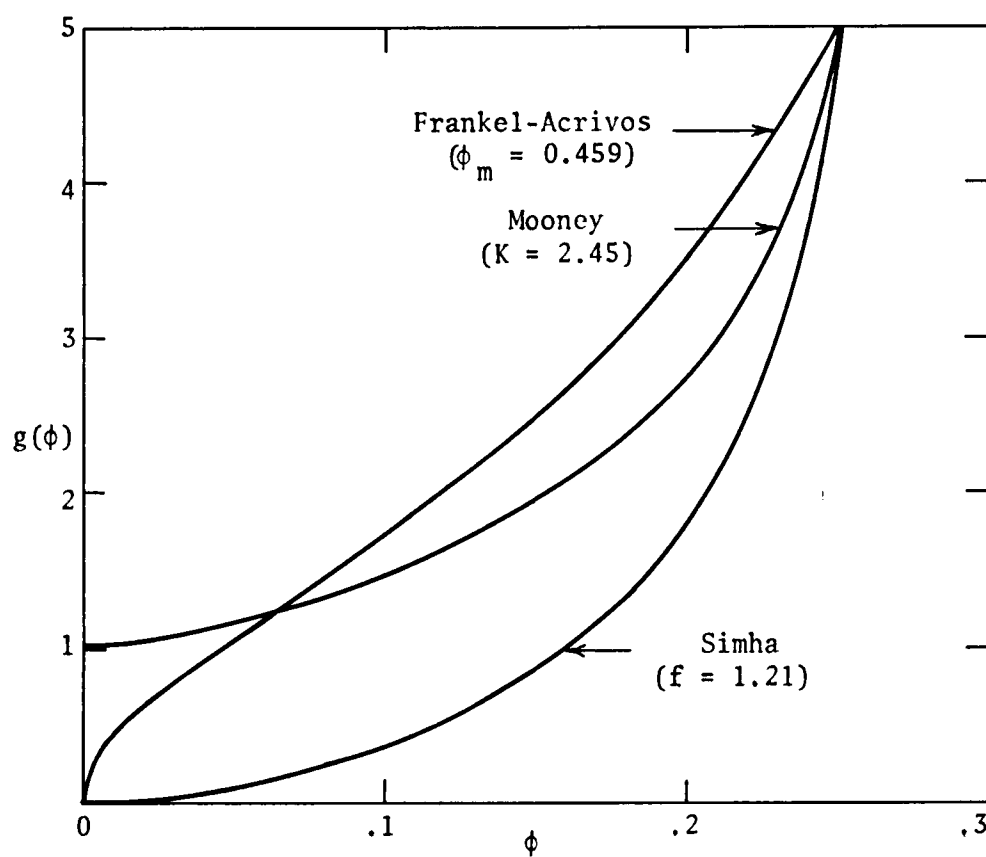


Figure VI-10. Hydrodynamic factor as a function of volume loading for various theories.

We can evaluate the constitutive model VI-21 for a more specific case of filled systems in steady state shear flows.

$$T_{12} = \left[g(\phi) + \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } H_o^2}} \right] \left(\sum_{i=1}^n \frac{G_i^o \tau_i^o \dot{\gamma}}{1 + b \dot{\gamma} \tau_i^o} \right) \quad (\text{VI-26})$$

The apparent shear viscosity ($\eta = \frac{P_{12}}{\dot{\gamma}}$) is plotted as a function of shear rate in Figure VI-11. The value $\underline{Y}$ for each loading ϕ is selected so that the theoretical curve most closely matches the experimental results. The effect of the yielding value is more dramatically illustrated in Figure VI-12 where the same shear viscosity data are plotted against shear stress. The yield values markedly increase with small increases in volume loadings over ten volume percent as illustrated in Table VI-2.

Using the tabulated parameters (Tables V-1, p. 89, VI-1 and VI-2) and the appropriate strain kinematics in the constitutive model (Eq. VI-21) we obtain the predictions for the primary normal stress difference in shearing flows illustrated in Figure VI-13. The resulting equation for this flow is

$$T_{11} - T_{22} = \left[g(\phi) + \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } H_o^2}} \right] \sum 2G_i (\tau_{i\text{eff}} \dot{\gamma})^2 \quad (\text{VI-27})$$

The data seem in fair agreement with the theory predictions but are not extensive enough to provide validation of the theory for a broad range

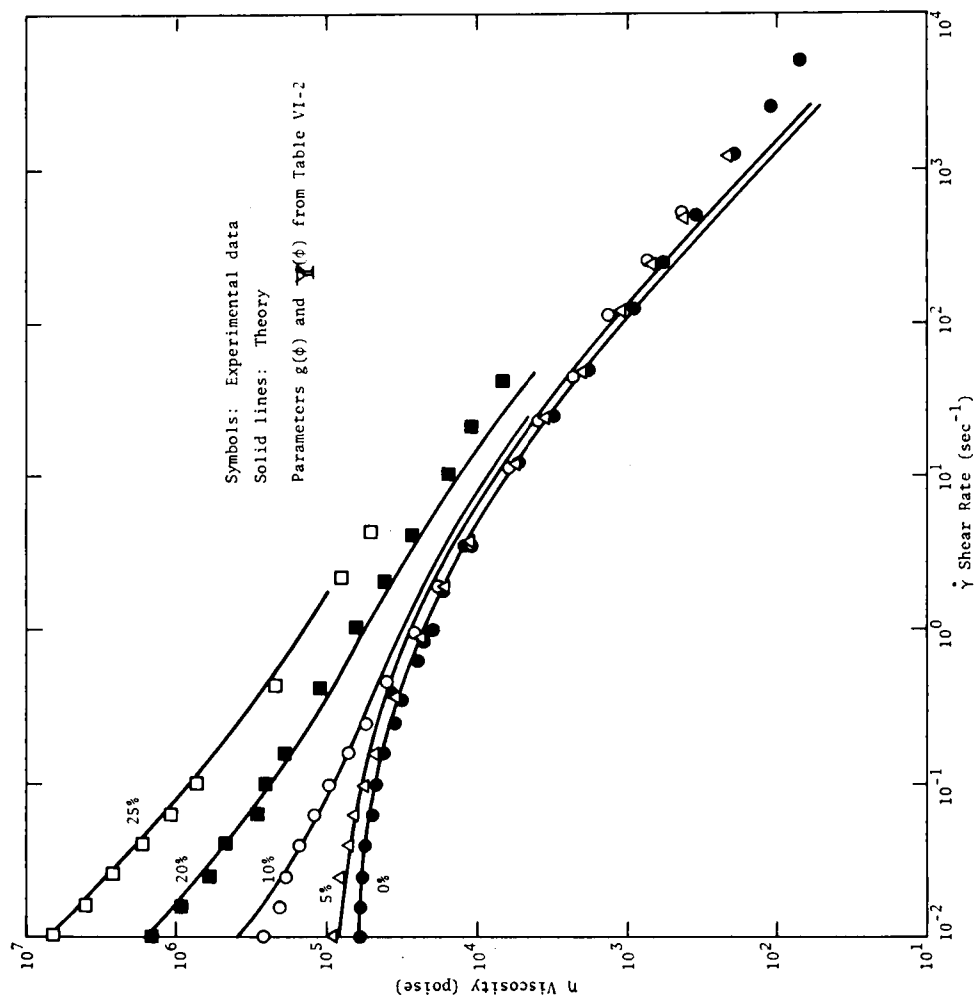


Figure VI-11. Shear viscosity as a function of shear rate theory and experiments for N110/PS678u at 170°C.

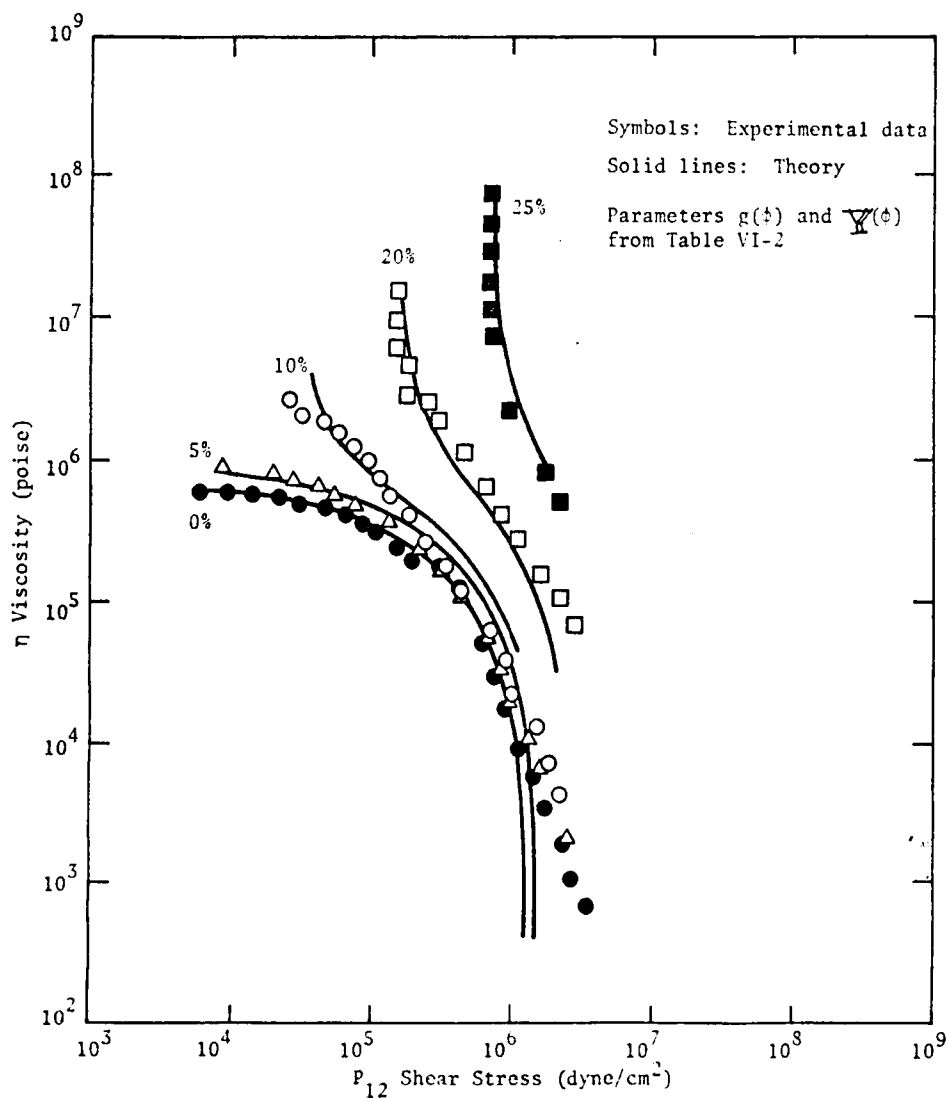


Figure VI-12. Shear viscosity as a function of shear stress theory and experiments for N110/PS678u at 170°C.

TABLE VI-2

YIELD VALUES FOR CARBON BLACK FILLED POLYSTYRENE MELTS
DETERMINED FROM SHEAR EXPERIMENTS AT 170°C

ϕ % by vol.	$\bar{Y}$ dynes/cm ²
0	0
5	8.00×10^2
10	3.00×10^4
20	1.5×10^5
25	7×10^5

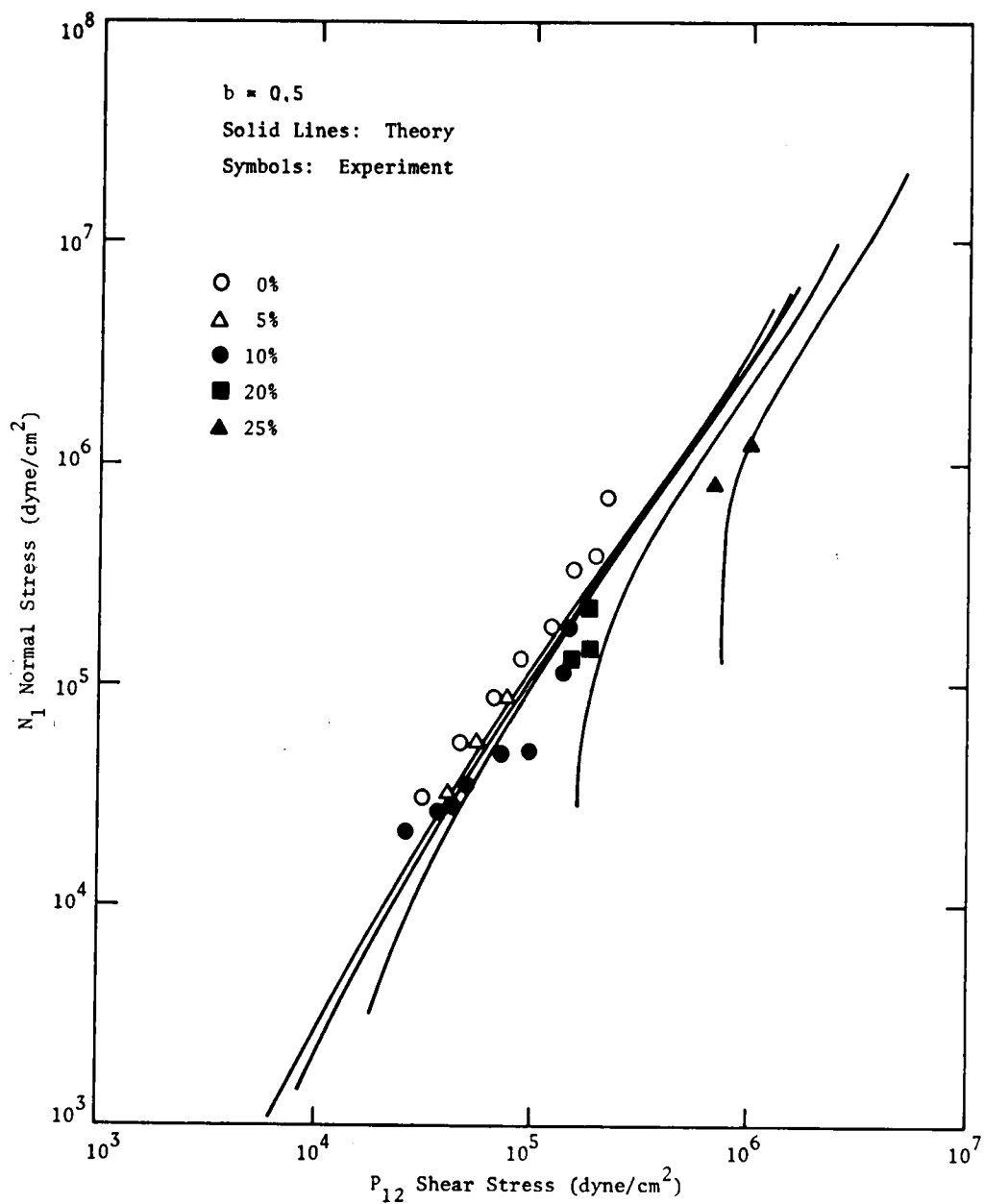


Figure VI-13. Normal stress as a function of shear stress theory and experiments for N110/PS678u at 170°C.

in stress and filler loading. Alternative values of the yield values do not provide discernably better fit of the data.

The transient extensional viscosity data for the highly filled systems (Figures IV-25 and IV-26, pp. 71, 72) appear to reach a steady state plateau over the range of deformation rates $\dot{E} = 6 \times 10^{-3}$ to $\dot{E} = 2 \times 10^{-1}$. We can replot this data in terms of extensional viscosity and tensile stress (Figure VI-14). This experimental data is compared with the constitutive model (Eq. V-21) evaluated for the steady state constant extension rate deformation.

$$P_{11} - P_{22} = \sqrt{3} \underline{Y} + 3g(\phi) \left(\sum_{i=1}^n \frac{G_i \tau_{i\text{eff}} \dot{E}}{(1 + \tau_{i\text{eff}} \dot{E})(1 - 2\tau_{i\text{eff}} \dot{E})} \right) \quad \text{VI-28}$$

While the theoretical parameters b , $g(\phi)$ and $\underline{Y}$ of this figure are the same as those determined to be optimum for shearing deformations (Tables V-1, VI-1, VI-2, pp. 89, 109, 114) we may use values better fit to this extensional deformation. The influence of changes in the parameters b and $\underline{Y}(\phi)$ are seen to improve the fit of the theory to the experiment and are discussed here.

Using Eq. VI-22 we can determine the critical deformation rate ($\dot{E}_c$). For deformation rates lower than $\dot{E}_c$ the theory predicts a steady state value in the transient stress development. For larger rates the stresses are predicted to increase without bound. The value of the critical deformation rate is determined by the maximum relaxation time (τ_m) and the value of the parameter b of the model.

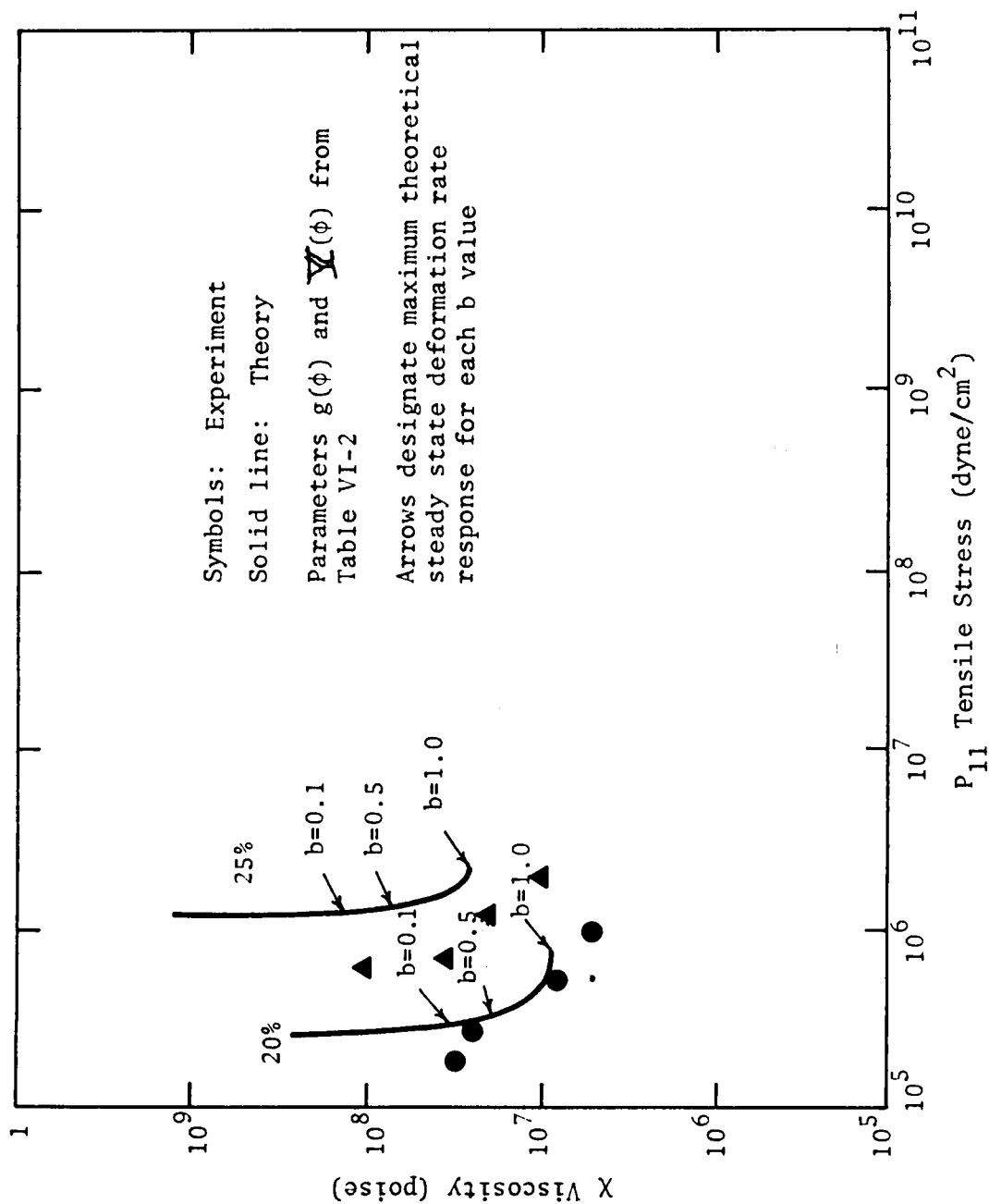


Figure VI-14. Steady state extensional viscosity theory and experiments for N110/PS678u at 170°C.

Larger values of the parameter b result in larger values of critical rate $\dot{E}_c$ for equivalent relaxation time τ_m . For example, for values of b of .1, .5 and 1.0 we would calculate values of $\dot{E}_c$ as .02, .04 and .16 for $\tau_m = 23.5$.

The theoretical extensional viscosity curve as a function of tensile stress is "u" shaped. The position of the minimum proceeds to lower values in viscosity and higher values in tensile stress as the critical extension rate increases (by increasing the value of the parameter b). The viscosity function increases at low values of tensile stress (with lower values of extension rate) due to the predominant influence of the yield function $\Psi(\phi)$. In this limit the effect of the b parameter is not apparent.

Questions of whether the observed "apparent" steady state viscosity is real (extends indefinitely with time) or not cannot be unequivocally resolved by any experimental apparatus at this time. We therefore would not change the value of the b parameter determined from other methods (i.e., various experiments in the unfilled system) to extend the range of theoretically steady extensional viscosity.

The position of the apparent yield value in extension is more critical than increasing the value of $\dot{E}_c$. The yield values in the extensional experiment of 1×10^5 (20%) and 3×10^5 (25%) dynes/cm² appear to best fit the data (Figure VI-15).

Because these values are different from those determined in shear we conclude that the yield surface need not be the Von Mises form as presumed for simplicity of calculation. We would recommend determining

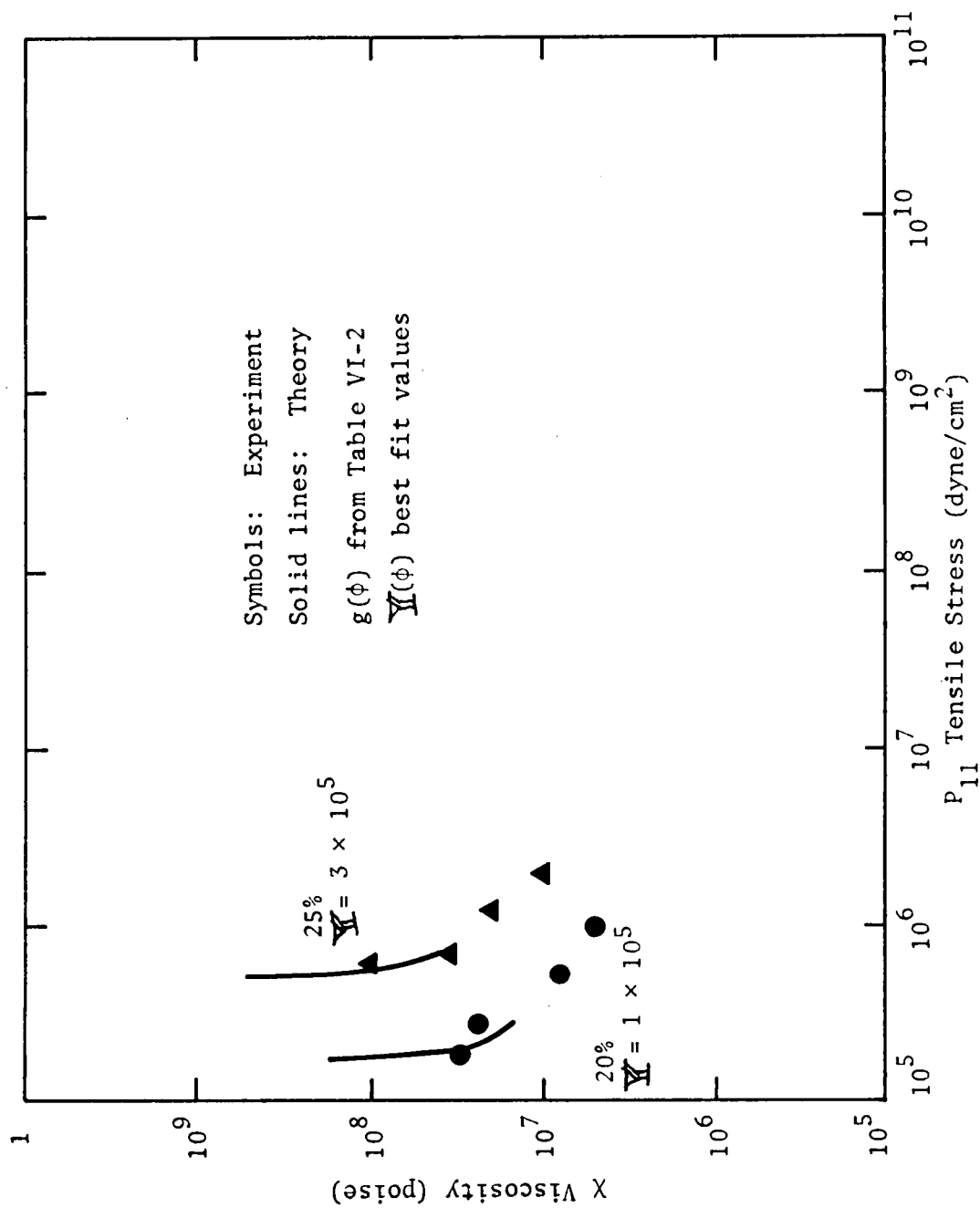


Figure VI-15. Steady state extensional viscosity theory and experiments for N110/PS678u at 170°C with best fit $\bar{Y}(\phi)$.

the yield values $\underline{Y}(\phi)$ for each experiment rather than selecting a best fit of $\underline{Y}$ for all experiments as was done for the parameter b in the case of unfilled materials.

A more complicated geometry for flow provides the opportunity to validate the theory in a broad range of deformation rates with the broad range of loadings. The flow used was that of the orthogonal rheometer. The flow was analyzed following the methods of Bird and Harris (28). The details of the analysis are provided in Appendix B. The resulting equations are given by

$$P_{13} = \left[g(\phi) + \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } H_o^2}} \right] \left[\sum \frac{G_i^o}{\tau_{i \text{eff}}^o} \gamma \left(\frac{\omega}{\left(\frac{1}{\tau_{i \text{eff}}^o} \right)^2 + \omega^2} \right) \right] \quad (\text{VI-29})$$

$$P_{23} = \left[g(\phi) + \frac{\underline{Y}}{\sqrt{\frac{1}{2} \text{tr } H_o^2}} \right] \left[\sum \frac{G_i}{\tau_{i \text{eff}}^o} \gamma \left(\tau_{i \text{eff}}^o - \frac{\frac{1}{\tau_{i \text{eff}}^o}}{\left(\frac{1}{\tau_{i \text{eff}}^o} \right)^2 + \omega^2} \right) \right] \quad (\text{VI-30})$$

The predictions of Eq. VI-29 for P_{13} using the parameters of Tables V-1, VI-1, VI-2, pp. 89, 109, 114, are observed to show the appropriate trends of experimental data (Figure VI-16).

The fit of the data in Figure VI-16 can be improved using different values of the yield value. Predictions for the dynamic experiment are shown for the 20% data ($\underline{Y} = 1.0 \times 10^5$) and 25% data ($\underline{Y} = 2 \times 10^5$) which are found to best fit this case. The values are in general agreement with those found in the shear viscosity experiment for the lower

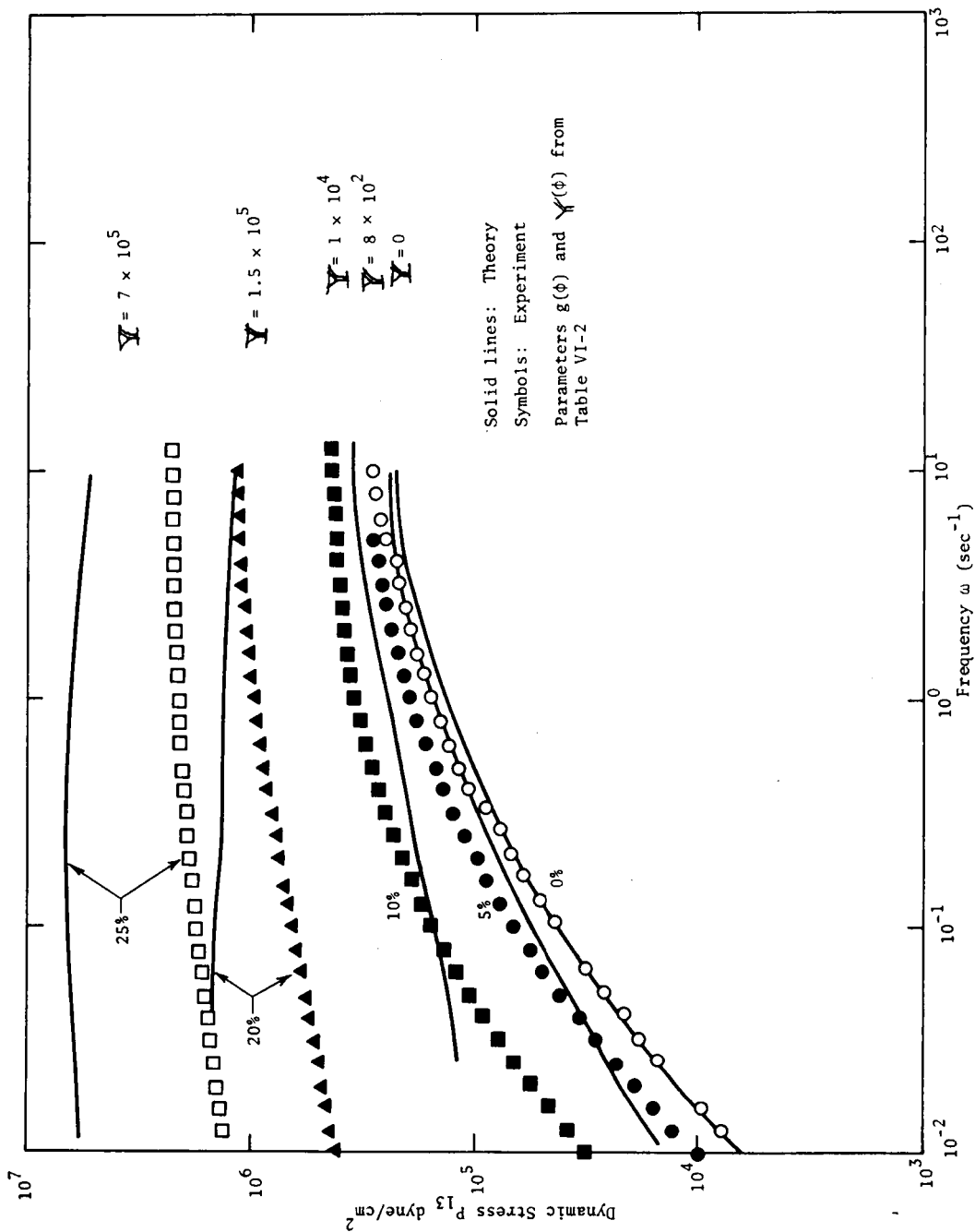


Figure VI-16. Dynamic stress theory and experiments for NI10/PS678u at 170°C.

loadings and seem to show significant deviation only in the highest loading case ($\bar{Y} = 7 \times 10^5$ vs. 2×10^5). This best fit of theory is shown in Figure VI-17. The value of the parameter b was found not to significantly change these curves especially in the cases of high carbon black loading samples.

The deviations in predictions of the yield value from steady state shear experiments support the recommendation to determine yield values $\bar{Y}(\phi)$ for each experiment. The difference in this yield value can be explained by changes in yield surface dimension (deviation from the Von Mises hypothesis) as in the case of the extensional experiments. This yield stress is in the shearing (P_{13}) dimension while the steady state shearing experiments are in the P_{12} directions. An alternate explanation of the lower observed yield function may be in thixotropic nature of the yielding structure. The dynamic experiment may cause the yielding structure to be broken down to a greater extent than in steady state experiments because of its continually changing kinematics.

D. CONCLUSIONS FROM THE INTERPRETATION OF NONLINEAR EXPERIMENTAL RESULTS FOR FILLED POLYSTYRENE MELTS

The experimental results of Chapter IV were interpreted using a plastic yielding nonlinear constitutive model. The model is characterized using parameters of the unfilled melt (τ_i , G_i , b) and parameters of the filled compound ($g(\phi)$, $\bar{Y}(\phi)$).

The nonlinear experiments on the unfilled melts can each be best represented using different values of the parameter b . It is seen,

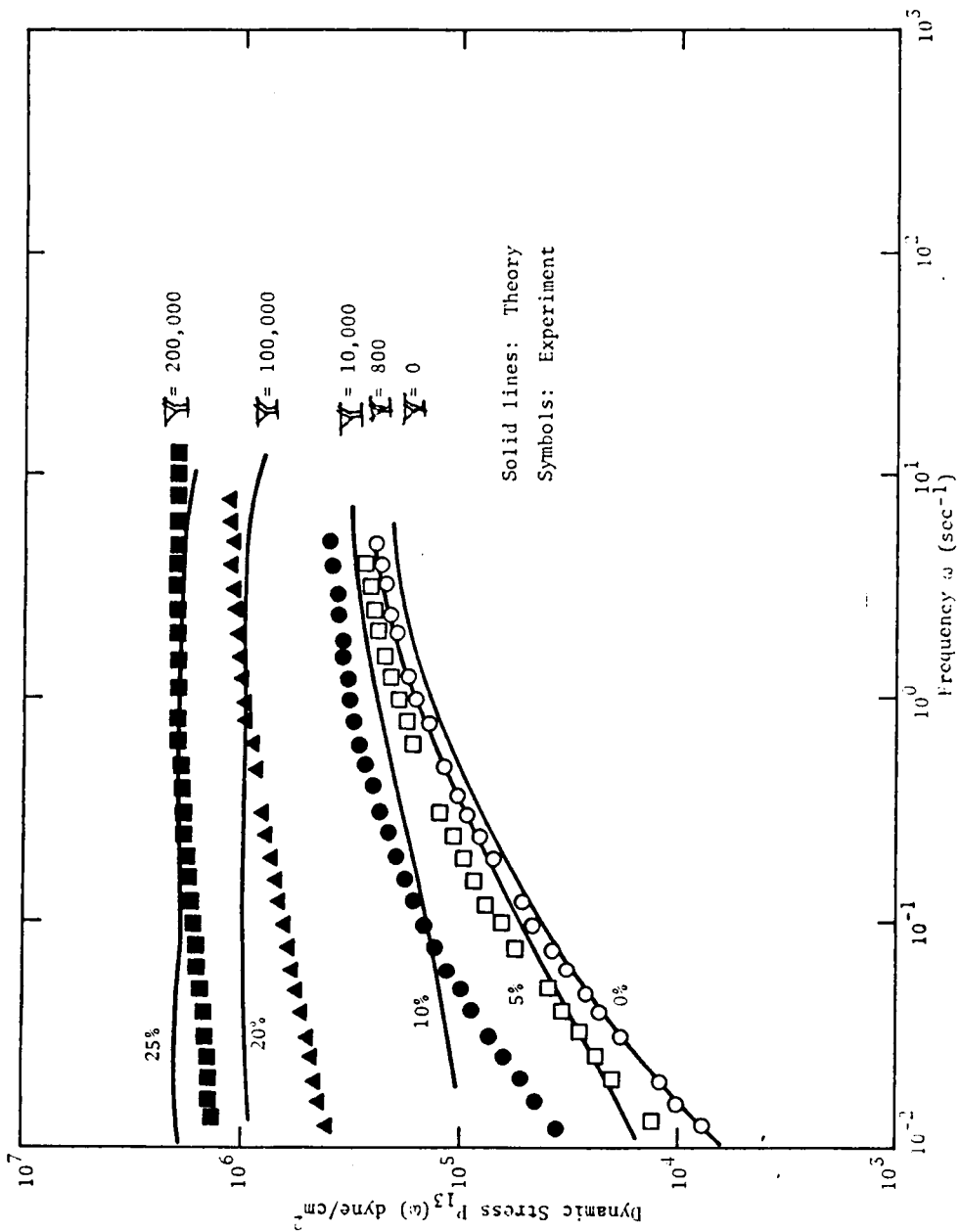


Figure VI-17. Dynamic stress theory and experiments for N110/PS678u at 170°C with best fit $\bar{Y}(\phi)$.

however, that a single value of the parameter ($b = 0.5$) can provide a reasonable fit of all of the experiments. The shear experiments were best fit by exactly this value, normal stress experiments would require a slightly lower value and extensional data would indicate values of about 0.1. The large sensitivity of the shear viscosity data to lower values of b would indicate that a best value for all experiments should be near $b = 0.5$.

The filled systems are characterized using the values of the unfilled system parameters along with the hydrodynamic function $g(\phi)$ and yielding factor $\Upsilon(\phi)$. The function $g(\phi)$ is determined using the Mooney equation for highly filled systems. The function $\Upsilon(\phi)$ is found to be best described by fitting the function to each experiment.

The value of the yield function for each experiment is shown in Table VI-3. The values of yield function determined in steady state shear are distinctly indicated by experiments. In the normal stress experiment the appropriate trends are observed but quantitative evaluation of the yield function is not possible. The extensional viscosity experiments and dynamic experiments in the orthogonal rheometer indicate substantially lower values of yield value in the 25% case but are in closer agreement for the lower values.

TABLE VI-3
YIELD FUNCTION $\bar{Y}(\phi)$ FOR VARIOUS EXPERIMENTS

% Volume Loading C.B. Stress	Steady State Shear P_{12}	Steady State Normal Stress $P_{11} - P_{22}$	Extensional Viscosity $P_{11} - P_{22}$	Orthogonal Dynamic Stress P_{13}
5	8×10^2	8×10^2		8×10^2
10	3×10^4	3×10^4		1×10^4
20	1.5×10^5	1.5×10^5	1×10^5	1×10^5
25	7×10^5	7×10^5	3×10^5	2×10^5

CHAPTER VII

RECOMMENDATIONS

This study introduces a nonlinear constitutive model with a yielding criterion that is intended to describe the reinforcing response of filled systems in a broad range of conventional experiments. A large number of experiments are suggested to expand this theory to describe other observed phenomena in filled systems.

The linear experiments could be compared with carefully controlled extension relaxation and creep experiments to quantitatively verify linearity and the frequency/time transformations. The frequency range might be extended in dynamic experiments using alternative equipment or time/temperature extrapolations.

Careful experiments in extension and compression might expand the determined yield surface which deviates from the presumed Von Mises yield surface. The constant extension rate experiments might be conducted over a broader range of extension rates if a different design extensional rheometer were used (enabling large deformations) to permit steady state evaluations with lower end effects.

The development and breakdown of the structure which leads to the observed yield phenomena is time dependent. The time dependence has not been treated in this dissertation but may be interpreted using the time dependent yielding functions of Slibar and Pasley (257,93).

Molecular and thermal effects should be developed for reinforced systems as they are being developed for the pure polymer systems.

Particle size and shape effects of the fillers also influence the stress response and should be investigated. This would lead to a theory of interacting particles .

LIST OF REFERENCES

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1. Acierno, D., F. P. LaMantia, B. DeCindio, and L. Nicodemo, Trans. Soc. Rheol., 21, 261 (1977).
2. Acierno, D., F. P. LaMantia, and G. Marrucci, J. Non-Newtonian Fluid Mech., 2, 271 (1977).
3. Acierno, D., F. P. LaMantia, G. Marrucci, G. Rizzo, and G. Titomanilo, J. Non-Newtonian Fluid Mech., 1, 147 (1976).
4. Acierno, D., F. P. LaMantia, G. Marrucci, and G. Titomanilo, J. Non-Newtonian Fluid Mech., 1, 125 (1976).
5. Acierno, D., F. P. LaMantia, and G. Titomanilo, Rheol. Acta., 15, 642 (1976).
6. Adam, G. and J. H. Gibbs, J. Chem. Phys., 43, 139 (1965).
7. Agrawal, P. K., W. K. Lee, J. M. Lorntson, C. I. Richardson, K. F. Wissbrun, and A. B. Metzner, Trans. Soc. Rheol., 21, 355 (1977).
8. Alfrey, T., Jr., Mechanical Behavior of High Polymers, Interscience, New York (1948).
9. Allen, T., Particle Size Measurement, Chapman and Hall Ltd., London, 1968.
10. Aris, R., Vectors, Tensors, and the Basic Equations of Fluid Dynamics, Prentice-Hall, Englewood Cliffs, N.J., 1962.
11. ASTM D-3182-73, "Standard Materials, Equipment and Procedures for Mixing Rubber Compounds and for Preparing Vulcanized Test Sheets."
12. Astarita, G., Ind. and Eng. Chem. Fund., 6, 257 (1967).
13. Bagley, E. B., J. Appl. Phys., 28, 624 (1957).
14. Bagley, E. B., Trans. Soc. Rheol., 5, 355 (1961).
15. Bagley, E. B. and J. H. Duffy, Trans. Soc. Rheol., 14, 545 (1970).
16. Ballman, R. L., Rheol. Acta., 4, 137 (1965).
17. Bernhardt, E. C., Processing of Thermoplastic Materials, Reinhold, New York, 1959.

18. Bernstein, B., *Int. J. Non-Linear Mech.*, 4, 183 (1969).
19. Bernstein, B., *Rheol. Acta*, 12, 95 (1973).
20. Bernstein, B., R. R. Huilgol, and R. I. Tanner, *Int. J. Eng. Sci.*, 10, 263 (1972).
21. Bernstein, B., E. A. Kearsley, and L. J. Zapas, *Trans. Soc. Rheol.*, 7, 391 (1963).
22. Bernstein, B., E. A. Kearsley, and L. J. Zapas, *J. Res. Nat. Bur. Stand.*, 68B, 103 (1964).
23. Bernstein, B., E. A. Kearsley, and L. J. Zapas, *Trans. Soc. Rheol.*, 7, 137 (1965).
24. Binding, D. M., J. F. Hutton, K. Walters, *Rheol. Acta*, 15, 540 (1976).
25. Bingham, E. C., Fluidity and Plasticity, McGraw-Hill, New York, 1923.
26. Bird, R. B., *Annual Review of Fluid Mechanics*, 8, 13 (1976).
27. Bird, R. B. and P. J. Carreau, *Chem. Eng. Sci.*, 23, 427 (1968).
28. Bird, R. B. and E. K. Harris, *A.I.Ch.E.J.*, 14, 758 (1968).
29. Bird, R. B., O. Hassager, and S. I. Abdel-Khalik, *A.I.Ch.E.J.*, 20, 1041 (1974).
30. Blatz, P. J., S. C. Sharda, and N. W. Tschoegl, *Trans. Soc. Rheol.*, 18, 145 (1974).
31. Bogue, D. C., *Ind. and Eng. Chem. Fund.*, 5, 253 (1966).
32. Bogue, D. C., "Nendonsei Ryutai no Riron to Oyo" (Viscoelastic Fluid Theory and Applications), in *Kagaku Kikai Gijutau No. 26*, Maruzen, Tokyo, Japan (1974).
33. Bogue, D. C., *Chem.-Mech. Eng. Technol.*, 26, 126 (1974).
34. Bogue, D. C. and J. O. Doughty, *Ind. and Eng. Chem. Fund.*, 5, 243 (1966).
35. Bogue, D. C., T. Masuda, Y. Einaga, and S. Onogi, *Polym. J.*, 1, 563 (1970).
36. Bogue, D. C. and J. L. White, Engineering Analysis of Non-Newtonian Fluids, NATO Agardograph 144, 1970.

37. Boguslawski, J. J., Rubber Chem. Technol., 45, 1424 (1972).
38. Bolen, W. R. and R. E. Colwell, A.C.S. Conference, Paper 98, 1004 (1960).
39. Boltzmann, L., Progg. Ann. Phys., 7, 624 (1876).
40. Boltzmann, L., Sitzungber Akad. Wiss Wien, 70, 275 (1874).
41. Bueche, F., Physical Properties of Polymers, Interscience, New York, 1962.
42. Caddell, R. M., R. S. Raghava, and A. G. Atkins, J. Mat. Sci., 8, 1641 (1973).
43. Caddell, R. M., R. S. Raghava, and A. G. Atkins, Mat. Sci. and Eng., 13, 113 (1974).
44. Carley, J. F., "Die Design" in Processing of Thermoplastic Materials, E. C. Bernhardt, ed., Reinhold, New York, 1959.
45. Carley, J. F., R. S. Mallouk, and J. M. McKelvey, Ind. Eng. Chem., 45, 974 (1953).
46. Carley, J. F. and R. A. Strub, Ind. Eng. Chem., 45, 970 (1953).
47. Carr, W., "Measurement of Pigment Dispersions in Paints and Printing Inks," Particle Size Analysis Conference, Paper 9, 1970.
48. Carreau, P. J., Trans. Soc. Rheol., 16, 99 (1972).
49. Caruthers, J. M., R. E. Cohen, and A. I. Medalia, Rubber Chem. and Tech., 49, 1076 (1976).
50. Chan, Y., M. S. Thesis, The University of Tennessee, Knoxville, 1977.
51. Chan, Y., J. L. White, and Y. Oyanagi, J. Rheol. 22, 507 (1978).
52. Chang, S. J. and B. Bernstein, Rheol. Acta 13, 721 (1974).
53. Chang, K. I., S. S. Yoo, and J. P. Hartnett, Trans. Soc. Rheol., 19, 155 (1975).
54. Chapman, T. F., private communication.
55. Chapman, F. M. and T. S. Lee, S.P.E.J., 26, 37 (1970).

56. Chen, I-J., Ph.D. Thesis, The University of Tennessee, Knoxville, 1972.
57. Chen, I-J. and D. C. Bogue, Trans. Soc. Rheol., 16, 59 (1972).
58. Chen, I-J., G. E. Hagler, L. E. Abbott, D. C. Bogue, and J. L. White, Trans. Soc. Rheol., 16, 473 (1972).
59. Cheng, D. C-H., Rheol. Acta, 12, 228 (1973).
60. Chung, C. I., S.P.E. ANTEC Tech. Papers, New York, p. 93, 1970.
61. Cogswell, F. N. and P. L. Lamb, Trans. J. Plastics Inst., 35, 809 (1967).
62. Coleman, B. D. and W. Noll, Arch. Rat. Mech. and Anal., 3, 289 (1959).
63. Coleman, B. D. and W. Noll, Arch. Rat. Mech. and Anal., 6, 355 (1960).
64. Colwell, R. E. and K. R. Nickolls, Ind. Eng. Chem., 51, 841 (1959).
65. Cotten, G. R., "Influence of Carbon Black on Processibility of Rubber Stocks. II. Extrusion Shrinkage," paper presented at the International Rubber Conference, Brighton, England, May, 1977.
66. Crawley, R. L. and W. F. Graessley, Trans. Soc. Rheol., 21, 19 (1977).
67. Crowder, J. W., M.S. Thesis, The University of Tennessee, Knoxville, 1973.
68. Crowl, V. T., J. Oil Col. Chem. Assoc., 55, 388 (1972).
69. Dealy, J. M., J. Non-Newtonian Fluid Mech., 4, 9 (1978).
70. DeWitt, T. W., J. Appl. Phys., 26, 889 (1955).
71. Denn, M. M. and G. Marrucci, A. I. Ch. E. J., 17, 101 (1971).
72. Dickie, R. A., J. Appl. Polym. Sci., 17, 45 (1973).
73. Dimarzio, E. A. and J. G. Gibbs, J. Polym. Sci., 40, 121 (1959).
74. Dominghaus, H., S.P.E.J., 28 (1972).
75. Doolittle, A. K., J. Appl. Phys., 22, 1471 (1951).

76. Eccher, S. and A. Balentinotti, Ind. Eng. Chem., 50, 829 (1958).
77. Eckert, R. E., J. Appl. Polym. Sci., 7, 1715 (1963).
78. Einstein, A., Ann. Physik, 19, 289 (1906).
79. Eisenberg, A. and M. C. Shen, "Glass Transitions in Polymers" in Progress in Solid State Chemistry, Vol. 3, Pergamon Press, New York, 1966.
80. Eisenschitz, R., B. Rabinowitsch, and K. Weissenberg, Mitt deut Material Pruf., 9, 91 (1929).
81. Everage, E. A. and R. L. Ballman, J. Appl. Polym. Sci., 20, 1137 (1976).
82. Eyring, H., J. Chem. Phys., 4, 283 (1936).
83. Ferry, J., Viscoelastic Properties of Polymers, Wiley, New York, 1961.
84. Ferry, J. D., R. G. Mancke, E. Maekawa, Y. Oyanagi, and R. A. Dickie, J. Phys. Chem., 68, 3414 (1964).
85. Fox, T. G. and P. J. Flory, J. Appl. Phys., 21, 581 (1950).
86. Frankel, N. A. and A. Acrivos, Chem. Eng. Sci., 22, 847 (1967).
87. Fredrickson, A. G., Principles and Applications of Rheology, Prentice-Hall, Englewood Cliffs, N.J., 1964.
88. Fujita, H., J. Appl. Phys., 29, 943 (1958).
89. Furuta, I., V. M. Lobe, and J. L. White, J. Non-Newtonian Fluid Mech., 1, 207 (1976).
90. Gaskell, R. E., J. Appl. Mech., Trans. A.S.M.E., 72, 334 (1950).
91. Goddard, J. D., Trans. Soc. Rheol., 11, 381 (1967).
92. Goldberg, W., B. Bernstein, and G. Lianis, Int. J. Non-Linear Mech., 4, 277 (1969).
93. Goldblatt, P. H., Ph.D. Thesis, The University of Tennessee, Knoxville, 1972.
94. Goldstein, C., Trans. Soc. Rheol., 18, 359 (1974).

95. Gore, W. L. and J. M. McKelvey, "Theory of Screw Extruders" in Rheology, Vol. 3, F. Eirich, ed., Academic Press, New York, 1960.
96. Graessley, W. S., S. D. Glasscock, and R. L. Crawley, Trans. Soc. Rheol., 14, 519 (1970).
97. Graessley, W. W., W. S. Park, and R. L. Crawley, Rheol. Acta, 16, 291 (1977).
98. Green, A. E. and R. S. Rivlin, Arch. Rat. Mech. and Anal., 1, 1 (1957).
99. Greener, Y. and S. Middleman, Polym. Eng. and Sci., 15, 1 (1975).
100. Gregory, R. B., Plastics and Polymers, 38, 120 (1970).
101. Gregory, R. B., S.P.E.J., 27, 49 (1971).
102. Griffith, R. M., I. and E.C. Fund., 1, 180 (1962).
103. Gross, L. H. and B. Maxwell, Trans. Soc. Rheol., 16, 577 (1972).
104. Gruver, J. T. and G. Kraus, J. Polym. Sci., A2, 797 (1964).
105. Guth, E., J. Appl. Phys., 16, 20 (1945).
106. Han, C. D., J. Appl. Polym. Sci., 17, 1289 (1973).
107. Han, C. D., J. Appl. Polym. Sci., 18, 821 (1974).
108. Han, C. D., K. U. Kim, N. Siskovic, and C. R. Huang, Rheol. Acta, 14, 533 (1975).
109. Hanan, S. E. and R. L. Bukowski, J. Paint Technol., 38, 527 (1966).
110. Happel, J. and H. Brenner, Low Reynolds Number Hydrodynamics with Special Applications to Particulate Media, Prentice-Hall, Englewood Cliffs, N.J., 1965.
111. Harwood, J. A. C., L. Mullins, and A. R. Payne, Journal of the I.R.I., 17 (1967).
112. Heijboer, J., Br. Polym. J., 1, 3 (1969).
113. Herbst, W., Prog. in Org. Coatings, 1, 267 (1972).
114. Hinrichs, D. R. and L. U. Lilleleht, Polym. Eng. and Sci., 10, 268 (1970).

115. Hlavacek, B., J. Stanislov, and I. Patterson, *Rheol. Acta*, 14, 812 (1975).
116. Hopper, J., *Rubber Chem. Technol*, 40, 463 (1967).
117. Huke, D. W., Introduction to Natural and Synthetic Rubbers, Chemical Publishing Co., Inc., New York, 1961.
118. Huang, D., Ph.D. Thesis, The University of Tennessee, Knoxville, in progress.
119. Hutton, J. F., *Rheol. Acta*, 14, 979 (1975).
120. Ide, Y., Ph.D. Thesis, The University of Tennessee, Knoxville, 1976.
121. Ide, Y. and J. L. White, *J. Appl. Polym. Sci.*, 18, 2997 (1974).
122. Ide, Y. and J. L. White, *J. Appl. Polym. Sci.*, 20, 2511 (1976).
123. Ide, Y. and J. L. White, *J. Non-Newtonian Fluid Mech.*, 2, 281 (1977).
124. Jeffreys, H., *The Earth*, Cambridge University Press, Cambridge, 1921.
125. Joye, D. D., G. W. Poehlein, and C. D. Denson, *Trans. Soc. Rheol.*, 16, 421 (1972).
126. Kaiser, H. and C. W. Smith, *J. of Basic Eng.*, 91, 479 (1969).
127. Kearsley, E. A. and L. J. Zapas, *Trans. Soc. Rheol.*, 20, 623 (1976).
128. Kim, H. T. and J. P. Darby, *S.P.E.J.*, 26, 31 (1970).
129. Klein, I. and Z. Tadmor, *Modern Plastics*, 46, 166 (1969).
130. Kotaka, T. and J. L. White, *Trans. Soc. Rheol.*, 17, 587 (1973).
131. Kraus, G., ed., Reinforcement of Elastomers, Interscience, New York, 1965.
132. Kraus, G., *Polym. Letters*, 8, 601 (1970).
133. Kraus, G., *J. Appl. Polym. Sci.*, 15, 1079 (1971).
134. Kraus, G., *Rubber Chem. Tech.*, 44, 199 (1971).

135. Kraus, G. and J. T. Gruver, J. Polym. Sci., A3, 105 (1965).
136. Kraus, G. and J. T. Gruver, J. Appl. Polym. Sci., 9, 739 (1965).
137. Kroesser, F. W. and S. Middleman, S.P.E. Trans., 5, 230 (1965).
138. Kuhn, W., O. Kanzle, and A. Preissman, Helv. Chim. Acta, 30, 307, 464, 839 (1947).
139. Laun, H. M. and H. Munstedt, Rheol. Acta, 16, 517 (1976).
140. Lee, B. and J. L. White, Trans. Soc. Rheol., 18, 467 (1974).
141. Lee, B. L. and J. L. White, Trans. Soc. Rheol., 19, 481 (1975).
142. Lenk, R. S., Rheologie der Kunststoffe, Carl Hanser Verlag, Munchen, 1971.
143. Lobe, V. M., unpublished data.
144. Lobe, V. M. and J. L. White, Polym. Eng. and Sci., 19, 617 (1979).
145. Lodge, A. S., Proc. Second Int. Rheol. Cong., Trans. Farad. Soc., 52, 120 (1956).
146. Lodge, A. S., Elastic Liquids, Academic Press, New York, 1964.
147. Lodge, A. S. and J. Meissner, Rheol. Acta, 12, 41 (1973).
148. Macdonald, I. F., Trans. Soc. Rheol., 18, 299 (1974).
149. Macdonald, I. F., Rheol. Acta, 14, 899 (1975).
150. Macdonald, I. F., Rheol. Acta, 14, 906 (1975).
151. Macosko, C. W. and W. M. Davis, Rheol. Acta, 13, 814 (1974).
152. Macosko, C. W. and Lornsten, SPE ANTEC Paper 22, 461 (1973).
153. Macosko, C. W. and J. Starita, S.P.E.J., 27, 38 (1971).
154. Macosko, C. W. and F. C. Weissert, ASTM, Philadelphia, 1974.
155. Maerker, J. M. and W. R. Schowalter, Rheol. Acta, 13, 627 (1974).
156. Mallouk, R. S. and J. M. McKelvey, Ind. Eng. Chem., 45, 987 (1953).

157. Maddock, B. H., S.P.E. Tech. Papers, 5, 45 (1959).
158. Marrucci, G. and G. Astarita, Rheol. Acta, 13, 754 (1974).
159. Matsui, M., Trans. Soc. Rheol., 20, 465 (1976).
160. Matsui, M. and D. C. Bogue, Polym. Eng. Sci. 16, 735 (1976).
161. Matsumoto, T., personal communication, 1977.
162. Matsumoto, T., C. Hitomi, and S. Onogi, Trans. Soc. Rheol., 19, 541 (1975).
163. Matsumoto, T., Y. Segawa, Y. Warashina, and S. Onogi, Trans. Soc. Rheol., 17, 47 (1973).
164. Matsumoto, T., A. Takashima, T. Masuda, and S. Onogi, Trans. Soc. Rheol., 14, 617 (1970).
165. Maxwell, B. and R. Chartoff, Trans. Soc. Rheol., 9, 41 (1965).
166. Maxwell, J. C., Phil. Trans. Roy. Soc., A157, 49 (1867).
167. Medalia, A. I., Rubber Chem. and Tech., 46, 877 (1973).
168. Medalia, A. I., Rubber World, 168, 49 (1973).
169. Medalia, A. I., Colloques Internationaux Du Centre National de la Recherche Scientifique, No. 231, Le Beschenberg-Obermal, p. 63 (1973).
170. Medalia, A. I., E. M. Dannenberg, F. A. Heckman, and G. R. Cotten, Rubber Chem. and Tech., 46, 1239 (1973).
171. Meissner, J., Rheol. Acta, 8, 78 (1969).
172. Meissner, J., Rheol. Acta, 10, 230 (1971).
173. Meissner, J., J. Trans. Soc. Rheol., 16, 405 (1972).
174. Meissner, J., J. Appl. Polym. Sci., 16, 2877 (1972).
175. Meister, B. J., Trans. Soc. Rheol., 15, 63 (1971).
176. Mendelson, R. A., F. L. Finger, and E. B. Bagley, J. Polym. Sci., C35, 177 (1971).
177. Mercer, H. A. and H. D. Weymann, Rheol. Acta, 13, 413 (1974).

178. Metzner, A. B., W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, 5, 133 (1961).
179. Middleman, S., *Trans. Soc., Rheol.*, 9, 83 (1965).
180. Middleman, S., *The Flow of High Polymers*, Interscience, New York, 1968.
181. Middleman, S., *Trans. Soc. Rheol.*, 13, 123 (1969).
182. Minagawa, N. and J. L. White, *J. Appl. Polym. Sci.*, 20, 501 (1976).
183. Minagawa, N. and J. L. White, *Polym. Eng. and Sci.*, 12, 825 (1975).
184. Morton, M., ed., *Rubber Technology*, Van Nostrand Reinhold Co., New York, 1973.
185. Mooney, M., "The Rheology of Raw Elastomers," in *Rheology*, Vol. 2, F. R. Eirich, ed., Academic Press, New York, 1958.
186. Mooney, M., *J. Colloid Sci.*, 6, 162 (1951).
187. Mooney, M., *J. Rheology*, 2, 210 (1931).
188. Mullins, L., *Rubber Chem. and Technol.*, 42, 339 (1969).
189. Mooney, M. and R. H. Ewart, *Physics*, 5, 350 (1939).
190. Mullins, L., *J. Rubber Reserve*, 16, 275 (1947).
191. Mullins, L., *J. Phys. Colloid Chem.*, 54, 239 (1950).
192. Mullins, L. and R. W. Wharlow, *Trans. Inst. Rubber Ind.*, 27, 55 (1958).
193. Mullins, L., *Proc. Second Rubber Technol. Conf.*, London, p. 179, 1948.
194. McCabe, C. C., *Trans. Soc. Rheol.*, 5, 329 (1961).
195. McKelvey, J. M., *Polymer Processing*, John Wiley and Sons, Inc., New York, 1962.
196. McKelvey, J. M., *Ind. Eng. Chem.*, 45, 982 (1953).
197. McKelvey, J. M., *Ind. Eng. Chem.*, 46, 660 (1954).
198. Nakajima, N., H. H. Bowerman, and E. A. Collins, *J. Appl. Polym. Sci.*, 21, 3063 (1977).

199. Nakajima, N. and E. A. Collins, Rubber Chem. and Tech., 48, 615 (1975).
200. Nakajima, N. and E. A. Collins, Rubber Chem. and Tech., 50, 791 (1977).
201. Nakajima, N. and M. Shida, Trans. Soc. Rheol., 10, 299 (1966).
202. Narkis, M. J. and A. Ram, Polym. Eng. and Sci., 7, 161 (1967).
203. Newman, S. and Q. A. Trementozzi, J. Appl. Polym. Sci., 9, 3071 (1965).
204. Nicodemo, L., B. DeCindio, and L. Nicolais, Polym. Eng. and Sci., 15, 679 (1975).
205. Nielsen, L., Mechanical Properties of Polymers, Reinhold, New York, 1962.
206. Ninomiya, K., S. Kasamizer, E. Maekawa, and G. Yasuda, "Application of Polymer Rheology to Rubber Technology," in Progress in Polymer Science, edited by M. Imoto and S. Onogi, Japan, 1, 377 (1971).
207. Ninomiya, K. and G. Yasuda, Rubber Chem. Tech., 42, 714 (1969).
208. Nitschmann, H. and J. Schrade, Helv. Chim. Acta, 31, 297 (1948).
209. Noll, W., Arch. Rat. Mech. and Anal., 2, 197 (1958).
210. Okano, M., Buss. Kenkyn, 3, 493 (1958).
211. Oono, R., J. Polym. Sci., 12, 1383 (1974).
212. Osmers, H. R. and P. F. Lobo, Trans. Soc. Rheol., 20, 239 (1976).
213. Oldroyd, J. G., Proc. Roy. Soc. (London), A200, 523 (1950).
214. Onogi, S., T. Masuda, and T. Matsumoto, Trans. Soc. Rheol., 14, 275 (1970).
215. Onogi, S., T. Matsumoto, and Y. Warashina, Trans. Soc. Rheol., 17, 175 (1973).
216. Oldroyd, J. G., Proc. Roy. Soc., A245, 278 (1958).
217. Parfitt, G. D., J. Oil Col. Chem. Assoc., 50, 822 (1967).
218. Paslay, P. R., Trans. A.S.M.E., 79, 602 (1957).

219. Payne, A. R., J. Appl. Polym. Sci., 6, 57 (1962).
220. Payne, A. R., J. Appl. Polym. Sci., 6, 368 (1962).
221. Payne, A. R., J. Appl. Polym. Sci., 9, 2273 (1965).
222. Payne, A. R. and E. R. Whittaker, Rubber Chem. Tech., 44, 440 (1971).
223. Pearson, J. R. A., Mechanical Principles of Polymer Melt Processing, Pergamon, New York, 1966.
224. Phan-Thien, N., J. Rheol., 22, 259 (1978).
225. Phan-Thien, N. and R. I. Tanner, J. of Non-Newtonian Fluid Mech., 2, 353 (1977).
226. Philippoff, W., Trans. Soc. Rheol., 4, 159, 169 (1960).
227. Philippoff, W., Trans. Soc. Rheol., 7, 45 (1963).
228. Philippoff, W. and F. H. Gaskins, Trans. Soc. Rheol., 2, 263 (1958).
229. Phillips, M., Trans. Soc. Rheol., 20, 185 (1976).
230. Phillips, M. C., J. Non-Newtonian Fluid Mech., 2, 109 (1977).
231. Phillips, M. C., J. Non-Newtonian Fluid Mech., 2, 123 (1977).
232. Phillips, M. C., J. Non-Newtonian Fluid Mech., 2, 139 (1977).
233. Piggot, W. T., Trans. Am. Soc. of Mech. Eng., 73, 947 (1951).
234. Pinto, G. and Z. Tadmor, Polym. Eng. and Sci., 5, 279 (1970).
235. Pliskin, I., Rubber Chem. Technol., 46, 1218 (1973).
236. Powell, R. L. and S. Middleman, Trans. Soc. Rheol., 13, 241 (1969).
237. Prager, W., Introduction to Mechanics of Continuum, Ginn and Co., New York, 1961.
238. Prager, W. and K. Hohenemser, ZfAMM, 12, 216 (1932).
239. Predecki, P. and W. O. Statton, Polym. Letters, 10, 87 (1972).
240. Raghava, R., R. M. Caddell, and G. S. Y. Yeh, J. Mat. Sci., 8, 225 (1973).

241. Reeve, T. B. and W. L. Dills, J. of Color and Appearance, 1, 25 (1971).
242. Reiner, M., Lectures on Theoretical Rheology, North Holland, Amsterdam, 1960.
243. Rivlin, R. S., "Large Elastic Deformations" in Rheology, Vol. 1, F. R. Eirich, ed., Academic Press, New York, 1956.
244. Rivlin, R. S., Proc. Roy. Soc., A193, 260 (1948).
245. Rivlin, R. S. and J. L. Ericksen, J. Rat. Mech. Anal., 4, 323 (1955).
246. Rokudai, M. and T. Fujiki, Appl. Polym. Sym., 20, 23 (1973).
247. Rowell, H. S. and D. Finlayson, Engineering, 17, 606 (1922).
248. Schubert, B., F. P. Ford, and F. Lyon, "Analysis of Carbon Black" in Encyclopedia of Industrial Chemical Analysis, Vol. 8, 179-243 (1969).
249. Schwarzl, F., Proc. Second Intern. Congress Rheol., Oxford, England, 1953.
250. Schwarzl, F. R., Rheol. Acta, 14, 581 (1975).
251. Schwarzl, F. R., and A. J. Staverman, Physica, 18, 791 (1952).
252. Schwarzl, F. and A. J. Staverman, Appl. Sci. Res., Section A, 4, 127 (1953).
253. Seth, B. R., "Generalized Strain Measure with Applications to Physical Problems" in Second-Order Effects in Elasticity Plasticity and Fluid Dynamics, M. Reiner and D. Abir, eds., Macmillan Co., New York, p. 162 (1964).
254. Shah, B. H. and R. Darby, Polym. Eng. and Sci., 16, 46 (1971).
255. Shenkel, G., Plastics Extrusion Technology and Theory, American Elsevier, New York, 1966.
256. Simha, R., J. Appl. Phys., 23, 1020 (1952).
257. Slibar, A. and P. R. Pasley, in Second Order Effects in Elasticity, Plasticity, and Fluid Dynamics, ed. by M. Reiner and D. Abir, Pergamon Press, London, 314 (1962).
258. Smit, P. P. A., Rheol. Acta, 10, 277 (1969).

259. Smith, M. J., J. Oil Col. Chem. Assoc., 56, 165 (1973).
260. Smith, M. J., Microscope, 19, 337 (1971).
261. Smith, D. and R. Christy, Rubber Chem. Technol., 45, 1434 (1972).
262. Snyder, J. W. and M. H. Leonard, "Carbon Black" in Introduction to Rubber Technol., M. Morton, ed., Reinhold, New York, 1959.
263. Spriggs, T. W., J. D. Huppler, and R. B. Bird, Trans. Soc. Rheol., 10, 191 (1966).
264. Squires, P. H. and C. F. Wolf, S.P.E.J., 27, 68 (1971).
265. Stern, H. J., Rubber: Natural and Synthetic, Palmerton Pub. Co., New York, 1967.
266. Stevens, M. J., Plastics and Polymers, 38, 107 (1970).
267. Stevenson, J. F., A.I.Ch.E.J., 18, 540 (1972).
268. Stevenson, J. F., S. C.-K. Chung, and J. F. Jenkins, Trans. Soc. Rheol., 19, 397 (1975).
269. Studebaker, M., Proc. Ind. Rubber Conf., London, p. 623, 1954.
270. Tadmor, Z. and I. Klein, Rubber Chem. and Technol., 42, 780 (1969).
271. Tadmor, Z. and I. Klein, Polym. Eng. and Sci., 9, 1 (1969).
272. Tadmor, Z. and I. Klein, Modern Plastics, 46, 166 (1969).
273. Tadmor, Z., I. J. Duvdevani, and I. Klein, Polym. Eng. and Sci., 7, 198 (1967).
274. Takahashi, Y., T. Masuda, and S. Onogi, J. Soc. Rheol., Japan, 1, 16 (1973).
275. Takahashi, M., T. Masuda, and S. Onogi, Trans. Soc. Rheol., 21, 337 (1977).
276. Takaki, T. and D. C. Bogue, J. Appl. Polym. Sci., 19, 419 (1975).
277. Tanaka, H., M.S. Thesis, The University of Tennessee, Knoxville (1979).
278. Tanner, R. I., J. Polym. Sci., A Z, 2067 (1970).
279. Tobolsky, A. V., Properties and Structures of Polymers, John Wiley, New York, 1960.

280. Tobolsky, A. V. and K. Murakami, J. Polym. Sci., 40, 443 (1959).
281. Tokita, N. and I. Pliskin, Rubber Chem. Technol., 46, 1166 (1973).
282. Tokita, N. and J. L. White, J. Appl. Polym. Sci., 10, 1011 (1966).
283. Toupin, R. A., J. Rat. Mech. and Anal., 5, 849 (1956).
284. Treloar, L. R. G., The Physics of Rubber Elasticity, Clarendon Press, Oxford, 1958.
285. Treloar, L. R. G., J. Appl. Polym. Sci., Polymer Symposium, 48, 107 (1974).
286. Trouton, F., Proc. Roy. Soc., A77, 426 (1906).
287. Truesdell, C., J. Rat. Mech. and Anal., 1, 125 (1952).
288. Truesdell, C., ed., The Rational Mechanics of Materials, Gordon and Breach Science Publishers, Inc., New York, 1965.
289. Truesdell, C., ed., Foundations of Elasticity Theory, Gordon and Breach Science Publishers, Inc., New York, 1965.
290. Truesdell, C., ed., Problems of Non-Linear Elasticity, Gordon and Breach Science Publishers, Inc., New York, 1965.
291. Tschoegl, N. W., Rheol. Acta, 10, 582 (1971).
292. Tschoegl, N. W., Rheol. Acta, 10, 545 (1971).
293. Turnbull, D. and M. H. Cohen, J. Chem. Phys., 21, 1850 (1953).
294. Van der Wahl, C. W., H. W. Bree, and F. R. Schwarzl, J. Appl. Polym. Sci., 9, 2143 (1965).
295. Van Es, H. E. and R. M. Christensen, Trans. Soc. Rheol., 17, 325 (1973).
296. Vila, G. R., Ind. Eng. Chem., 36, 1113 (1944).
297. Vinogradov, G. V., Rheol. Acta, 14, 942 (1975).
298. Vinogradov, G. V., N. I. Insarova, B. B. Boiko, and E. K. Borisenkova, Polym. Eng. Sci., 12, 323 (1971).
299. Vinogradov, G. V. and A. Ya. Malkin, J. Polym. Sci. A-2, 4, 135 (1966).

300. Vinogradov, G. V., A. Ya. Malkin, E. P. Plotnikova, C. Yu. Sabsai, and N. E. Nikolayeva, *Intern. J. Polymeric Mat.*, 2, 1 (1972).
301. Vinogradov, G. V., B. V. Radushkevich, and V. D. Fikhman, *J. Polym. Sci.*, A-2, 8, 1 (1970).
302. Vinogradov, G. V., Yr. G. Yanovsky, A. I. Iaayev, V. P. Shatalov, and V. G. Shalganova, *Int. J. Polym. Mat.*, 1, 17 (1971).
303. Von Mises, R., *Gottinger Nachrichten, Math.-Phys. Klasse*, 582 (1913).
304. Wahl, E. F., G. G. Pangborn, and H. A. McCurdy, *J. Paint Technol.*, 44, 98 (1972).
305. Walters, K., *Rheometry*, John Wiley, New York, 1970.
306. Walters, K., *Z. Angew. Math. Phys.*, 21, 592 (1970).
307. Ward, I. M., *J. Mat. Sci.*, 6, 1397 (1971).
308. Ward, I. M., *Mechanical Properties of Solid Polymers*, Wiley-Interscience, New York, 1971.
309. Watson, W. F., "Chemical Interaction of Fillers and Rubbers During Cold Milling" in *Reinforcement of Elastomers*, G. Kraus, ed., Interscience, New York, 1965.
310. Whitby, G. S., ed., *Synthetic Rubber*, John Wiley and Sons, New York, 1954.
311. White, J. L., *J. Appl. Polym. Sci.*, 8, 1129, 2339 (1964).
312. White, J. L., *Rubber Chem. Technol.*, 42, 257 (1969).
313. White, J. L., *Trans. Soc. Rheol.*, 13, 3 (1969).
314. White, J. L., *Proc. of the Fifth Int. Cong. on Rheol.*, 3, 17 (1970).
315. White, J. L., *Applied Polymer Symposium*, 20, 155 (1973).
316. White, J. L., *Rheol. Acta*, 14, 600 (1975).
317. White, J. L., *Trans. Soc. Rheol.*, 19, 271 (1975).
318. White, J. L., *Rubber Chem. Tech.*, 50, 163 (1976).
319. White, J. L., in *Science and Technology of Rubber*, ed. by F. R. Eirich, Academic Press, New York (1978).

- 320. White, J. L. and D. C. Bogue, S.P.E. RETEC, The University of Tennessee, p. 15, 1972.
- 321. White, J. L. and J. W. Crowder, J. Appl. Polym. Sci., 18, 1013 (1974).
- 322. White, J. L. and Y. Ide, Appl. Polym. Symp., 27, 61 (1975).
- 323. White, J. L. and Y. Ide, J. Appl. Polym. Sci., in press as of July 19, 1977.
- 324. White, J. L. and T. Kotaka, Macromolecules, 7, 106 (1974).
- 325. White, J. L. and H. L. Landreth, ed., S.P.E. RETEC, The University of Tennessee, 1972.
- 326. White, J. L. and B. L. Lee, Trans. Soc. Rheol., 19, 457 (1975).
- 327. White, J. L. and Y. M. Lin, J. Appl. Polym. Sci., 17, 2373 (1973).
- 328. White, J. L. and A. B. Metzner, J. Appl. Polym. Sci., 7, 1867 (1963).
- 329. White, J. L. and J. F. Roman, The University of Tennessee Polym. Sci. and Eng. Report 36, 1975.
- 330. White, J. L., D. G. Salladay, D. C. Quisenberry, and D. L. Maclean, J. Appl. Polym. Sci., 16, 2811 (1972).
- 331. White, J. L. and N. Tokita, J. Appl. Polym. Sci., 9, 1929 (1965).
- 332. White, J. L. and N. Tokita, J. Appl. Polym. Sci., 10, 1011 (1966).
- 333. White, J. L. and N. Tokita, J. Appl. Polym. Sci., 11, 321 (1967).
- 334. White, J. L. and N. Tokita, J. Appl. Polym. Sci., 12, 1589 (1968).
- 335. White, J. L., R. C. Ufford, K. R. Dharod, and R. L. Price, J. Appl. Polym. Sci., 16, 1313 (1972).
- 336. Willey, S. J., W. M. Davis, C. W. Macosko, and C. Goldstein, Trans. Soc. Rheol., 18, 515 (1974).
- 337. Williams, M. C. and R. B. Bird, A.I.Ch.E.J., 8, 378 (1962).
- 338. Williams, M. C. and R. B. Bird, Physics of Fluids, 5, 1126 (1962).
- 339. Williams, M. C. and R. B. Bird, Ind. Eng. Chem. Fund., 3, 42 (1964).

- 340. Williams, M. L., R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).
- 341. Winspar, G. G., ed., The Vanderbilt Rubber Handbook, R. T. Vanderbilt Company Inc., New York, 1968.
- 342. Yamamoto, M., J. Phys. Soc., Japan, 12, 1148 (1957).
- 343. Yamamoto, M., Trans. Soc. Rheol., 15, 783 (1971).
- 344. Zamodits, H. J. and J. R. A. Pearson, Trans. Soc. Rheol., 13, 357 (1969).
- 345. Zapas, L. J., paper presented at Fifth Int. Conf. on Rheol., Japan, 1968.
- 346. Zapas, L. J., J. Res. Nat. Bur. Std., 70A, 525 (1966).
- 347. Zapas, L. J. and T. Craft, J. Res. Nat. Bur. Std., 69A, 541 (1965).
- 348. Zapas, L. J. and J. C. Phillips, J. Res. Nat. Bur. Std., A. Physics and Chemistry, 75A, 33 (1971).
- 349. Zaremba, S., Bull. Intern. Acad. Sci., Cracovie, 594 (1903).

APPENDIXES

APPENDIX A

DETERMINATION OF THE RELAXATION SPECTRUM $H(\tau)$ FROM THE SHEAR RELAXATION SPECTRUM $G(t)$

The shear relaxation modulus is defined in Equation V-2 as

$$G(t) = \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad (A-1)$$

Performing a Laplace transform on Equation A-1 with change of variable $\tau = \frac{1}{\zeta}$ we obtain

$$G(t) = \int_0^{\infty} \zeta^{-1} H(\zeta^{-1}) e^{-t\zeta} d\zeta \quad (A-2)$$

This transform may be inverted using a "Post-Widder" inversion formula
(291)

$$H(\zeta^{-1}) \lim_{K \rightarrow \infty} = H_K(\zeta^{-1}) \quad (A-3)$$

where

$$H_K(\tau) = \frac{(-t)^K}{(K-1)!} \left. \frac{d^K G(t)}{dt^K} \right|_{t=K\tau} \quad (A-4)$$

(K has positive integer values.)

From this formula we obtain the "order" approximations as follows:

for $K = 1$

$$H_1(\tau) = - t \left. \frac{d G(t)}{dt} \right|_{t=\tau} = - \left. \frac{d G(t)}{d \ln \tau} \right|_{t=\tau} \quad (A-5)$$

This approximation involves only the first derivative of the source function $G(t)$ and therefore is said to be a first order approximation. It was introduced by Alfrey (8) in 1948 and has been called "Alfrey's rule" (83).

For higher order approximations the value of t in the experimental time scale spectrum corresponds to $\frac{\tau}{K}$ in the relaxation spectrum. Since

$$\frac{d^2 G}{d \ln^2 t} = t \left(\frac{dt \cdot \left(\frac{dG}{dt} \right)}{dt} \right) = t \left(t \frac{d^2 G}{dt^2} + \frac{dG}{dt} \right) \quad (A-6)$$

we have for $K = 2$

$$H_2\left(\frac{\tau}{2}\right) = t^2 \left. \frac{d^2 G(t)}{dt^2} \right|_{t=\tau} = - \left. \frac{d G(t)}{d \ln t} \right|_{t=\tau} + \left. \frac{d^2 G(t)}{d \ln^2 t} \right|_{t=\tau} \quad (A-7)$$

and for $K = 3$

$$H_3\left(\frac{\tau}{3}\right) = - \frac{1}{2} t^3 \left. \frac{d^3 G(t)}{dt^3} \right|_{t=\tau} \quad (A-8)$$

$$H_3\left(\frac{\tau}{3}\right) = - \left. \frac{d G(t)}{d \ln t} \right|_{t=\tau} + \frac{3}{2} \left. \frac{d^2 G(t)}{d \ln^2 t} \right|_{t=\tau} - \frac{1}{2} \left. \frac{d^3 G(t)}{d \ln^3 t} \right|_{t=\tau}$$

These higher order approximations were introduced by Schwarzl and Staverman (251,252). They based the approximation on the inversion of the Laplace transform. This transform is not unique. Other transforms may also be used. Tschoegl (292) develops a more general method as follows.

$$H_K(\tau, r_0) = \mathcal{P}_K(G(t)) \Big|_{t=\tau} \quad (A-9)$$

$\mathcal{P}_K$ is a logarithmic differential operator on $G(t)$ defined by

$$\mathcal{P}_K = \sum_{n=1}^{n=K} a_n \frac{d}{d \ln^n t} \quad (A-10)$$

where a and r_0 are numerical coefficients. Applying this operator to Eq. A-5 we obtain

$$\mathcal{P}_K(G(t)) \Big|_{t=\tau} = H_K(\tau, r_0) \quad (A-11)$$

where

$$H_K(\tau, r_0) = \int_{-}^{\infty} H(\tau) \mathcal{P}_K[e^{-t/\tau}] d \ln \tau \Big|_{t=\tau} \quad (A-12)$$

The function $\mathcal{P}_K[e^{-t/\tau}]$ is called an "intensity function." This intensity function must be normalized to unity and have only one peak. These conditions permit the evaluation of the numerical coefficients in Eq. A-11. This results in Alfrey's rule (8,83) ($a_1 = -1$) uniquely for the first order approximation and to two new higher order approximations

$$H_2\left(\frac{\tau}{\sqrt{2}}\right) = -\frac{dG(t)}{d \ln t} + \frac{1}{3} \frac{d^2 G(t)}{d \ln^2 t} \Big|_{t=\tau} \quad (\text{A-13})$$

and

$$H_3\left(\frac{\tau}{\sqrt{6}}\right) = -\frac{dG(t)}{d \ln t} + \frac{6}{5} \frac{d^2 G(t)}{d \ln^2 t} - \frac{1}{5} \frac{d^3 G(t)}{d \ln^3 t} \Big|_{t=\tau} \quad (\text{A-14})$$

In general there will be K approximations of order κ . The root r_0 shifts the maximum of the intensity function such that the time scale of the relaxation spectrum τ is properly adjusted with respect to the source function time scale t .

APPENDIX B

ANALYSIS OF FLOWS IN THE ORTHOGONAL RHEOMETER USING A YIELDING-SINGLE INTEGRAL CONSTITUTIVE MODEL

To evaluate the parameters of the constitutive model

$$\tilde{T} = \left[g(\phi) + \frac{\tilde{Y}}{\sqrt{\frac{1}{2} \text{tr } H_o^2}} \right] H_o \quad (B-1)$$

We analyze the orthogonal rheometer experiments in terms of a single integral model following Bird and Harris (28) and Macasko (151). The single integral model we use here is defined by

$$\tilde{H}^o = \int_0^\infty \mu(z) \left[\left(1 + \frac{\epsilon}{2}\right) \tilde{C}^{-1} - \left(-\frac{\epsilon}{2}\right) \tilde{C} \right] dz \quad (B-2)$$

This appendix illustrates the evaluation of each of the components of $\tilde{H}^o$. The $\tilde{H}^o$ tensor is used, along with the functions $g(\phi)$ and $\tilde{Y}(\phi)$ to describe the stress response in the orthogonal rheometer.

To evaluate $\tilde{H}^o$ we must evaluate the strain measure $\left[\left(1 + \frac{\epsilon}{2}\right) \tilde{C}^{-1} - \left(-\frac{\epsilon}{2}\right) \tilde{C} \right]$ and the memory function $\mu(z)$. The strain measures are determined by direct analysis of the flow field. We describe the flow field by:

$$x = X \cos \omega z - [Y - \gamma Z] \sin \omega z$$

$$y = X \sin \omega z + (Y - \gamma Z) \cos \omega z + \gamma Z \quad (\text{B-3})$$

$$z = Z$$

The conventional strain measures are given by

$$C^{-1} = \begin{vmatrix} 1 + \gamma^2 \sin^2 \omega z & \gamma^2 \sin \omega z (1 - \cos \omega z) & \gamma \sin \omega z \\ \gamma^2 \sin \omega z (1 - \cos \omega z) & 1 + \gamma^2 (1 - \cos \omega z)^2 & \gamma (1 - \cos \omega z) \\ \gamma \sin \omega z & \gamma (1 - \cos \omega z) & 1 \end{vmatrix} \quad (\text{B-4})$$

$$C = \begin{vmatrix} 1 & 0 & -\gamma \sin \omega z \\ 0 & 1 & -\gamma (1 - \cos \omega z) \\ -\gamma \sin \omega z & -\gamma (1 - \cos \omega z) & 1 + 2\gamma^2 (1 - \cos \omega z) \end{vmatrix}$$

The deviatoric stress measure defined as

$$\tilde{C} = C - \frac{1}{3} \text{tr } C$$

and

(B-5)

$$\tilde{C}^{-1} = C^{-1} - \frac{1}{3} \text{tr } C^{-1}$$

is given by

$$\begin{aligned}
 \tilde{C}^{-1} &= \begin{vmatrix} \frac{\gamma^2}{3}(3\sin^2\omega z - 2(1-\cos\omega z)) & \gamma^2\sin\omega z(1-\cos\omega z) & \gamma\sin\omega z \\ \gamma^2\sin\omega z(1-\cos\omega z) & \frac{\gamma^2}{3}(4(1-\cos\omega z) - 3\sin^2\omega z) & \gamma(1-\cos\omega z) \\ \gamma\sin\omega z & \gamma(1-\cos\omega z) & -\frac{\gamma^2}{3}(2(1-\cos\omega z)) \end{vmatrix} \\
 \tilde{C} &= \begin{vmatrix} -\frac{2\gamma^2}{3}(1-\cos\omega z) & & -\gamma\sin\omega z \\ 0 & -\frac{2\gamma^2}{3}(1-\cos\omega z) & -\gamma(1-\cos\omega z) \\ -\gamma\sin\omega z & -\gamma(1-\cos\omega z) & \frac{4}{3}\gamma^2(1-\cos\omega z) \end{vmatrix} \quad (B-6)
 \end{aligned}$$

Knowing the parameter ϵ we can then evaluate the strain measure (bracketed) of H^0 .

The memory function $\mu(z)$ is determined by the discrete relaxation parameters (τ_i^0, G_i^0) and the effective relaxation time function $\tau_{i_{eff}}$. The discrete relaxation spectrum (G_i^0, τ_i^0) is determined by methods described in Appendix A or in Chapter V (i.e., from linear dynamic experiments or linear stress relaxation experiments of the unfilled polymer melt).

The effective relaxation time function is determined from the history of the velocity flow field. The velocity field is presumed to be at steady state with

$$\begin{aligned}
 v_x &= -\omega y + \gamma\omega z \\
 v_y &= \omega x \\
 v_z &= 0
 \end{aligned} \quad (B-7)$$

The symmetric rate of deformation tensor with components

$$d_{ij} = \frac{1}{2} \left| \frac{dv_i}{dx^j} + \frac{dv_j}{dx^i} \right| \text{ is given by}$$

$$\underline{d} = \frac{\omega\gamma}{2} \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} \quad (\text{B-8})$$

The second invariant of $\underline{d}$ is

$$II_d = \text{tr } d^2 = \frac{(\omega\gamma)^2}{4} \quad (\text{B-9})$$

and the time averaged second invariant is

$$\langle II_d^{\frac{1}{2}} \rangle = \frac{\int_0^Z II_d^{\frac{1}{2}} dz}{Z} = \frac{\omega\gamma}{2} \quad (\text{B-10})$$

The effective relaxation time function defined by

$$\tau_{i\text{eff}} = \frac{\tau_i}{1 + b \langle II_d^{\frac{1}{2}} \rangle \tau_i} \text{ is then}$$

$$\tau_{i\text{eff}} = \frac{\tau_i}{1 + b \left(\frac{\omega\gamma}{2} \right) \tau_i} \quad (\text{B-11})$$

Evaluating the integral H^0 of Eq. B-2 over the infinite past we obtain

$$\begin{aligned}
 H_{13} &= \sum \int_0^{\infty} \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}} [\gamma \sin \omega z] dz \\
 &= \sum \left(\frac{G_i}{\tau_{i\text{eff}}} \right) \gamma \left[\frac{\omega}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 + \omega^2} \right]
 \end{aligned} \tag{B-12}$$

$$\begin{aligned}
 H_{23} &= \sum \int_0^{\infty} \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}} [\gamma(1 - \cos \omega z)] dz \\
 &= \sum \left(\frac{G_i}{\tau_{i\text{eff}}} \right) \gamma \left[\tau_{i\text{eff}} - \frac{\frac{1}{\tau_{i\text{eff}}}}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 + \omega^2} \right]
 \end{aligned} \tag{B-13}$$

$$\begin{aligned}
 H_{12} &= \sum \int_0^{\infty} \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}} \left[\left(\left(1 + \frac{\epsilon}{2} \right) \gamma^2 \sin(\omega z) - \sin(\omega z) \cos(\omega z) \right) \right] dz \\
 &= \sum \left(\frac{G_i}{\tau_{i\text{eff}}} \right) \gamma^2 \left(1 + \frac{\epsilon}{2} \right) \left[\frac{\omega}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 + \omega^2} - \frac{\omega}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 + 4\omega^2} \right]
 \end{aligned} \tag{B-14}$$

$$\begin{aligned}
 H_{11} &= \sum \int_0^{\infty} \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}} \left[\left(\left(1 + \frac{\epsilon}{2} \right) \gamma^2 \sin^2(\omega z) - \frac{2}{3} \gamma^2 (1 - \cos(\omega z)) \right) \right] dz \\
 &= \sum \frac{G_i}{\tau_{i\text{eff}}} \gamma^2 \left[\frac{\left(1 + \frac{\epsilon}{2} \right) 2\omega^2 \tau_{i\text{eff}}}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 + 4\omega^2} - \frac{2}{3} \left[\tau_{i\text{eff}} - \frac{\frac{1}{\tau_{i\text{eff}}}}{\left(\frac{1}{\tau_{i\text{eff}}} \right)^2 - \omega^2} \right] \right]
 \end{aligned} \tag{B-15}$$

$$\begin{aligned}
H_{22} &= \int_0^\infty e^{-z/\tau_{i\text{eff}}} \left\{ \left(1 + \frac{\epsilon}{2}\right) \left[\frac{4}{3} \gamma^2 (1 - \cos \omega z) - \gamma^2 \sin^2 \omega z \right] \right. \\
&\quad \left. + \left(\frac{\epsilon}{2}\right) \frac{2}{3} \gamma^2 (1 - \cos \omega z) \right\} dz \\
&= \int \left(\frac{G_i}{\tau_{i\text{eff}}} \right) \gamma^2 \left[\left(1 + \frac{\epsilon}{2}\right) \left[\tau_{i\text{eff}} - \frac{\frac{1}{\tau_{i\text{eff}}}}{\left(\frac{1}{\tau_{i\text{eff}}}\right)^2 + \omega^2} \right] \right. \\
&\quad \left. - \left(1 + \frac{\epsilon}{2}\right) \frac{2\omega^2 \tau_{i\text{eff}}}{\left(\frac{1}{\tau_{i\text{eff}}}\right)^2 + 4\omega^2} \right] dz \quad (B-16)
\end{aligned}$$

$$\begin{aligned}
H_{33} &= \int_0^\infty \int \frac{G_i}{\tau_{i\text{eff}}} e^{-z/\tau_{i\text{eff}}} \left[\left(1 + \frac{\epsilon}{2}\right) \left(-\frac{2}{3} \gamma^2\right) (1 - \cos \omega z) \right. \\
&\quad \left. + \left(\frac{\epsilon}{2}\right) \left(\frac{4}{3} \gamma^2\right) (1 - \cos \omega z) \right] dz \\
&= \int \left(\frac{G_i}{\tau_{i\text{eff}}} \right) \gamma^2 \frac{2}{3} \left(-1 + \frac{\epsilon}{2}\right) \left[\tau_{i\text{eff}} - \frac{\frac{1}{\tau_{i\text{eff}}}}{\left(\frac{1}{\tau_{i\text{eff}}}\right)^2 + \omega^2} \right] dz \quad (B-17)
\end{aligned}$$

Having evaluated each of the components of $\tilde{H}^0$ we can evaluate the trace of $(\tilde{H}^0)^2$ and all parameters of Eq. B-1 with the exception of $g(\phi)$ which is obtained from the Mooney equation and $\underline{\Upsilon}(\phi)$ which is fit to the experimental data.

VITA

The author, Vincent Michael Lobe, was born in Ely, Minnesota, on September 21, 1947. He is the eldest son of Mr. and Mrs. John M. Lobe. After completing his primary education from kindergarten through high school in Ely, Minnesota, he was admitted to the University of Minnesota Institute of Technology in Minneapolis, Minnesota, June 1965. There he studied chemical engineering with an elected minor in biochemical engineering. He received his Bachelor of Chemical Engineering degree in June of 1969.

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