VISCOELASTIC PROPERTIES OF POLYMER FILMS

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ABSTRACT

Thirteen samples of molten polymers were used to test Spriggs and Carreau Models. Two empirical equations, one for apparent viscosity and the other which is new, for primary normal stress difference, were checked with these samples also.

In order to test the models, material functions were sought for some specific flow patterns under which the experimental data were collected, and then these functions were compared with data.

Carreau Model was found to be better than Spriggs Model in representing molten polymer properties but still yield large deviations. Two empirical equations fitted data quite well and were expected to be useful in some applications.

A considerable amount of molten polymer data was added to the open literature.

Some ways of modifying Carreau Model to describe polymer melts better were recommended.

APPROVAL OF THESIS

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1 INTRODUCTION

According to Newton's law of viscosity for the flow of a fluid, the shear force per unit area (shear stress) is proportional to the negative of the local velocity gradient (shear rate),

$$\tau_{rz} = -\mu \frac{dV_z}{dr} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

τ_{rz} = shear stress

$\frac{dV_z}{dr}$ = shear rate

μ = viscosity

A fluid obeying Newton's law of viscosity is called a Newtonian fluid. The Newtonian fluid cannot store mechanical energy but dissipates it entirely.

On the other hand the ideal elastic body which follows Hooke's law:

$$\tau = G \gamma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where τ = shear stress

γ = shear strain

G = constant

can store mechanical energy, and return to its original length immediately, as the force which caused its deformation is removed.

Between these two extremes lie viscoelastic materials which have the characteristics of both ideal elastic body and Newtonian fluids.

In order to illustrate this point consider a simple experiment. Let us stretch a piece of rubber. When the rubber is released, it snaps back substantially to its original length. However, if we examine it carefully, we find that it does not quite return immediately to its original length. There is a slight residual elongation, which gradually reduces with time. Such time-dependent elastic recovery may be thought of as a retarded elastic recovery. Alternatively, if we apply a constant bending deformation to a piece of rubber, it is found that the force applied to the strip is not constant, but diminishes slightly with time, that is, stress relaxation takes place.

Again, if instead of applying a constant force or constant deformation, we apply a force or deformation which varies sinusoidally with time, then if the deformation is small enough we find that, respectively, the deformation or force also varies sinusoidally with time; in general, however the deformation is not in phase with the force but lags behind. The stress-strain plot under these conditions is thus an ellipse; this implies that during such cyclic deformation mechanical work is converted into heat. Many materials perform similarly to rubber in that, when undergoing deformation, partly store mechanical energy and partly dissipate it as heat. This is known as viscoelastic behavior.

One of the most important sort of materials which possess viscoelastic behavior is synthetic high polymers. An understanding of the mechanics of them is needed in connection with the processing and utilization of polymer liquids, for which the technology of Newtonian fluids has proved to be inadequate. The flow problems which have been solved for Newtonian fluids must be resolved for viscoelastic materials. New correlations must be developed for old systems and new and strange phenomena must be sought for and explained. In order that the mechanics of viscoelastic fluids might be systematically developed, it is necessary to obtain constitutive equations which can adequately describe the behavior of these materials, but which are simple enough so that calculations for various flow systems can be performed.

A number of constitutive equations have been developed These have proven successful in describing the behavior of polymer solutions. However, few data for polymer melts have been tested. The purposes of this work are not only to test existing constitutive equations with molten polymer rheological data (much of it presented for the first time in this study) but also to develop appropriate rheological equations for polymer melts.

II CONSTITUTIVE RELATIONS

General Description

In forming a constitutive equation, the theoretician is guided in his assignment of properties to the ideal material by the behavior of some actual materials over a range of experimental conditions. He begins with a decision concerning the general nature of the stress-deformation relation. The form of the relation is then simplified by demanding compliance with a set of physically reasonable principles and by taking advantage of the properties of the tensors that occur in the relation.

Some important principles in forming constitutive equations are summarised below:

(1) Coordinate invariance. Every constitutive equation must be stated in such a way that it is unaffected by the choice of the coordinate system; that is, the body should be "unaware" of the particular coordinate system which we happen to employ. If the equations are stated in tensorial form, this rule will be satisfied.

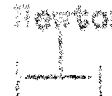
(2) Isotropy. The constitutive equation must reflect the symmetry of the material represented. If, for example, the material is isotropic then any rotation of the material coordinates must leave the constitutive equation unchanged when the reference configuration is taken to be an undistorted state. Not only is a fluid isotropic, but any configuration can be taken as the reference configuration—an undistorted state. If the fluid is held in any configuration for a long time, the stress must eventually reduce to a hydrostatic pressure.

(3) Material indifference. To be consistent with our notion that the response of a material is independent of the observer, the constitutive equation must have a form such that it is not changed by an arbitrary rigid rotation of the frame of reference. In other words, if both the material and reference system are rotated at the same time, the constitutive equation remains the same. Even though the constitutive equation must satisfy the requirement of material indifference, it is to be noted that the laws of motion do not; apparent forces must be invoked in comparisons of the experimental results of observers who are rotating with respect to each other.

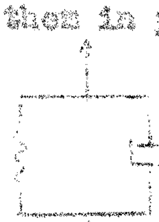
A special case is that when viscoelastic behavior is linear, under which the behavior become amenable to simple mathematical treatment. A linear viscoelastic material is defined as one which, under stress, gives a response that is a combination of linear elastic and linear viscous behaviour. Such materials are often represented by mechanical models which are designed to duplicate the observed time dependent.

A. <u>Linear model 1 - The Voigt Model.</u> One of the simplest models exhibiting viscoelastic behavior is the Voigt element. We represent the Hooke's elastic body by a spring,

of shear modulus G, and the Newtonian fluid by a dashpot



of viscosity η. Connect them in parallel we get the Voigt element



If we apply Hooke's law for elasticity and Newton's law for viscosity to this model we arrive at

$$\tau_{ij}(t) = G\gamma_{ij} + \eta\dot{\gamma}_{ij} \qquad \text{...........(1)}$$

where

$\dot{\gamma}_{ij}$ = shear rate

γ_{ij} = shear component of a strain tensor

$= \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$

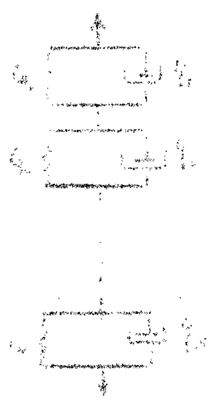
u_i, u_j = component of displacement

The solution of equation (1) is

$$\gamma_{ij} = \frac{\tau}{2G}\{1 - \exp(-\frac{G}{\eta}t)\} \qquad \text{...........(2)}$$

τ = constant stress

In order to extend the Voigt model into a more realistic system for describing viscoelastic behavior, it is convenient to consider a set of N Voigt elements connected in series as shown below:



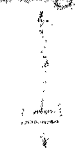
for nth element

$$\tau_{ij} = 2G_n\gamma_{ij,n} + 2\eta_n\dot{\gamma}_{ij,n} \qquad \text{.......... (3)}$$

The total strain is

$$\gamma_{ij} = \sum_{n=1}^{N}\gamma_{ij,n}(t) \qquad \text{...........(4)}$$

<u>Linear model 2 - The Maxwell Model.</u> Another simple model used to describe viscoelastic behavior is the Maxwell Model, consisting of a spring and a dashpot in series



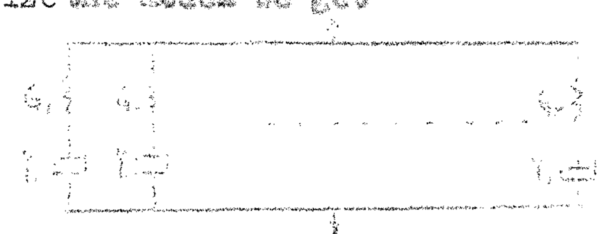
The differential equation is then given by

$$2\dot{\gamma}_{ij} = \frac{1}{\eta}\tau_{ij} + \frac{1}{G}\dot{\tau}_{ij} \qquad \ldots\ldots\ldots\ldots(5)$$

The solution is (subject, at time t = 0, to a constant strain γ_{ij})

$$\tau_{ij} = 2\gamma_{ij} G \exp\left(-\frac{G}{\eta}t\right) \qquad \ldots\ldots\ldots\ldots(6)$$

If we generalize the model we get



The relationship between stress and strain for nth element is

$$2\dot{\gamma}_{ij} = \frac{1}{\eta_n}\tau_{ij(n)} + \frac{1}{G_n}\dot{\tau}_{ij(n)} \qquad \ldots\ldots\ldots\ldots(7)$$

and total stress is

$$\tau_{ij} = \sum_{n=1}^{N} \tau_{ij(n)}(t) \qquad \ldots\ldots\ldots\ldots(8)$$

For an infinite set of Maxwell elements the constants (G_n, η_n) are replaced by the function G(λ) which gives the amount of elastic modulus associated with the relaxation time $\lambda = \frac{\eta}{G}$. This function is often refered to as the "distribution of relaxation time". The total stress is given by

$$\tau_{ij}(t) = \int_0^\infty \tau_{ij}(t,\lambda)\,d\lambda \qquad \ldots\ldots\ldots\ldots(9)$$

__Non-linear model.__ The Voigt and Maxwell models illustrate the procedure of obtaining linear constitutive equations. The approach can be used in a variety of ways, all of which describe the behavior of the material in some degree of realty. Generally, however, such equations have always been found to be inadequate in predicting several viscoelastic characteristics simultaneously. They are suitable, therefore, for limited cases only.

The linear constitutive equations however can be used as a starting point. They are then modified to yield non-linear equations.

As an example, Spriggs (1) has generalized the Jeffrey's model:

$$(1+\lambda_1 \frac{\partial}{\partial t})\underline{\underline{\tau}} = -2\eta_0(1+\lambda_2 \frac{\partial}{\partial t})\underline{\underline{e}} \qquad \text{.........(10)}$$

by first replacing

$$\lambda_1^{(n)} \text{ for } \lambda_1, \ \lambda_2^{(n)} \text{ for } \lambda_2, \ \underline{\underline{\tau}}^{(n)} \text{ for } \underline{\underline{\tau}}$$

it becomes

$$\left.\begin{aligned} (1+\lambda_1^{(n)} \frac{\partial}{\partial t})\underline{\underline{\tau}}^{(n)} &= -2\eta_n(1+\lambda_2^{(n)} \frac{\partial}{\partial t})\underline{\underline{e}} \\ \underline{\underline{\tau}} &= \sum_n \underline{\underline{\tau}}^{(n)} \end{aligned}\right\} \qquad \text{.........(11)}$$

Where $\lambda_1^{(n)}$, $\lambda_2^{(n)}$ are characteristic time which depend on the summation index n and η_n has the dimension of viscosity. Next he extended equation (11) by replacing $\mathcal{F}_{a,\epsilon}$ for $\frac{\partial}{\partial t}$ and got

$$\left.\begin{aligned} (1+\lambda_1^{(n)}\mathcal{F}_{a,\epsilon})\underline{\underline{\tau}}^{(n)} &= -2\eta_n(1+ \\ &\quad \lambda_2^{(n)}\mathcal{F}_{a,\epsilon})\underline{\underline{e}} \\ \underline{\underline{\tau}} &= \sum_n \underline{\underline{\tau}}^{(n)} \end{aligned}\right\} \qquad \text{..........(12)}$$

where $\mathcal{F}_{ab}$ is defined by

$$\mathcal{F}_{ab}\underline{\underline{A}} = \frac{\partial \underline{\underline{A}}}{\partial t} + \{\underline{v}\cdot\nabla\underline{\underline{A}}\} + \{\underline{\underline{\omega}}\cdot\underline{\underline{A}}\} - \{\underline{\underline{A}}\cdot\underline{\underline{\omega}}\} - a\{(\underline{\underline{e}}\cdot\underline{\underline{A}}) + (\underline{\underline{A}}\cdot\underline{\underline{e}})\} + b(\underline{\underline{e}}:\underline{\underline{A}})\underline{\underline{\delta}} + c(\underline{\underline{\delta}}:\underline{\underline{A}})\underline{\underline{e}} \quad \ldots\ldots\ldots\ldots(13)$$

As another example, we can integrate equations (7),(8) then it becomes

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t}\left(\sum_{p=1}^{\infty}\frac{\eta_p}{\lambda_p}\, e^{-\frac{t-t'}{\lambda_p}}\right)\dot{\underline{\underline{\gamma}}}(t')\,dt' \quad \ldots\ldots\ldots\ldots(14)$$

Integrate by part again, we get

$$\underline{\underline{\tau}} = \int_{-\infty}^{t}\left(\sum_{p=1}^{\infty}\frac{\eta_p}{\lambda_p^2}\, e^{-\frac{t-t'}{\lambda_p}}\right)\underline{\underline{\gamma}}(t')\,dt' \quad \ldots\ldots\ldots\ldots(15)$$

where t is the current time, and t' denotes the past time.

Carreau, P.J., and Bird, R.B. (2) guided by this form modified the memory function

$$\left(\sum_{p=1}^{\infty}\frac{\eta_p}{\lambda_p^2}\, e^{-\frac{t-t'}{\lambda_p}}\right)$$

by

$$\mu(t-t', II(t')) = \sum_{p=1}^{\infty}\frac{\eta_p}{\lambda_{2p}^2}\,\frac{e^{-\frac{t-t'}{\lambda_{2p}}}}{1+\frac{1}{2}\lambda_{1p}^2 II(t')}$$

and used the strain tensor

$$\left\{\left(1-\frac{\epsilon}{2}\right)\underline{\underline{C}}^{-1} + \frac{\epsilon}{2}\underline{\underline{C}}\right\}$$

Then the model became

$$\underline{\underline{\tau}} = \int_{-\infty}^{t}\mu(t-t', II(t'))\left\{\left(1-\frac{\epsilon}{2}\right)\underline{\underline{C}}^{-1} + \frac{\epsilon}{2}\underline{\underline{C}}\right\}dt' \quad \ldots\ldots\ldots(16)$$

where $II(t')$ is the second invariant of rate of strain tensor, $\underline{\underline{C}}$, $\underline{\underline{C}}^{-1}$ are Cauchy and Finger tensor respectively, ϵ, η_p, λ_{1p}, λ_{2p} are constant.

Complex Constitutive Equations

The complex constitutive equations published in the literatures may be divided into two types: differential and integral models.

All of the differential models involve special forms of a differential operator used by Oldroyd(3). He derived the simplest general form of the equation of state for isotropic, incompressible fluid, which was linear in the stresses alone, and included terms of the second degree in the stresses and velocity gradients taken together.

$$\tau_{ij} + \lambda_1 \frac{\mathcal{D}}{\mathcal{D}t}\tau_{ij} + \mu_0 \tau_{mm} e_{ij} - \mu_1 (\tau_{im} e_{mj} + \tau_{jm} e_{mi})$$

$$+ \nu_1 \tau_{mn} e_{mn} \delta_{ij} = 2\eta_0 \left(e_{ij} + \lambda_2 \frac{\mathcal{D} e_{ij}}{\mathcal{D}t} - 2\mu_2 e_{im} e_{mj} + \nu_2 e_{mn} e_{mn} \delta_{ij}\right) \quad (17)$$

where $\frac{\mathcal{D}}{\mathcal{D}t}$ is the material derivative

$$\frac{\mathcal{D} A_{ij}}{\mathcal{D}t} = \frac{\partial A_{ij}}{\partial t} + v_m \frac{\partial A_{ij}}{\partial x_m} + \omega_{im} A_{mj} - A_{im} \omega_{mj} \quad \ldots\ldots\ldots(18)$$

and

e_{ij} = element of rate-of-strain tensor

$$= \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \quad \ldots\ldots\ldots(19)$$

ω_{ij} = element of vorticity tensor

$$= \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right) \quad \ldots\ldots\ldots(20)$$

Now we combine the material derivative with the other expressions in the Oldroyd's equation and define the new derivative operator $F_{a,\mu,\nu}$ by equation(13) we can write the Oldroyd's equation in a more compact form

$$(1 + \lambda_1 F_{a_1,\mu_1,\nu_1})\, \underline{\underline{\tau}} = 2\eta_0 (1 + \lambda_2 F_{a_2,\mu_2,\nu_2})\, \underline{\underline{e}} \quad \ldots\ldots\ldots(21)$$

The operator $\frac{\mathcal{D}}{\mathcal{D}t}$ is constructed so that the resulting equations preserve their form when the reference frame undergoes a rigid body motion, and it reduces to $\frac{\partial}{\partial t}$ for small enough motions.

The integral models can be considered as a merger of two ideas. The first of these is Boltzmann's theory of materials with memory for which the stress is a time integral over the history of the strain. For a linear elastic material subjected to infinitesimal strain at time t_0, responds with an infinitesimal stress given by

$$d\tau_{ij} = G\, d\gamma_{ij} \quad , \quad t > t_0 \qquad \text{.......(22)}$$

Viscoelasticity is then introduced by replacing the shear modulus G by a relaxation function $\phi(t-t_0)$, so that

$$d\tau_{ij}(t) = \phi(t-t_0)\, d\gamma_{ij}(t_0) \qquad \text{.......(23)}$$

One may then conceive of a material having been subjected to a sequence of infinitesimal strains $d\gamma_{ij}^{(i)}$ at times t_i. By assuming that the infinitesimal stresses resulting from each strain increment simply add in a linear fashion, with each strain weighted by a relaxation function reckoned from the time of imposition of that strain, then the stress at time t may be written as

$$\tau_{ij}(t) = \sum_{i=0}^{i} \phi(t-t_i)\, d\gamma_{ij}(t_i) \qquad \text{.......(24)}$$

If the sequence of infinitesimal strains is replaced by a continuous strain history $\gamma_{ij}(t')$, the resultant stress may be written as an integral with the result

$$\tau_{ij}(t) = \int_{-\infty}^{t} \phi(t-t')\, d\gamma_{ij}(t') \qquad \text{......(25)}$$

We can write it alternately by integrating the above equation by parts, then get

$$\tau_{ij}(t) = \phi(0)\gamma_{ij}(t) + \int_{-\infty}^{t} \mu(t-t')\gamma_{ij}(t')\,dt' \quad \text{..........(26)}$$

The Bolzmann's equations, such as the one shown above, are limited to small strain because the infinitesimal strain tensor γ_{ij} was used.

The second idea of representing an integral model originates in the equations of Finger for finite-strain elasticity. The distance between two points at time t may be written in terms of the metric tensor g of the chosen coordinate system

$$ds^2 = g_{ij}\, d\xi^i d\xi^j \quad \text{..........(27)}$$

Define Cauchy's and Finger's deformation tensor by

$$c_{ij} = \frac{\partial \xi'^m}{\partial \xi^i} \frac{\partial \xi'^n}{\partial \xi^j} g_{mn}(\xi') \quad \text{..........(28)}$$

$$(c^{-1})^{ij} = \frac{\partial \xi^i}{\partial \xi'^m} \frac{\partial \xi^j}{\partial \xi'^n} g^{mn}(\xi') \quad \text{..........(29)}$$

We can write more general equations with these deformation tensors.

The integral model can be considered especial case which resulted from replacing Bolzmann's infinitesimal strain tensor by Finger's measure of finite deformation.

A summary of existing differential and integral equations are given on the following pages.

Table I: Differential Models

Name	constant	function	Equation	Ref.
Oldroyd 3-constant	$\eta_0, \lambda_1, \lambda_2$		$(1+\lambda_1 F_{1,\frac{2}{3},0})\boldsymbol{\tau} = -2\eta_0 (1+\lambda_2 F_{1,\frac{2}{3},0})\boldsymbol{e}$	5
Oldroyd 8-constant	$\eta_0\ \lambda_1\ \lambda_2\ \mu_0$ $\mu_1\ \mu_2\ \nu_1\ \nu_2$		$(1+\lambda_1 F_{\mu_1,\nu_1,\mu_0})\boldsymbol{\tau} = -2\eta_0 (1+\lambda_2 F_{\mu_2,\nu_2,0})\boldsymbol{e}$	3
Oldroyd (1962)	$\eta_0\ \mu_n\ \lambda_n$		$(1+\sum_{n=1}^{N}\lambda_n F^{n}_{000})\boldsymbol{\tau} = -2\eta_0 (1+\sum_{n=1}^{N}\mu_n F^{n}_{000})\boldsymbol{e}$	7
Spriggs-Bird	$\eta_0\ \ \lambda$		$(1+a_n F^{n}_{1,\frac{2}{3},0})\boldsymbol{\tau} = -2\eta_0 (1+b_n F^{n}_{1,\frac{2}{3},0})\boldsymbol{e}$ $a_n = \frac{\pi^{2n}\lambda^{n}}{(2n+1)!} = \frac{1}{3}(2n+3)\,b_n$	6
Spriggs 4-constant	$\eta_0, \lambda, \alpha, \epsilon$		$(1+\lambda_1 n^{-\alpha} F_{1+\epsilon,\frac{2}{3}(1+\epsilon),0})\boldsymbol{\tau}^{(n)} = -2\eta_0 \left(\frac{n^{-\alpha}}{Z(\alpha)}\right)\boldsymbol{e}, \quad \boldsymbol{\tau} = \sum_{n=1}^{\infty}\boldsymbol{\tau}^{(n)}$	1,4
Spriggs 6-constant	$\eta_0\ \lambda_1\ \lambda_2\ \alpha$ $\epsilon_1\ \epsilon_2$		$(1+\lambda_1 n^{-\alpha} F_{1+\epsilon_1,\frac{2}{3}(1+\epsilon_1),0})\boldsymbol{\tau}^{(n)} = -2\eta_0 \frac{n^{-\alpha}}{Z(\alpha)}$ $\times(1+\lambda_2 F_{1+\epsilon_2,\frac{2}{3}(1+\epsilon_2),0})\boldsymbol{e}, \quad \boldsymbol{\tau} = \sum_{n=1}^{\infty}\boldsymbol{\tau}^{(n)}$	1
Roscoe	$\eta_0\ \lambda_n\ \mu_n$ $\gamma\ s\ \rho$		$\prod_{n=1}^{N}(1+\lambda_n F_{rsp})\boldsymbol{\tau} = -2\eta_0 \prod_{n=1}^{N}(1+\mu_n F_{rsp})\boldsymbol{e}$	8
Williams	$\eta_0\ \lambda_1\ \lambda_2\ \omega$		$(1+\lambda_1 F_{1,2\omega,0})\boldsymbol{\tau} = -2\eta_0 (1+\lambda_2 F_{1,2\omega,0})\boldsymbol{e}$	9
White-Metzner	G	μ	$\left[1+\frac{\mu}{G F_{100}}\right]\boldsymbol{\tau}' = -2\mu\boldsymbol{e}, \quad \boldsymbol{\tau} = \boldsymbol{\tau}' - \frac{1}{3}(\boldsymbol{\tau}:\boldsymbol{\delta})\boldsymbol{\delta}$ μ is a function of $(\boldsymbol{e}:\boldsymbol{e})$	10
Tanner	λ	μ	$(1+\lambda F_{100})\boldsymbol{\tau} = -2\mu\boldsymbol{e}$ μ is a function of $(\boldsymbol{e}:\boldsymbol{e})$	11

Table I: Differential Models (cont'd)

Name	Constant	Function	Equation	Ref.
Unsymmetrical Maxwell	η_0 λ ϵ ξ		$(1+\lambda F_{1+\epsilon,\frac{2}{3}(1+\epsilon),0})\underline{\underline{\tau}} - \xi[(\underline{\underline{e}}\cdot\underline{\underline{\tau}}) - \frac{1}{3}(\underline{\underline{\tau}}:\underline{\underline{e}})\underline{\underline{\delta}}] = -2\eta_0\underline{\underline{e}}$	1 2
Coleman-Noll 2nd Order Fluid	η_0 β γ		$\underline{\underline{\tau}} = 2\eta_0\underline{\underline{e}} - 4\beta(\underline{\underline{e}}\cdot\underline{\underline{e}}) - 2\gamma F_{100}\underline{\underline{e}}$	13
Reiner-Rivlin	~~α_1 α_2~~	α_1, α_2	$\underline{\underline{\tau}} = -2\alpha_1\underline{\underline{e}} - 4\alpha_2(\underline{\underline{e}}\cdot\underline{\underline{e}})$	14
Bird-William-Spriggs		η, ξ, β	$\underline{\underline{\tau}} = -2\eta\underline{\underline{e}} - 2(\xi - 2\beta)[(\underline{\underline{e}}\cdot\underline{\underline{e}}) - \frac{1}{3}(\underline{\underline{e}}:\underline{\underline{e}})\underline{\underline{\delta}}] + 2\xi F_{100}\underline{\underline{e}}$ η, ξ, β are function of invariants of $\underline{\underline{e}}$	15
Rivlin-Ericksen		f	$\underline{\underline{\tau}} = -f(\underline{\underline{e}}, F_{100}\underline{\underline{e}}, \cdots, F_{100}^{n}\underline{\underline{e}})$	16
Yamamoto	β, ϵ ϕ G		$\underline{\underline{\tau}} = -G[\underline{\underline{\delta}} + \epsilon\phi(\underline{\underline{\lambda}} - \underline{\underline{\delta}})](\underline{\underline{\lambda}} - \underline{\underline{\delta}})$ $F_{100}\underline{\underline{\lambda}} = -\beta[\underline{\underline{\delta}} + \phi(\underline{\underline{\lambda}} - \underline{\underline{\delta}})]\cdot(\underline{\underline{\lambda}} - \underline{\underline{\delta}})$	17

Table II: Integral Models

Name	Equation	Ref.
Lodge (1956)	$\underline{\underline{\tau}} = -\int_{-\infty}^{t} m(t-t')\,\underline{\underline{C}}^{-1}(t,t')\,dt'$	18
Lodge (1964)	$\underline{\underline{\tau}} = -\int_{-\infty}^{t} m(t-t', II(t))\,\underline{\underline{C}}^{-1}(t,t')\,dt'$ $m(t-t', II(t)) =$ [illegible]	18
Lodge (1965)	$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \{ \mu_1(t-t', II(t))\,\underline{\underline{C}}^{-1}(t,t')$ $+ \mu_2(t-t', II(t))\,\underline{\underline{C}}(t,t') \}\,dt'$	12
Ward-Jenkins	$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \{ \mu_1(t-t')\,\underline{\underline{C}}^{-1}(t,t')$ $+ \mu_2(t-t')\,\underline{\underline{C}}(t,t') \}\,dt'$	19
WJFLMB	$\underline{\underline{\tau}} = -\int_{-\infty}^{t} m(t-t', II(t'))\,[(1-\frac{\epsilon}{2})\underline{\underline{C}}^{-1} + \frac{\epsilon}{2}\underline{\underline{C}}]\,dt'$ $m(t-t', II(t')) = \frac{\sum \frac{\eta_p}{\lambda_p} \frac{1}{1+[\text{illegible}]} e^{-s/\lambda_p}}{\sum \lambda_p}$ $\lambda_p = \frac{\lambda}{p^{\alpha}}$	12
Analog of WJFLMB	$\underline{\underline{\tau}} = -\int_{-\infty}^{t}$ [illegible] $\underline{\underline{C}}^{-1}$ [illegible] [illegible] $\underline{\underline{C}}$ [illegible] dt' [illegible] $= \frac{1}{\sum \lambda_p} \sum \frac{e^{[\text{illegible}]}}{1+[\text{illegible}]}$	1
Oldroyd-Walters-Fredricksen	$\underline{\underline{\tau}} = -\int_{-\infty}^{t}$ [illegible] $\frac{\partial}{\partial t'}\underline{\underline{C}}$ [illegible] dt'	20, 21
Walters	$(1-$ [illegible] $)\,\underline{\underline{\tau}} = \int_{-\infty}^{t} \psi(t-t')$ $\frac{\partial}{\partial t'}\underline{\underline{C}}$ [illegible] $dt' - 2\eta_0$ [illegible] $\underline{\underline{e}}$	21

Table II: Integral Models (cont'd)

Name	Equation	Ref.
Bernstein -Kearsley -Zapas	$\underline{\underline{\tau}} = -\int_{-\infty}^{t}$ [illegible] $\underline{\underline{C}}^{-1}(t')\,dt'$	22
Coleman-Noll 2nd order theory of viscoelasticity	$\underline{\underline{\tau}} = -\int_{-\infty}^{t}$ [illegible] dt' [illegible] $\int_{-\infty}^{t}\int_{-\infty}^{t}$ [illegible] $dt'\,dt''$	23
Waters-Walters	$\underline{\underline{\tau}} = -2\int_{-\infty}^{t}$ [illegible] $\underline{\underline{F}}$ [illegible] dt' $-4\int_{-\infty}^{t}$ [illegible] $\underline{\underline{F}}$ [illegible] dt'	24
Carreau -Bird	$\underline{\underline{\tau}} = -\int_{-\infty}^{t}$ [illegible] dt'; [illegible] $\sum \frac{\eta_p}{\lambda_{\cdot}} \frac{e^{[illegible]}}{1 + [illegible]}$; $\eta_p = \eta_0 \frac{\lambda_{\cdot}}{\sum \lambda_{\cdot}}$, $\lambda_{1n} = \lambda_1 \left(\frac{[illegible]}{[illegible]}\right)^{\alpha_1}$, $\lambda_{2n} = \lambda_2 \left(\frac{[illegible]}{[illegible]}\right)^{\alpha_2}$	2

Discussion:

The constitutive equations are always judged by the following experimental criteria.

(a) Non-Newtonian viscosity $\eta(\dot{\gamma})$

An adequate constitutive equation must be able to describe the most commonly measured property of viscoelastic fluids which is the variation of viscosity with shear rate.

(b) Primary normal stress coefficient $\theta(\dot{\gamma})$

A constitutive equation must be able to describe the shear rate dependence of the primary normal stress coefficient

(c) Secondary normal stress coefficient $\beta(\dot{\gamma})$

A constitutive equation must be able to describe the shear rate dependence of the second normal stress coefficient

(d) Complex viscosity $\eta^*(\omega)$

A constitutive equation should be able to describe the complex viscosity or an equivalent material function from linear viscoelasticity.

(e) Shear-stress relaxation after steady shearing $\eta(\dot{\gamma}, t)$

This property is interesting because it serves as a link between linear and nonlinear viscoelasticity. An interesting phenomenon which has been observed by some investigators is that the rate of stress relaxation depends on the initial shear rate

(f) Normal-stress relaxation after steady shearing $\theta(\dot{\gamma}, t)$

One of the most important phenomena noted for this property is that the normal stresses relax slower than the shear stresses.

(g) Elongational flow phenomena

Elongation is one of the simplest flows which have been studied other than simple shearing. However, the experimental difficulties have not yet been satisfactorily overcome.

(h) Recoil

This is another property for which very little experimental information is available.

(i) Material objectivity

From continuum mechanics we have the requirement of material objectivity. This means that an acceptible constitutive equation should be independent of rigid body motions.

(j) Simplicity

From engineering practice, there arises the requirement that a constitutive equation should be simple.

Most appraisal of the constitutive equations have been made by using the polymer solutions rather than polymer melts as experimental samples. Also more attention has been paid to such properties as non-Newtonian viscosity, complex viscosity and first normal stress coefficient, because experimental work is relatively easier for these properties. For the other properties, only qualitative comparisons have been possible.

In general, all of the models listed here meet the test of material objectivity, but few of them are simple.

Some restrictions apply to several of the proposed models have been found as follow:

(A) very low deformation rates

Lodge(1956), Oldroyd-Water-Fredrickson, Ward-Jenkins

(B) Very slowly changing flow, any deformation rate

Bird-William-Spriggs, Rivlin-Erickson

(C) very low deformation rate, very slowly changing flow

Coleman-Noll second order Fluid

(D) low deformation rates

Oldroyd 3-constant, Oldroyd 8-constant, Williams, Unsymmetrical Maxwell, Coleman-Noll Second Order Fluid

(E) can not describe all stress relaxation phenomena

Oldroyd 3-constant, Oldroyd 8-constant, Williams, Unsymmetrical Maxwell, Coleman-Noll Second Order Fluid, Tanner, White-Metzner, Lodge(1964), Lodge(1969), Walters, Water-Walters

(F) can not describe both normal stress differences

Oldroyd 8-constant, Oldroyd(1962), Spriggs-Bird, Tanner White-Metzner, Oldroyd-Water-Fredrickson, Reiner-Rivlin (can't describe $\theta(\dot{\gamma})$), Lodge(1964) (can't describe $\beta(\dot{\gamma})$)

As stated before, since most comparisons have been made for polymer solutions, more effort should be directed to polymer melts.

Empirical Rheological Equation

The complex rheological equations derived from the continuum mechanics theory and molecular theories etc., are desirable in that they (i) apply to many kinds of materials , (ii) describe many phenomena simultaneously, (iii) permit extrapolation, (iv) apply to any flow system as they are derived in such a way that they are unaffected by the choice of the particular system.

Empirical equations, however, have the advantage of being easily manipulated. They are particularly useful when only one behavior of data such as viscosity or normal stress is needed.

Among them the power law is the most widely used one.

$$\tau_{12} = m\dot{\gamma}^{n} \qquad \cdots\cdots\cdots(39)$$

Some more of them are listed below:(25)

The Binghan Model

$$\tau_{12} = -\mu_0 \dot{\gamma} \pm \tau_0 \qquad \text{if } |\tau_{12}| > \tau_0$$

$$\dot{\gamma} = 0 \qquad \text{if } |\tau_{12}| < \tau_0$$

The Eyring Model

$$\tau_{12} = A \operatorname{arcsinh}\left(-\frac{1}{B}\dot{\gamma}\right)$$

The Ellis Model

$$-\dot{\gamma} = \left(\varphi_0 + \varphi_1 |\tau_{12}|^{\alpha-1}\right)\tau_{12}$$

The Reiner-Philippoff Model

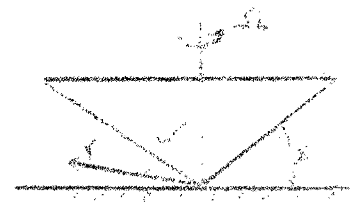
$$-\dot{\gamma} = \left(\frac{1}{\mu_\infty + \dfrac{\mu_0 - \mu_\infty}{1 + \left(\dfrac{\tau_{12}}{\tau_s}\right)^2}} \right)$$

III EXPERIMENTAL

Apparatus - Weissenberg Rheogoniometer

The Weissenberg Rheogoniometer operated as a cone-and-plate instrument is a powerful one to measure rheological properties such as shear stress, primary normal stress difference, the complex viscosity etc. This instrument can b e used in many ways, among which, the rotational and forced oscillatory testings are most important ones and are illustrated below.

Rotational testing. Consider the flow between a stationary flat plate and a rotating cone with a very small angle α. If inertial forces are neglected and edge effects at the periphery of the cone are ignored, the equation of motion is:



$$\frac{1}{r}\frac{\partial}{\partial r}(r^2\tau_{r\phi}) + \frac{\partial \tau_{\theta\phi}}{\partial \theta} + \tau_{r\phi} + 2\tau_{\theta\phi}\cot\theta = 0 \quad ....(1)$$

The only non-zero velocity component is v_ϕ , and, by the symmetry of the flow in the ϕ-direction, the only non-zero components of the rate of deformation tensor are:

$$\Delta_{r\phi} = \Delta_{\phi r} = r\frac{\partial}{\partial r}\left(\frac{v_\phi}{r}\right) \quad ....(2)$$

$$\Delta_{\theta\phi} = \Delta_{\phi\theta} = \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\left(\frac{v_\phi}{\sin\theta}\right) \quad ....(3)$$

Assume

$$v_\phi = r\,f(\theta) \quad ....(4)$$

which satisfies the boundary conditions:

$$V_\phi = \Omega r \sin(\frac{\pi}{2} - \alpha), \quad at \quad \theta = \frac{\pi}{2} - \alpha \qquad \text{.......(5)}$$

$$V_\phi = 0 \quad , at \quad \theta = \frac{\pi}{2} \qquad \text{.......(6)}$$

$$V_\phi = 0 \quad , at \quad r = 0 \qquad \text{.......(7)}$$

where Ω is the angular velocity of cone.

Then equation(4) substitutes into rate of deformation tensor, we have

$$\Delta_{r\phi} = 0$$

and from symmetry

$$\tau_{r\phi} = \tau_{r\theta} = 0$$

The equation of motion become

$$\frac{1}{r}\frac{d\tau_{\theta\phi}}{d\theta} - \frac{2\cot\theta}{r}\tau_{\theta\phi} = 0 \qquad \text{.......(8)}$$

$$\tau_{\theta\phi} = \frac{C_1}{\sin^2\theta} \cong \frac{C_1}{\sin^2\frac{\pi}{2}} = constant \qquad \text{.......(9)}$$

The torque T equals the total shear stress exerted on the surface of plate

$$T = \int_0^R 2\pi\tau_{\theta\phi} r^2 dr \cong 2\pi \cdot \frac{R^3}{3} C_1 \qquad \text{.......(10)}$$

$$\therefore \quad C_1 = \frac{3T}{2\pi R^3}$$

$$\tau_{\theta\phi} = \frac{3T}{2\pi R^3 \sin^2\theta} \qquad \text{.......(11)}$$

Since $\tau_{\theta\phi}$ is nearly constant, it follows that $\dot{\gamma}$ is also nearly constant*

$$\dot{\gamma} = -\frac{1}{r}\frac{dV_1}{d\theta} \qquad \ldots\ldots\ldots(12)$$

$$V_1 = r\dot{\gamma}\left(\frac{\pi}{2} - \theta\right) \qquad \ldots\ldots\ldots(13)$$

From the boundary conditions, we get

$$\dot{\gamma} = \frac{\Omega}{\alpha} \qquad \ldots\ldots\ldots(14)$$

and

$$V_1 = r\Omega\left(\frac{\pi}{2} - \theta\right)/\alpha \qquad \ldots\ldots\ldots(15)$$

If we express the torque

$$T = \Delta_1 K_1 \qquad \ldots\ldots\ldots(16)$$

where

Δ_1 = movement of torsion head transducer in microns

K_1 = torsion bar consta t in dyne cm per micron movement of the transducer

and

β = angular rotation of the platen in radian per second

$t = 2\pi/\beta$ (sec./rev)

Then equation(14) becomes

$$\dot{\gamma} = \frac{\Omega}{\alpha} = \frac{180\beta}{\pi\alpha} = \frac{360}{\alpha t} \qquad \ldots\ldots\ldots(17)$$

and equation(11) becomes

$$\tau_{12} = \frac{3T}{2\pi R^3} = \frac{3.82\,T}{d^3} \qquad \ldots\ldots\ldots(18)$$

$$\eta = \frac{\tau_{12}}{\dot{\gamma}} = \frac{\alpha t}{360}\cdot\frac{3.82\,T}{d^3}$$

$$= \frac{T\alpha t}{94.25\,d^3} = \frac{t\,\alpha\,\Delta_1 K_1}{94.25\,d^3}\ \text{poise} \qquad \ldots\ldots\ldots(19)$$

In order to get the expression for the primary normal stress difference, we write down the r-component ; of the equation of motion

$$-\rho \frac{v_\phi^2}{r} = -\frac{\partial p}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} - \frac{\tau_{\theta\theta} + \tau_{\phi\phi} - 2\tau_{rr}}{r} \qquad \ldots\ldots\ldots(20)$$

Since τ is a function of $\dot{\gamma}$ which in turn independent of r, so $\frac{\partial \tau_{rr}}{\partial r}$ is vanished. Furthermore

$$T_{\theta\theta}(r,\theta) = -p(r,\theta) + \tau_{\theta\theta} \qquad \ldots\ldots\ldots(21)$$

$$\frac{\partial T_{\theta\theta}}{\partial r} = -\frac{\partial p}{\partial r} \qquad \ldots\ldots\ldots(22)$$

Substitute equation(22) into equation(20), we get

$$\frac{\partial T_{\theta\theta}}{\partial r} = -\left(\frac{\rho v_\phi^2}{r} - \frac{\tau_{\theta\theta} + \tau_{\phi\phi} - 2\tau_{rr}}{r} \right) \qquad \ldots\ldots\ldots(23)$$

At $\theta = \frac{\pi}{2}$, $v = 0$, the above equation becomes

$$\frac{\partial T_{\theta\theta}}{\partial r} = -\frac{\tau_{\theta\theta} - \tau_{\phi\phi} - 2\tau_{rr}}{r} = -\frac{\tau_{\theta\theta}}{r}$$

or

$$\frac{\partial T_{\theta\theta}}{\partial \ln r} = -3\tau_{\theta\theta} = \text{constant} \qquad \ldots\ldots\ldots(24)$$

For the small cone angle, the vertical force exerted against the cone, F may be calculated from

$$F = -2\pi \int_0^R T_{\theta\theta}\, r\, dr \qquad \ldots\ldots\ldots(25)$$

Integrate by parts

$$F = -2\pi \left(\frac{R^2}{2} T_{\theta\theta}(R) - \int_0^R \frac{r^2}{2} \frac{\partial T_{\theta\theta}}{\partial r}\, dr \right) \qquad \ldots\ldots\ldots(26)$$

Substitute equation(24) into the previous equation

$$F = -2\pi\left(\frac{R^2}{2}\tau_{zz}(R) + \frac{1}{2}\tau_{11}\frac{R^2}{2}\right)$$

$$= -\pi R^2\left[(-p(R) - \tau_{22}) + \frac{1}{2}(\tau_{11} - \tau_{22})\right] \qquad \text{.......(27)}$$

If the system isin equilibrium with the atmosphere on its outer boundary, then

$$-p(R) + \tau_{22} = \tau_{rr}(R) = 0 \qquad \text{...... .(28)}$$

and it follows that

$$\tau_{11} - \tau_{22} = \frac{2F}{\pi R^2} \qquad \text{.......(29)}$$

<u>Forced oscillatory testing.</u> For small amplitude oscillatory motion, the flow behavior is linear. A simple harmonic input of shear strain, with a certain frequency, amplitude and phase, will produce a simple harmonic output of shear stress with the same frequency, but with a different amplitude and phase. Hence, one may describe the shear strain and shear stress as function of time, viz:

$$\gamma_{21}(t) = \gamma_0\cos(\omega t - \delta_\gamma) \qquad \text{.......(30)}$$

$$\tau_{21}(t) = P_0\cos(\omega t - \delta_\tau)$$

$$= \mathrm{Re}\left(P_0 e^{-i\delta_\tau} e^{i\omega t}\right) \qquad \text{.......(31)}$$

$$= \mathrm{Re}\left(\tau_{21}^{*} e^{i\omega t}\right) \qquad \text{.......(32)}$$

where

γ_0, P_0 = amplitude of shear strain, shear stress

δ_γ, δ_τ = phase of shear strain, shear stress

$\tau_{21}^{*} = P_0 e^{-i\delta_\tau}$ = complex amplitude of shear stress

.......(33)

Differentiate equation(30), the result is

$$\dot{\gamma} = \dot{\gamma}_a = \omega S_a \sin(\omega t - \delta_s)$$

$$= R_e[-i\omega S_a e^{-i\delta_s} e^{i\omega t}] = R_e(\dot{\gamma}^* e^{i\omega t}) \quad \text{.......(34)}$$

where

$$\dot{\gamma}^* = -i\omega S_a e^{-i\delta_s} \quad \text{.......(35)}$$

-complex amplitude of rate -of-shear

Define

$$\eta^* = \eta'(\omega) - i\eta''(\omega) = -\frac{\tau^*}{\dot{\gamma}^*} \quad \text{.......(36)}$$

From equations (33),(34) we have

$$\eta^* = -\frac{P_a e^{-i\delta_f}}{i\omega S_a e^{-i\delta_s}} = \frac{1}{i\omega} G_r(\omega) e^{-i(\delta_f - \delta_s)}$$

$$= \frac{1}{i\omega} G_r(\omega) e^{-i\varphi} = \frac{1}{\omega} G_r \sin\varphi - i\frac{G_r}{\omega}\cos\varphi \quad \text{........(37)}$$

$$\eta' = \frac{1}{\omega} G_r \sin\varphi \quad \text{......(38)}$$

$$\eta'' = \frac{1}{\omega} G_r \cos\varphi = \eta' \cot\varphi \quad \text{......(39)}$$

where

$$G_r = \frac{P_a}{S_a}$$

$$\varphi = \delta_f - \delta_s$$

The maximum value of shear strain is

$$S_a = \frac{A_a}{[illegible]} \quad \text{.......(40)}$$

where

peak value of input oscillation measured in microns of movement of the wormshaft

From force balance similar to equation(10),(11) we have

$$P_s = \frac{P_T \, 2(K - J\omega^2)}{3\pi A^2}$$

$$= \frac{[illegible] \, d_{tt} \, K \left(1 - \left(\frac{f}{f_n}\right)^2\right)}{d^3} \quad \text{dynes/cm}^2 \qquad \ldots\ldots\ldots(42)$$

where

K = torsional elastic constant for torsionbar

J = moment of inertia

f = frequency of the imposed oscillation in cycles/sec

d_{tt} = peak movement of the torsion head transducer measured in microns

f_n = natural frequency of torsion head in cycles/sec.

<u>Data</u>

Data from several sources are used in testing the models, and are listed as follows:

(a) Polyethylene samples studied in the Newark College of Engineering rheological laboratory are as follow: (23)

(i) Marlex 646 (160°C)

(ii) Marlex 646 (180°C)

(iii) Marlex 646 (200°C)

(iv) Alathon 10 (190°C)

(v) Celanese (190°C)

A Weissenberg Rheogoniometer Model R-18 made by Sangamo Control Limited, with a small cone angle $\alpha = 4°$, was used to get the viscosity and normal stress data.

Equations (17),(19),(29) are used to calculate the shear rate, apparent viscosity and primary normal stress difference of Marlex 646. The oscillatory data of Alathon 10 and Celanese can be calculated by equations (38) and (39), or through the relation with shear moduli

$$\eta_M = \frac{1}{\omega} \tau_A(\omega) \sin\phi \qquad \text{.........(42)}$$

$$\eta_F = \frac{\tau_A(\omega)}{\omega \sin\phi} \qquad \text{.........(43)}$$

by

$$\eta' = \eta_M = \sin^2\phi \, \eta_F \qquad \text{.........(44)}$$

$$\eta'' = \cot\phi \, \eta' \qquad \text{.........(45)}$$

Detailed data are given in the appendix.

(b) King's Data (29)

(i) Polyethylene; density = 0.95 gm/cc,
melt flow index = 0.35,
narrow M.Wt. spread.

(ii) Polyethylene; density = 0.95 gm/cc,
melt flow index = 0.31,
broad M.Wt. spread.

(iii) Polyethylene; density = 0.95 gm/cc,
melt flow index = 0.28,
medium M.Wt. spread.

These data were obtained with the Weissenberg Rheogoniometer Model R-16 with 4 degree, 5.0 cm cone, and a capillary rheometer. Temperature kept on 190 ± 0.5 degree C.

(c) Carreau and Bird's data (2)

Phenoxy-A; at 212 degree C, manufactured by Union Carbide company.

(d) Nakajima & Wong's data (30)

(i) Pure resin A ; density = 0.95, melt index = 0.4

(ii) 80% of resin A and 20% of high molecular weight component (polyethylene of Phillips type, melt index 0.74, density 0.945)

Resin A is Polyethylene of Phillips type with melt index 0.4 and density 0.950.

(e) Hogan, Levett and Werkman's data (31)

(i) Polyethylene; melt index = 0.21

(ii) Polyethylene; melt index = 0.20

IV. RESULTS AND DISCUSSION

Recently, C.D. Denson et. al. (32) used the Spriggs Model to compare the viscosity and elasticity of some poly-mer melts. A little earlier, R.B. Bird and P.J. Carreau tested their model against one sample of polymer melt.

In this work, thirteen samples have been selected (see the previous chapter) to compare their steady viscosity, com-plex viscosity, and primary normal stress difference with Spriggs Model, Carreau and Bird Model, and two empirical models.

Evaluation of Spriggs 4-constant, WJFLMB, AND OWFS Models. These three models are taken together because they give exactly the same material function η, η^* (33) defined for simple flow which has the velocity distribution

$$v_1 = v_1(x_2, t) = \dot{\gamma}(t)\, x_2 \qquad \text{.......(1)}$$

$$v_2 = v_3 = 0 \qquad \text{.......(2)}$$

and the shear rate, shear stress

$$\dot{\gamma}(t) = \dot{\gamma} = \frac{dv_1}{dx_2} \text{ ; for steady-shear motion} \qquad \text{.......(3)}$$

$$\dot{\gamma}(t) = Re(\dot{\gamma}^0 e^{i\omega t}) \text{ for small amplitude sinusoidal} \qquad \text{..(4)}$$

$$\tau_{12} = Re(\tau_{12}^0 e^{i\omega t}) \text{ shear flow} \qquad \text{.......(5)}$$

by

$$\tau_{12} = -\eta\, \dot{\gamma} \qquad \text{.......(6)}$$

$$\tau_{11} - \tau_{22} = -\Theta\, \dot{\gamma}^2 \quad \text{for steady shear motion} \qquad \text{.......(7)}$$

$$\tau_{12}^0 = -\eta^*\, \dot{\gamma}^0 \qquad \text{.......(8)}$$

where $\dot{\gamma}^0$ and τ_{12}^0 are the complex amplitudes of $\dot{\gamma}$ and τ_{12}

The model

(a) Spriggs Model:

$$\tau^{(p)} + \lambda_p \frac{\delta}{\delta t}\Big|_{\frac{1+\epsilon}{2}(1+\epsilon),0} \tau^{(p)} = -\left(2\eta_0 \, p^{-\alpha}/Z(\alpha)\right) \dot{\gamma} \qquad \ldots\ldots(9)$$

$$\tau = \sum_{p=1}^{\infty} \tau^{(p)} \qquad \ldots\ldots(10)$$

The time constant λ_p are taken to be of the form

$$\lambda_p = \lambda \, p^{-\alpha} \qquad \ldots\ldots(11)$$

and $Z(\alpha)$ is the Riemann Zeta function

$$Z(\alpha) = \sum_{n=1}^{\infty} n^{-\alpha} \qquad \ldots\ldots(12)$$

(b) WJFLMB Model:

$$\tau = -\int_{-\infty}^{t} M(t-t', II(t')) \left[\left(1+\frac{\epsilon}{2}\right) C^{-1} - \frac{\epsilon}{2} C\right] dt' \qquad \ldots\ldots(13)$$

$$M(t-t', II(t')) = \frac{\eta_0}{\sum_{p=1}^{\infty} \lambda_p} \sum_{p=1}^{\infty} \frac{1}{\lambda_p} \frac{\exp[-(t-t')/\lambda_p]}{1 + 2\, II(t') \lambda_p^2} \qquad \ldots\ldots(14)$$

$$\lambda_p = \lambda \, p^{-\alpha} \qquad \ldots\ldots(15)$$

$II(t') = (\dot{\gamma} : \dot{\gamma})$ = the second invariant of the e tensor. ......(16)

C and C^{-1} are Cauchy and Finger tensors respectively with the compounents given by

$$C_{ij} = \frac{\partial x^m}{\partial x'^i} \frac{\partial x^n}{\partial x'^j} g_{mn}(x) \qquad \ldots\ldots(17)$$

$$(C^{-1})^{ij} = \frac{\partial x'^i}{\partial x^m} \frac{\partial x'^j}{\partial x^n} g^{mn}(x) \qquad \ldots\ldots(18)$$

(c) CWPS Model:

$$\tau = \int_{-\infty}^{t} \left[m(t-t', II) \right] \left[\left(1 + \frac{\epsilon}{2}\right) \frac{\partial \gamma}{\partial t'} + \frac{\epsilon}{2} \frac{\partial \gamma}{\partial t'} \right] dt' \qquad \cdots\cdots\cdots(19)$$

where

$$m(t-t', II) = \frac{\eta_0}{\lambda} \sum \frac{\exp(-(t-t')/\lambda_p)}{1 + \frac{1}{2} II \lambda_p^2} \qquad \cdots\cdots\cdots(20)$$

Material Functions.

In this section, the Spriggs Model is tried to solve for simple flow defined by equations (1) through (5). For this kind of motion

$$\tau = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{12} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix} \qquad \cdots\cdots\cdots(21)$$

$$\nabla v = \sum_i \sum_j \delta_i \delta_j \left(\frac{\partial v_j}{\partial x_i}\right) = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdots(22)$$

$$(\nabla v)^T = \begin{pmatrix} 0 & \dot{\gamma}(t) & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdots(23)$$

$$\dot{\gamma} = \frac{1}{2}\left[\nabla v + (\nabla v)^T \right] \qquad \cdots\cdots\cdots(24)$$

$$= \frac{\dot{\gamma}(t)}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdots(25)$$

$$\underline{\underline{\omega}} = \frac{1}{2}\left((\nabla \underline{v}) - (\nabla \underline{v})^T\right) = \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(26)$$

$$\underline{\underline{\omega}} \cdot \underline{\underline{\tau}} = \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} -\tau_{21} & -\tau_{22} & 0 \\ \tau_{11} & \tau_{12} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(27)$$

$$\underline{\underline{\tau}} \cdot \underline{\underline{\omega}} = \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} \tau_{12} & -\tau_{11} & 0 \\ \tau_{22} & -\tau_{21} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(28)$$

$$\underline{\underline{e}} \cdot \underline{\underline{\tau}} = \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} \tau_{21} & \tau_{22} & 0 \\ \tau_{11} & \tau_{12} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(29)$$

$$\underline{\underline{\tau}} \cdot \underline{\underline{e}} = \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} \tau_{12} & \tau_{11} & 0 \\ \tau_{22} & \tau_{21} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(30)$$

$$\underline{\underline{e}} : \underline{\underline{\tau}} = tr(\underline{\underline{e}} \cdot \underline{\underline{\tau}}) = \dot{\gamma}(t)\,\tau_{12} \qquad \cdots\cdots\cdot(31)$$

$$\underline{v} \cdot \nabla \underline{\underline{\tau}} = 0 \qquad \cdots\cdots\cdot(32)$$

$$\frac{D\underline{\underline{\tau}}}{Dt} = \frac{\partial}{\partial t}\underline{\underline{\tau}} + \frac{\dot{\gamma}(t)}{2}\begin{pmatrix} -2\tau_{12} & \tau_{11}-\tau_{22} & 0 \\ \tau_{11}-\tau_{22} & 2\tau_{12} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \cdots\cdots\cdot(33)$$

$$\frac{\mathcal{D}\underline{\underline{\tau}}}{\mathcal{D}t} = \frac{\partial \underline{\underline{\tau}}}{\partial t} - (1-\varepsilon)\frac{\dot{\gamma}(t)}{2}\begin{pmatrix} 2\tau_{12} & \tau_{22}-\tau_{11} & 0 \\ \tau_{11}+\tau_{22} & -2\tau_{12} & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{2}{3}(1-\varepsilon)\dot{\gamma}(t)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\tau_{12} \qquad \cdots\cdots\cdot(34)$$

We can then write equation(9) as :

$$\begin{pmatrix} \tau_{11}^{(1)} & \tau_{12}^{(1)} & 0 \\ \tau_{21}^{(1)} & \tau_{22}^{(1)} & 0 \\ 0 & 0 & \tau_{33}^{(1)} \end{pmatrix} + \lambda_0 \left\{ \frac{\partial}{\partial t} \begin{pmatrix} \tau_{11}^{(1)} & \tau_{12}^{(1)} & 0 \\ \tau_{21}^{(1)} & \tau_{22}^{(1)} & 0 \\ 0 & 0 & \tau_{33}^{(1)} \end{pmatrix} \right.$$

$$+ \frac{\dot\gamma(t)}{2} \begin{pmatrix} -2\tau_{12}^{(1)} & \tau_{11}^{(1)} - \tau_{22}^{(1)} & 0 \\ \tau_{11}^{(1)} - \tau_{22}^{(1)} & 2\tau_{12}^{(1)} & 0 \\ 0 & 0 & 0 \end{pmatrix} - \frac{(1+\epsilon)\dot\gamma(t)}{2} \begin{pmatrix} 2\tau_{12}^{(1)} & \tau_{11}^{(1)} + \tau_{22}^{(1)} & 0 \\ \tau_{11}^{(1)} + \tau_{22}^{(1)} & 2\tau_{12}^{(1)} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\left. + \frac{2}{3}(1+\epsilon)\dot\gamma(t)\tau_{12}^{(1)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}$$

$$= - \frac{2\eta_0 n^*}{Z(x)} \frac{\dot\gamma(t)}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ - - - - - - - - (25)}$$

From the above equations we get :

$$\tau_{11}^{(1)} + \lambda_0 \frac{\partial \tau_{11}^{(1)}}{\partial t} - \frac{\lambda_0}{3}(4+\epsilon)\dot\gamma(t)\tau_{12}^{(1)} = 0 \text{ - - - - - - - (26)}$$

$$\tau_{12}^{(1)} + \lambda_0 \frac{\partial \tau_{12}^{(1)}}{\partial t} - \frac{\lambda_0}{2}\epsilon\dot\gamma(t)\tau_{11}^{(1)} - \frac{\lambda_0}{2}(2+\epsilon)\dot\gamma(t)\tau_{22}^{(1)}$$

$$= - \frac{\eta_0 n^* \dot\gamma(t)}{Z(x)} \text{ - - - - - - - (27)}$$

$$\tau_{22}^{(1)} + \lambda_0 \frac{\partial \tau_{22}^{(1)}}{\partial t} + \frac{\lambda_0}{3}\dot\gamma(t)(2-\epsilon)\tau_{12}^{(1)} = 0 \text{ - - - - - - (28)}$$

$$\tau_{33}^{(1)} + \lambda_0 \frac{\partial \tau_{33}^{(1)}}{\partial t} + \frac{2}{3}\lambda_0(1+\epsilon)\dot\gamma(t)\tau_{12}^{(1)} = 0 \text{ - - - - - (29)}$$

For steady state simple shearing, the above four equations reduce to:

$$\tau_{11}^{(i)} - \frac{\lambda_i}{2}(a+c)\dot{\gamma}(t)\,\tau_{12}^{(i)} = 0 \qquad \text{.......(40)}$$

$$\tau_{12}^{(i)} - \frac{\lambda_i}{2}c\,\dot{\gamma}\,\tau_{11}^{(i)} - \frac{\lambda_i}{2}(c+e)\,\dot{\gamma}\,\tau_{22}^{(i)} = -\frac{\eta_0\, a^{i\alpha}\dot{\gamma}}{Z(\alpha)} \qquad \text{.......(42)}$$

$$\tau_{22}^{(i)} + \frac{\lambda_i}{2}\dot{\gamma}(a-c)\,\tau_{12}^{(i)} = 0 \qquad \text{.......(42)}$$

$$\tau_{33}^{(i)} + \frac{\lambda_i}{2}(c-e)\,\dot{\gamma}\,\tau_{12}^{(i)} = 0 \qquad \text{.......(43)}$$

Solve for $\tau_{12}^{(i)}$, $\tau_{11}^{(i)}$, $\tau_{22}^{(i)}$, $\tau_{33}^{(i)}$

$$\tau_{12}^{(i)} = -\frac{\eta_0}{Z(\alpha)}\,\frac{a^{i\alpha}\dot{\gamma}}{1+\frac{\lambda_i^2}{4}(1-\epsilon^2)\dot{\gamma}^2} = -\frac{\eta_0\, a^{i\alpha}\dot{\gamma}}{Z(\alpha)(1+c^2\lambda_i^2\dot{\gamma}^2)} \qquad \text{.......(44)}$$

$$\tau_{11}^{(i)} = +\frac{\lambda_i}{2}(a+c)\,\dot{\gamma}\,\tau_{12}^{(i)} \qquad \text{.......(45)}$$

$$\tau_{22}^{(i)} = -\frac{\lambda_i}{2}\dot{\gamma}(a-c)\,\tau_{12}^{(i)} \qquad \text{.......(46)}$$

$$\tau_{33}^{(i)} = -\frac{\lambda_i}{2}(c-e)\,\dot{\gamma}\,\tau_{12}^{(i)} \qquad \text{.......(47)}$$

where

$$c^2 = 1 - a - \frac{e^2}{4} \qquad \text{.......(48)}$$

From equations (10), (11)

$$\tau_{12} = \sum_{i=1}^{\infty} \tau_{12}^{(i)}$$

$$= -\frac{\eta_0}{Z(\alpha)} \sum_{i=1}^{\infty} \frac{a^{i\alpha}}{1+c^2\lambda_i^2\dot{\gamma}^2}\,\dot{\gamma}$$

$$= -\frac{\eta_0}{Z(\alpha)} \sum_{i=1}^{\infty} \frac{a^{\alpha}}{a^{i\alpha}+c^2\lambda^2\dot{\gamma}^2}\,\dot{\gamma} \qquad \text{.......(49)}$$

$$\tau_{11} - \tau_{22} = \sum_{i=1}^{\infty}(\tau_{11}^{(i)} - \tau_{22}^{(i)})$$

$$= -\frac{\eta_0}{Z(\alpha)} \sum_{i=1}^{\infty} \frac{[illegible]}{[illegible]}\,\dot{\gamma}^2 \qquad \text{.......(50)}$$

From equations (6) and (7)

$$\eta = -\frac{\tau_{12}}{\dot{\gamma}} = \frac{\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{n^{\alpha}}{n^{2\alpha}+c^2\lambda^2\dot{\gamma}^2} \qquad \text{.......(51)}$$

$$\theta = -\frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = \frac{2\lambda\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{1}{n^{2\alpha}+c^2\lambda^2\dot{\gamma}^2} \qquad \text{.......(52)}$$

For small amplitude oscillatory simple shearing flow neglect the terms of order $O(\dot{\gamma}^3)$, that is $\dot{\gamma}\tau_{11}$, $\dot{\gamma}\tau_{12}$, etc., then equation (37) becomes

$$Re\{\tau_{12}^{(n)0}e^{i\omega t}\} + \lambda_n Re\{i\omega\tau_{12}^{(n)0}e^{i\omega t}\}$$
$$= -\frac{\eta_0 n^{-\alpha}}{\zeta(\alpha)}Re\{\dot{\gamma}^0 e^{i\omega t}\} \qquad \text{.......(53)}$$

$$\tau_{12}^{(n)0} = -\frac{\eta_0 n^{-\alpha}\dot{\gamma}^0}{\zeta(\alpha)(1+i\omega\lambda_n)} \qquad \text{.......(54)}$$

$$\tau_{12}^{0} = \sum_{n=1}^{\infty}\tau_{12}^{(n)0} = -\frac{\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{n^{-\alpha}}{1+i\omega\lambda_n}\dot{\gamma}^0$$
$$= -\frac{\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{n^{\alpha}-i\omega\lambda}{n^{2\alpha}+\omega^2\lambda^2}\dot{\gamma}^0 \qquad \text{.......(55)}$$

From equation (8)

$$\eta^* = -\frac{\tau_{12}^0}{\dot{\gamma}^0} = \frac{\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{n^{\alpha}-i\omega\lambda}{n^{2\alpha}+\omega^2\lambda^2} \qquad \text{.......(56)}$$

$$\eta' = \frac{\eta_0}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{n^{\alpha}}{n^{2\alpha}+\omega^2\lambda^2} \qquad \text{.......(57)}$$

$$\eta'' = \frac{\eta_0\lambda\omega}{\zeta(\alpha)}\sum_{n=1}^{\infty}\frac{1}{n^{2\alpha}+\omega^2\lambda^2} \qquad \text{.......(58)}$$

<u>Comparison of data and model.</u> In order to get the parameters of the model for each sample, two sets of master curves are prepared. Rearranging equation (51)

$$\frac{\eta(\dot\gamma)}{\eta_0} = \frac{1}{Z(\alpha)} \sum_{n=1}^{\infty} \frac{n^{\alpha}}{n^{2\alpha} + (\lambda\dot\gamma)^2}, \quad Z(\alpha) = \sum_{n=1}^{\infty} n^{-\alpha} \quad \text{.......(59)}$$

and plotting the dimensionless groups $\frac{\eta}{\eta_0}$ vs. $\lambda\dot\gamma$ of the above equation on log-log scale for several values of α (see Appendix for computer program), we get the master curves for apparent viscosity (Fig. A-1).

For preparing the master curves of the primary normal stress difference, we can do much the same way. However, since most normal stress data are reported in the form of $-(\tau_{11}-\tau_{22})$ rather than $\theta = -\frac{(\tau_{11}-\tau_{22})}{\dot\gamma^2}$ vs. $\dot\gamma$, a new dimensionless group including $-(\tau_{11}-\tau_{22})$ and excluding the variable $\dot\gamma$ is preferable. From equation (52)

$$\theta = -\frac{\tau_{11}-\tau_{22}}{\dot\gamma^2} = \frac{2\lambda\eta_0}{Z(\alpha)} \sum_{n=1}^{\infty} \frac{1}{n^{2\alpha} + (\lambda\dot\gamma)^2} \quad \text{.......(60)}$$

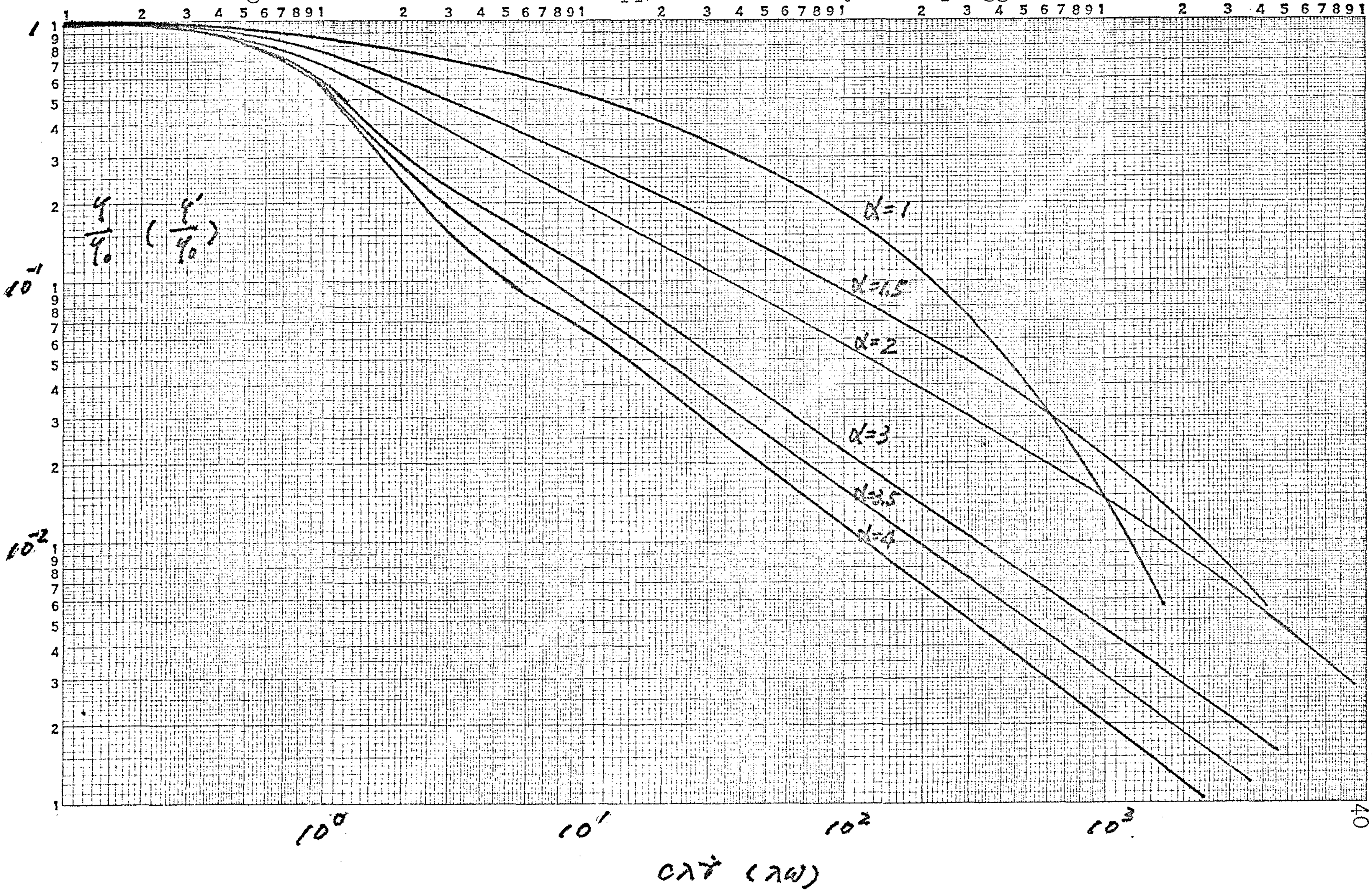
we multiply each side by $\dot\gamma^2\lambda/\eta_0$ then get

$$\left(-\frac{(\tau_{11}-\tau_{22})\lambda}{\eta_0}\right) = \frac{2(\lambda\dot\gamma)^2}{Z(\alpha)} \sum_{n=1}^{\infty} \frac{1}{n^{2\alpha} + (\lambda\dot\gamma)^2} \quad \text{.......(61)}$$

The left-hand side of equation(61) is dimensionless, we plot it against $\lambda\dot\gamma$ on log-log scale by using the same α in making the apparent viscosity master curves, and get the set of master curves for primary normal stress difference. (Fig. A-2)

LOGARITHMIC
3 CYCLES X 5 CYCLES

Fig. A-1 Master Curves of Apparent Viscosity for Spriggs Model



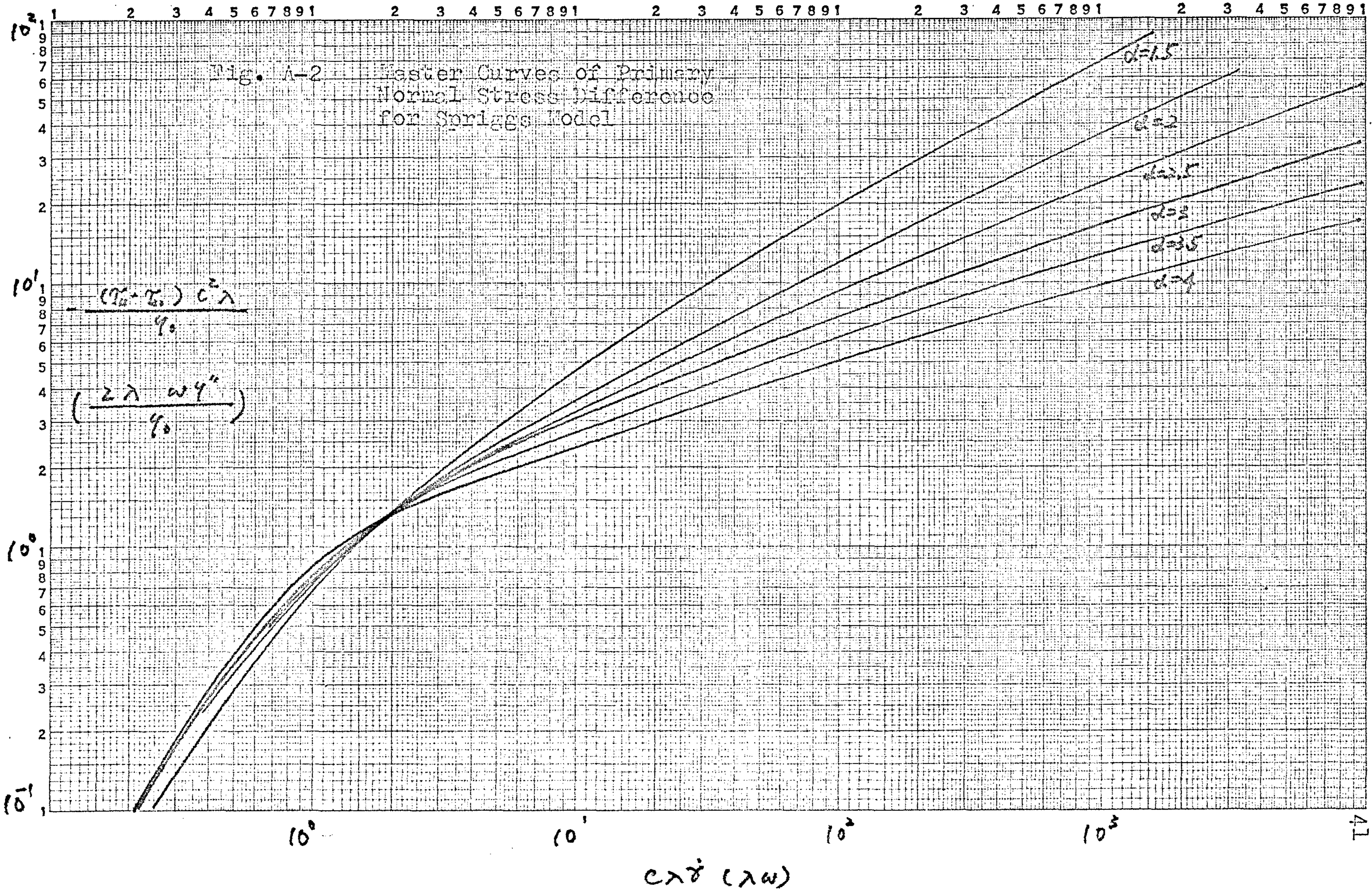


Fig. A-2 Master Curves of Primary Normal Stress Difference for Spriggs Model

From equations (51),(52),(57),(58) we can see that these models predict analogies between the steady and oscillatory shear-dependent material functions, namely

$$\eta(\dot{\gamma}) = \eta'(c\dot{\gamma}) \qquad \text{.......(62)}$$

$$\frac{1}{c}(\dot{\gamma}^2 \beta(\dot{\gamma})) = \eta''(c\dot{\gamma}) \qquad \text{.......(63)}$$

Using these relations we can get the parameters from the oscillatory data without seeking new sets of master curves.

By comparing the apparent viscosity data with master curves Fig. A-1 for best fit, we can get the constants η_0, α and $c\lambda$, let

$$c\lambda = p \qquad \text{.......(64)}$$

where p is a known number.

Next, use these constants in the comparison of the primary normal stress difference and master curves Fig. A-2, and get the constant c, substitute c into equation (64) the other constant λ we can easily obtain. This procedure can most easily done by coinciding the abscissa of the data sheet (log $(\tau_{11}-\tau_{22})$ vs. log $\dot{\gamma}$) with (log p) times that of the master curves (log $(\tau_{11}-\tau_{22})c\lambda/\eta_0$ vs. log $c\lambda\dot{\gamma}$) and fitting the data with the α curve, we then read the ratio of the ordinates of the two sheets, suppose the ratio is q, then

$$\frac{c\lambda}{\eta_0} = q \qquad \text{.......(65)}$$

From equations (64) and (65), we are able to obtain c and λ. When all constants are known, plug them into the model and use the computer to calculate the model prediction as shown in Fig. A-3 through A-13. We can also try to get the parameters by comparing the primary normal stress first, as shown in Fig. A-8', but since the viscosity data, in general, are more reliable and have broader range, the previous procedure is preferable. Sometimes we do not have enough data, we can get only very rough values of parameters or even can not determine them.

For oscillatory data, we can use similar procedure to get the parameters by noticing the relations of equations (62) and (63). From equation (62), we can see that $\lambda\omega$ is equivalent to $\lambda\dot{\gamma}$ and η' is equivalent to η in steady shear motion. Rearrange equation (58) as

$$\left(\frac{2\lambda\omega\eta''}{\eta_0}\right) = \frac{2\lambda^2\omega^2}{Z(\alpha)}\sum_{p=1}^{\infty}\frac{1}{p^{2\alpha}+\lambda^2\omega^2}$$

and compare qith equation(61), we know that $\omega\eta''$ vs. ω for oscillatory data is equivalent to $(\tau_{11}-\tau_{22})$ vs. $\dot{\gamma}$ and can use Fig. A-2 for comparison.

3 CYCLES X 5 CYCLES

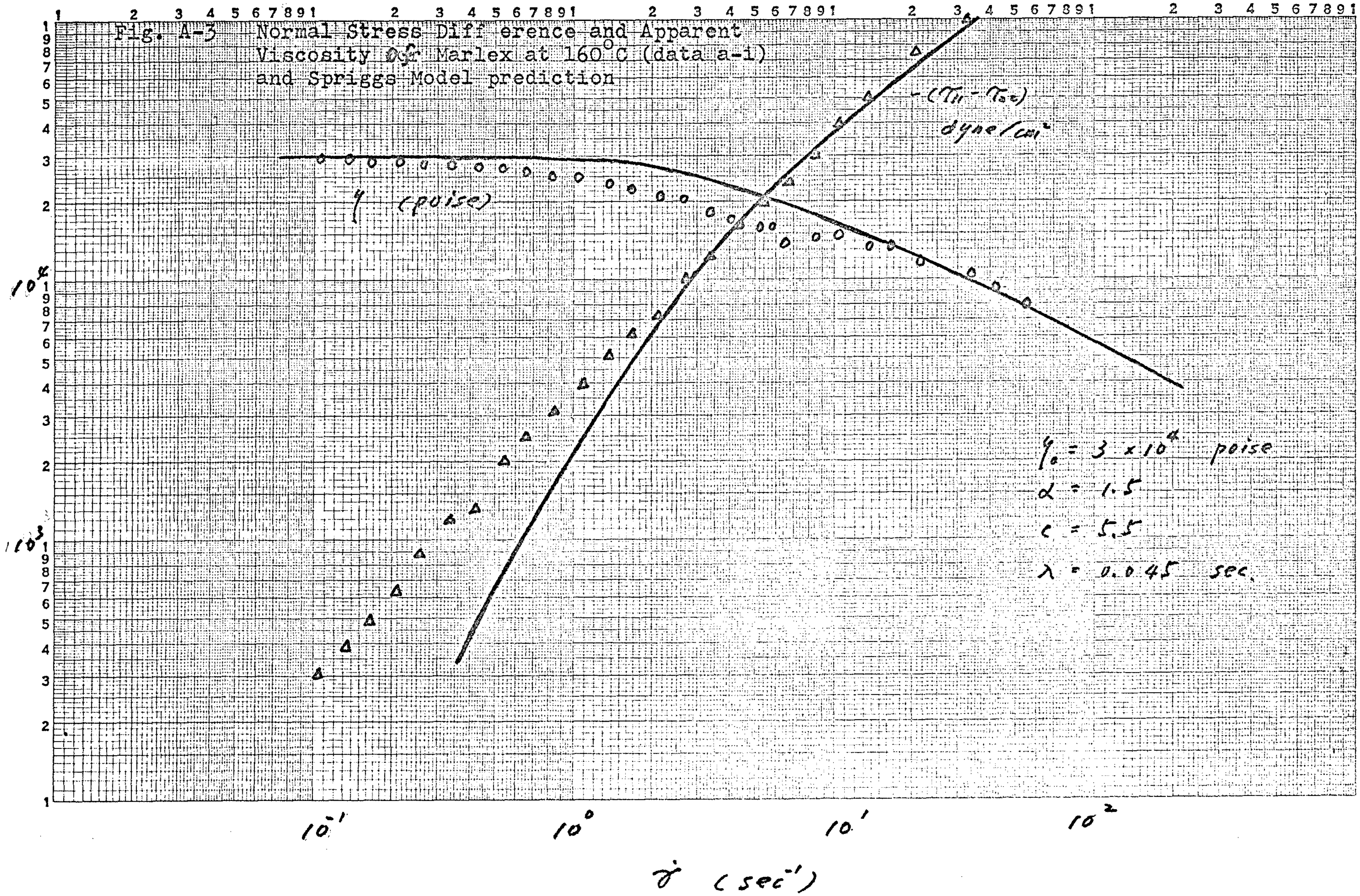


Fig. A-3 Normal Stress Difference and Apparent Viscosity of Marlex at 160°C (data a-1) and Spriggs Model prediction

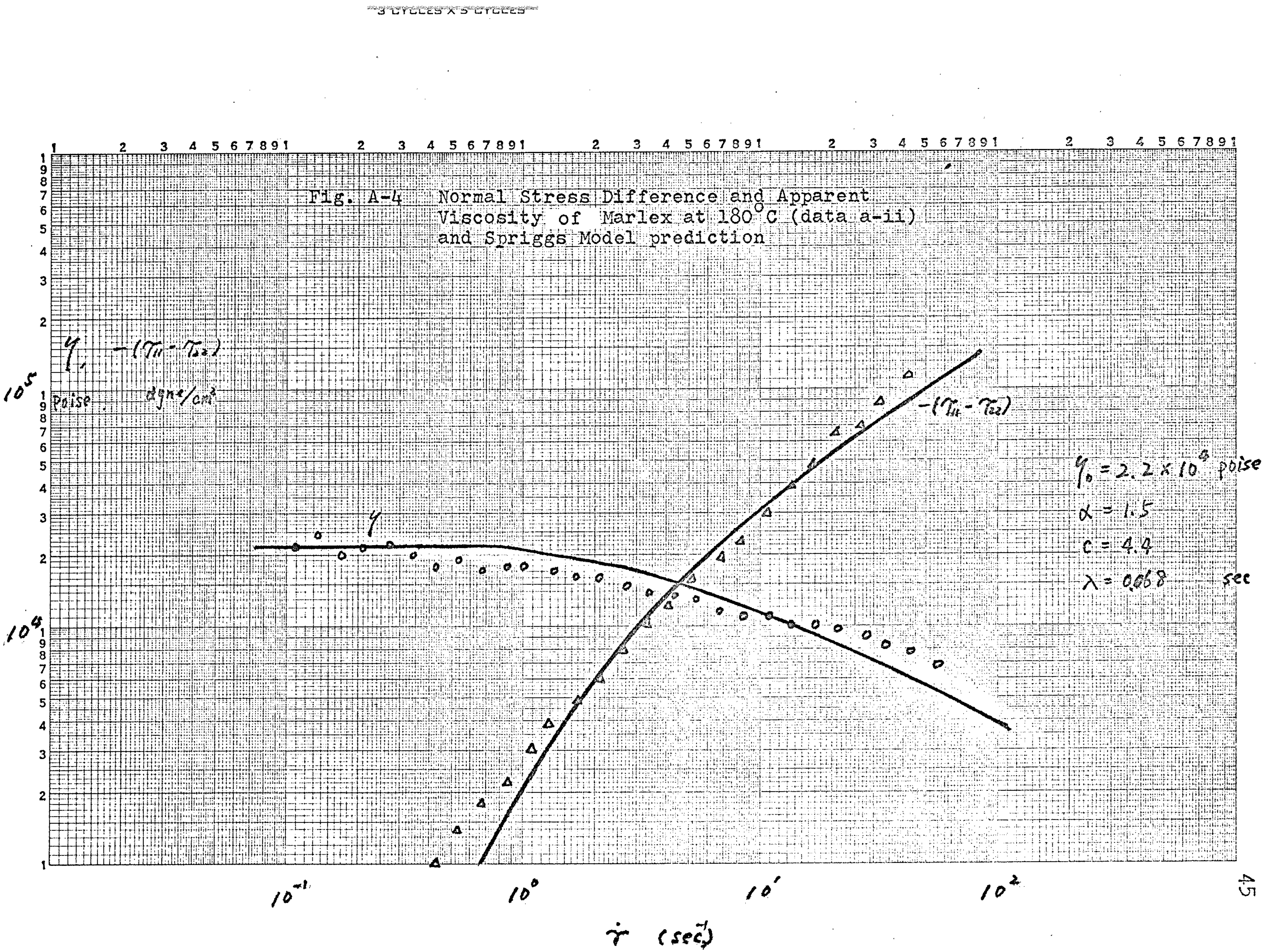


Fig. A-4 Normal Stress Difference and Apparent Viscosity of Marlex at 180°C (data a-ii) and Spriggs Model prediction

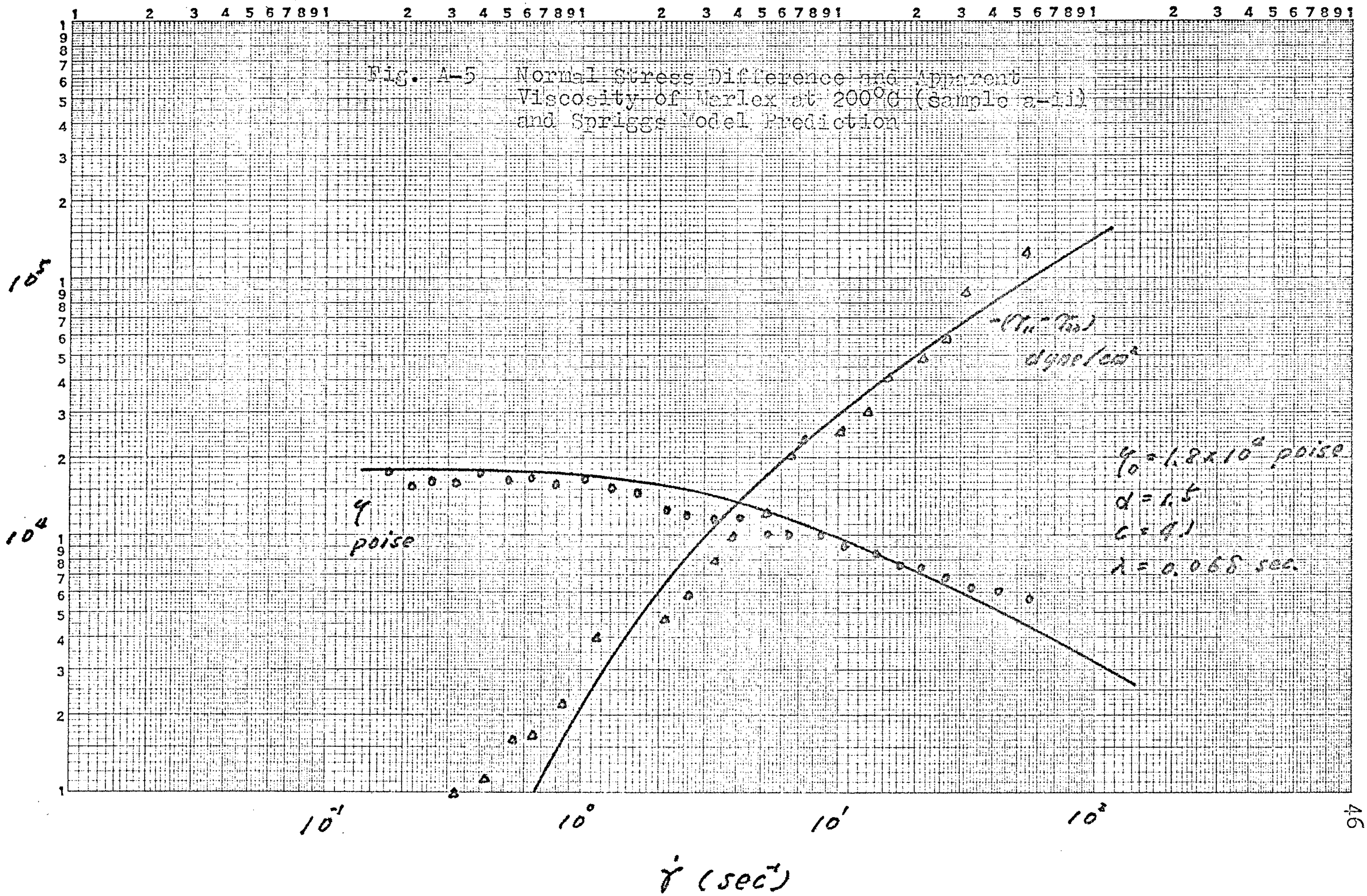


Fig. A-5 Normal Stress Difference and Apparent Viscosity of Marlex at 200°C (sample a-ii) and Spriggs Model Prediction

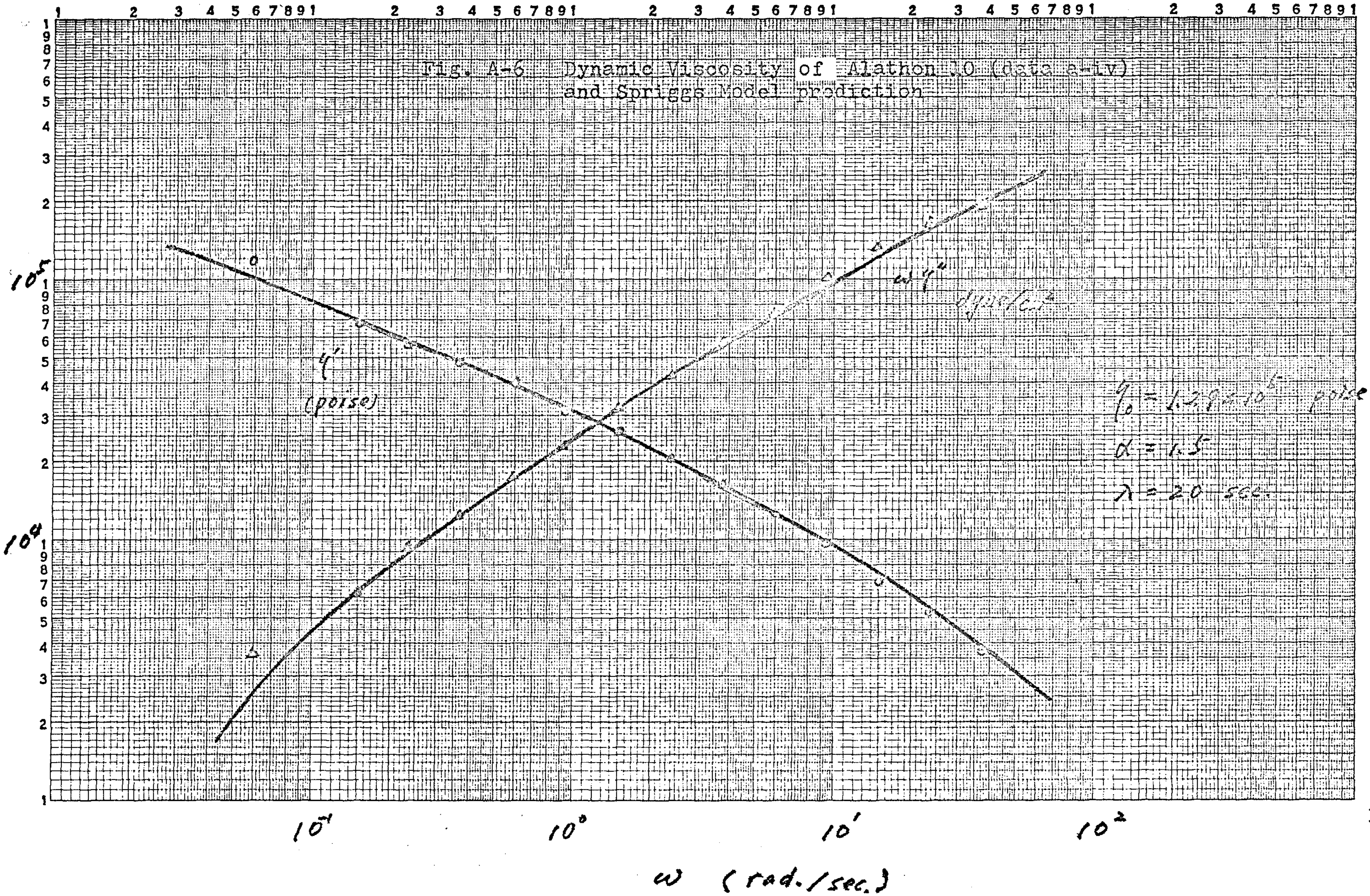


Fig. A-6 Dynamic Viscosity of Alathon 10 (data a-iv)
and Spriggs Model prediction
η'
(poise)
ωη''
dyne/cm²
$\eta_0 = 1.29 \times 10^5$ poise
$\alpha = 1.5$
$\lambda = 20$ sec.
10^5
10^4
10^{-1}
10^0
10^1
10^2
ω (rad./sec.)

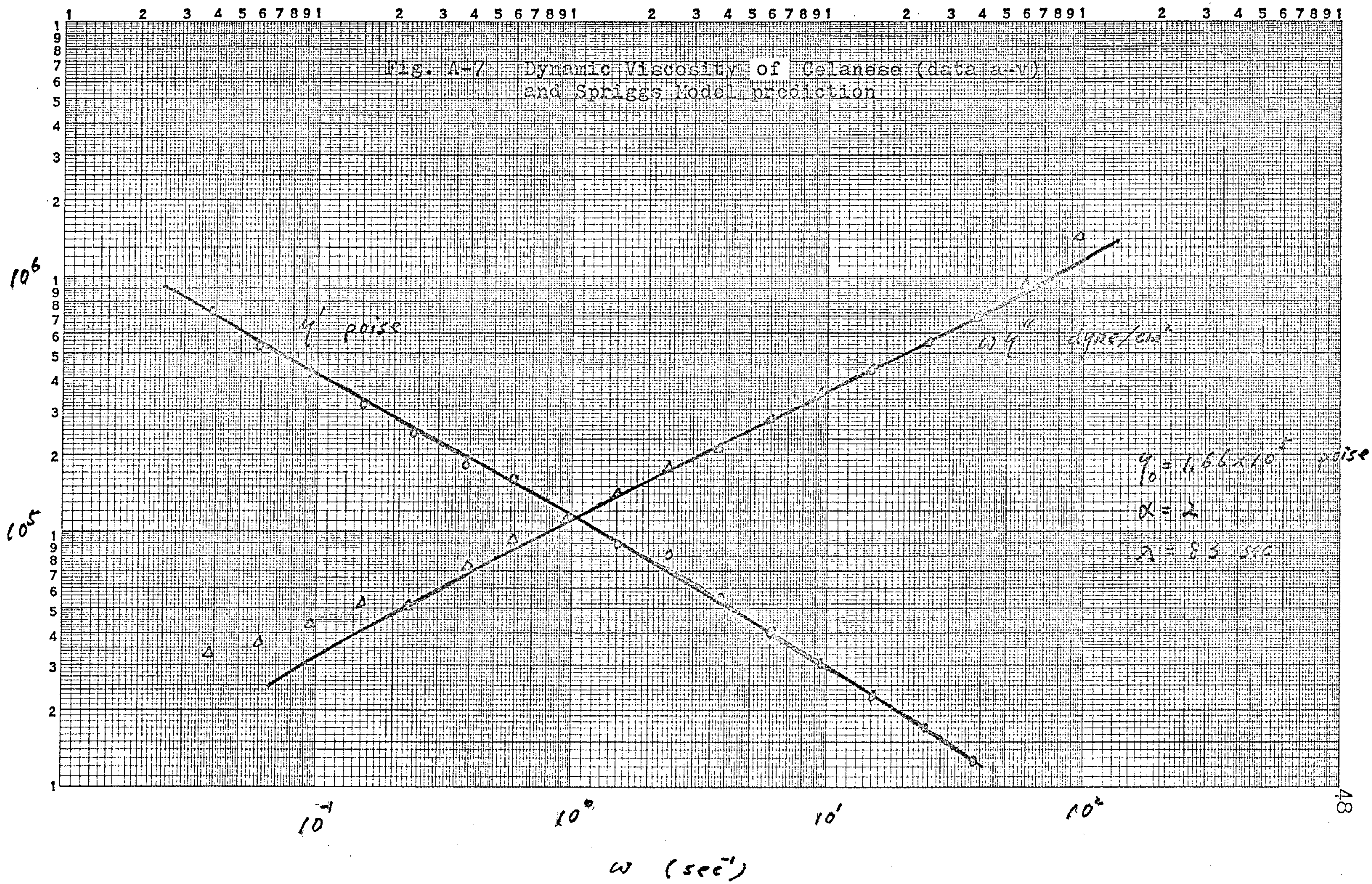
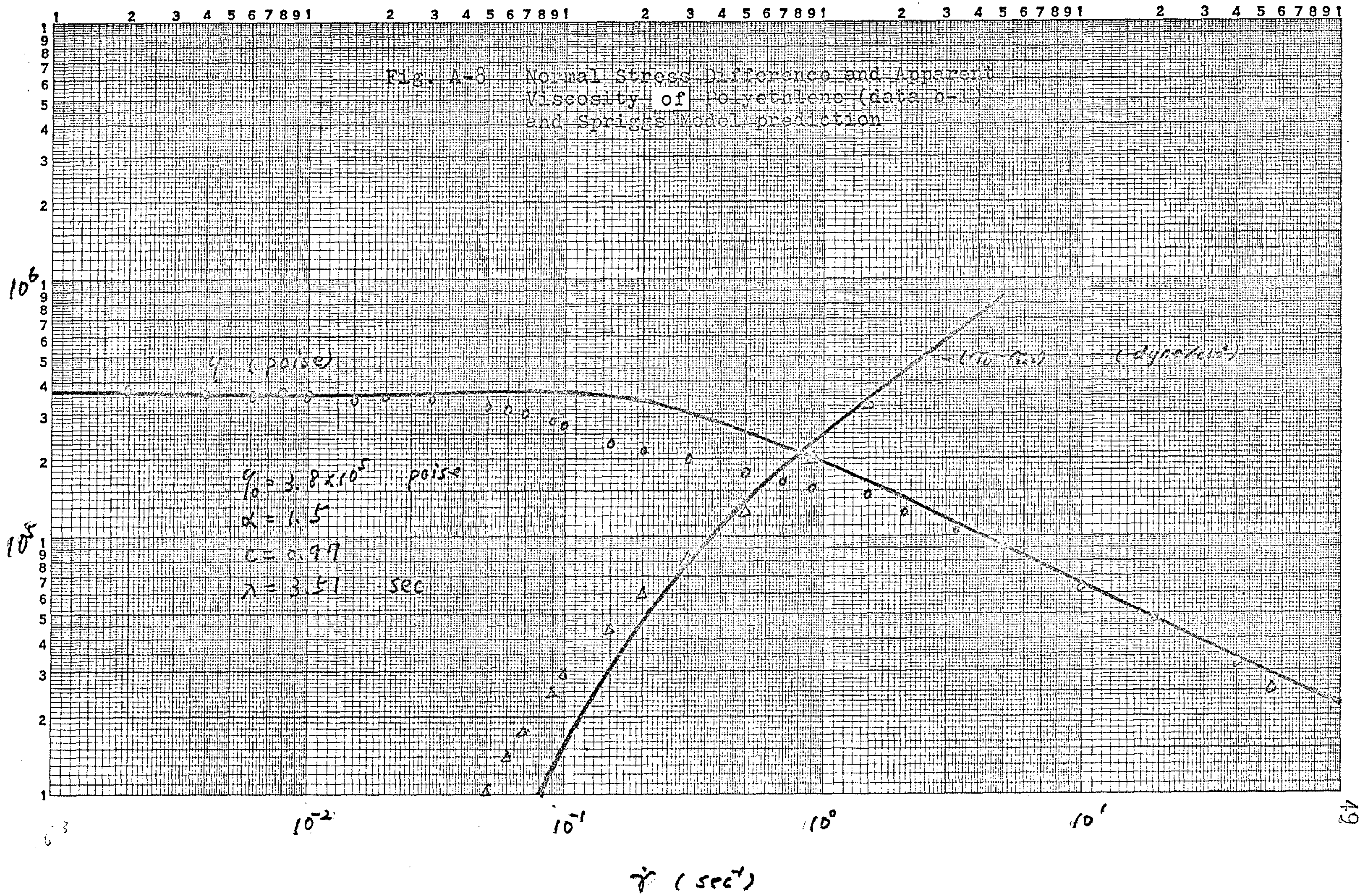


Fig. A-7 Dynamic Viscosity of Celanese (data a-v) and Spriggs Model prediction

Fig. A-8 Normal Stress Difference and Apparent Viscosity of Polyethlene (data b-1) and Spriggs Model prediction



LOGARITHMIC
3 CYCLES X 5 CYCLES

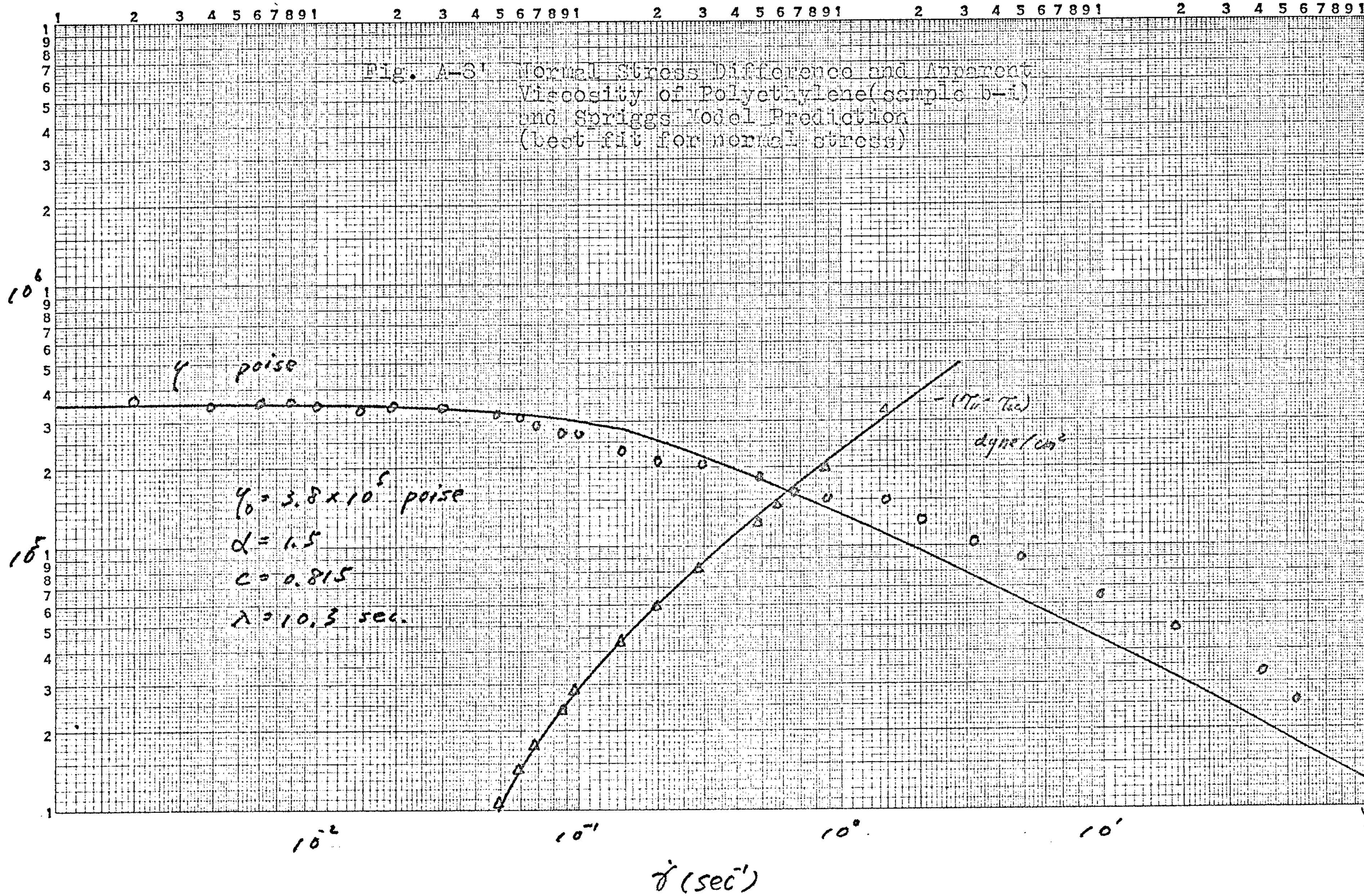


Fig. A-3' Normal Stress Difference and Apparent Viscosity of Polyethylene(sample b-1) and Spriggs Model Prediction (best fit for normal stress)

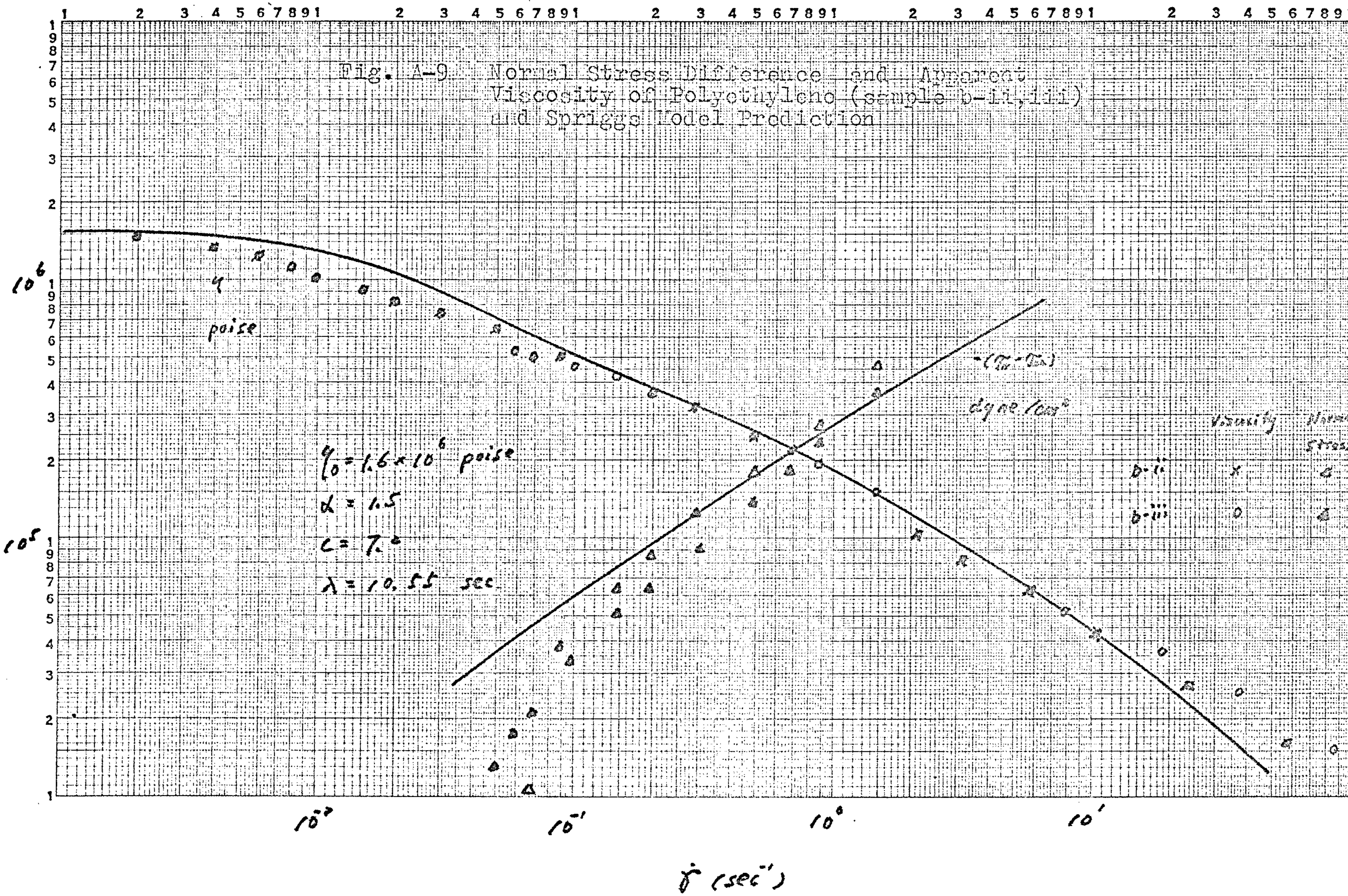
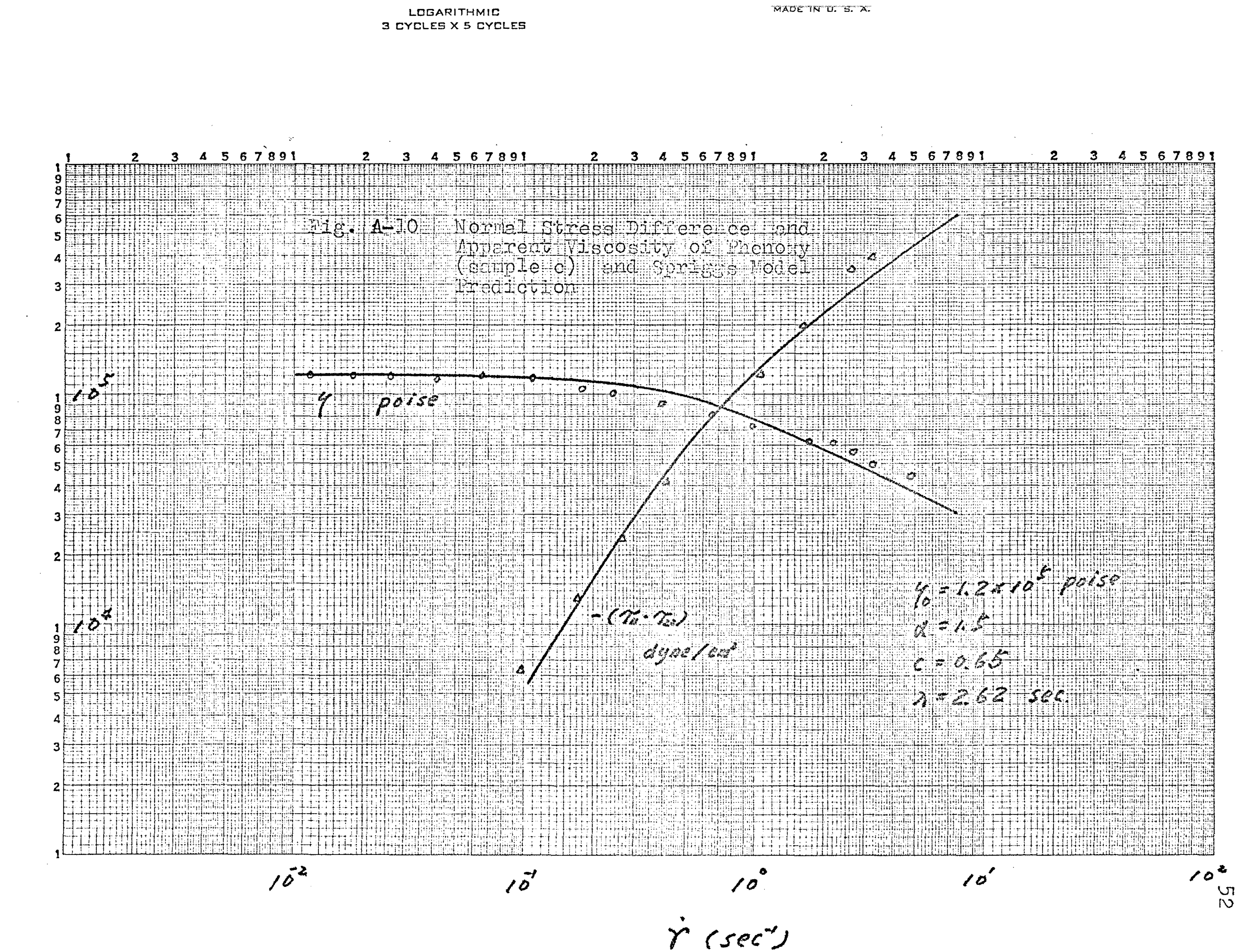
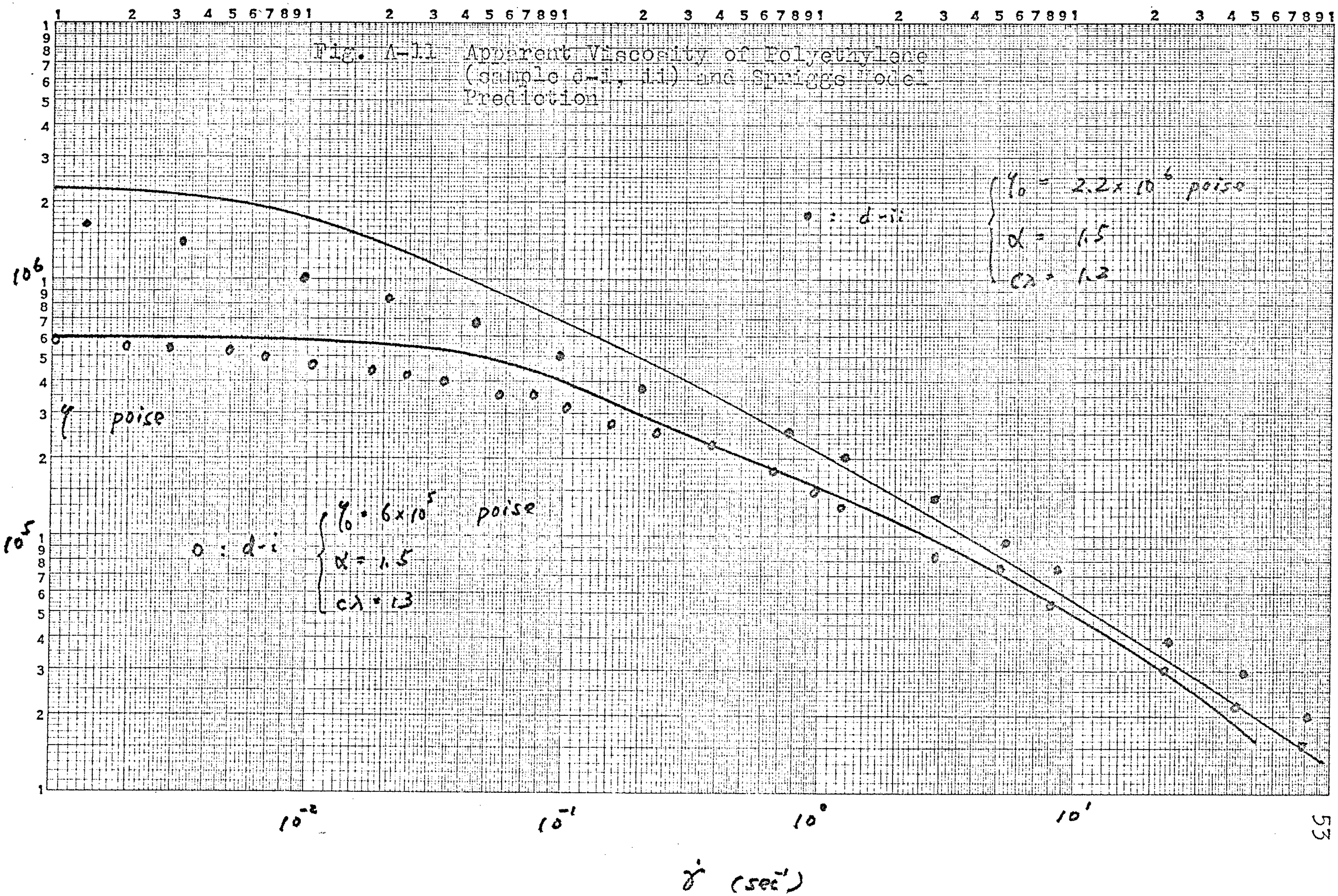


Fig. A-9 Normal Stress Difference and Apparent Viscosity of Polyethylene (sample b-ii,iii) and Spriggs Model Prediction


LOGARITHMIC
3 CYCLES X 5 CYCLES
MADE IN U. S. A.
Fig. A-10 Normal Stress Difference and Apparent Viscosity of Phenoxy (sample c) and Spriggs Model Prediction
10^5
η poise
10^4
$-(\tau_{11}-\tau_{22})$
dyne/cm²
$\eta_0 = 1.2 \times 10^5$ poise
$\alpha = 1.5$
$c = 0.65$
$\lambda = 2.62$ sec.
10^{-2}
10^{-1}
10^0
10^1
10^2
$\dot{\gamma}$ (sec⁻¹)

3 CYCLES X 5 CYCLES



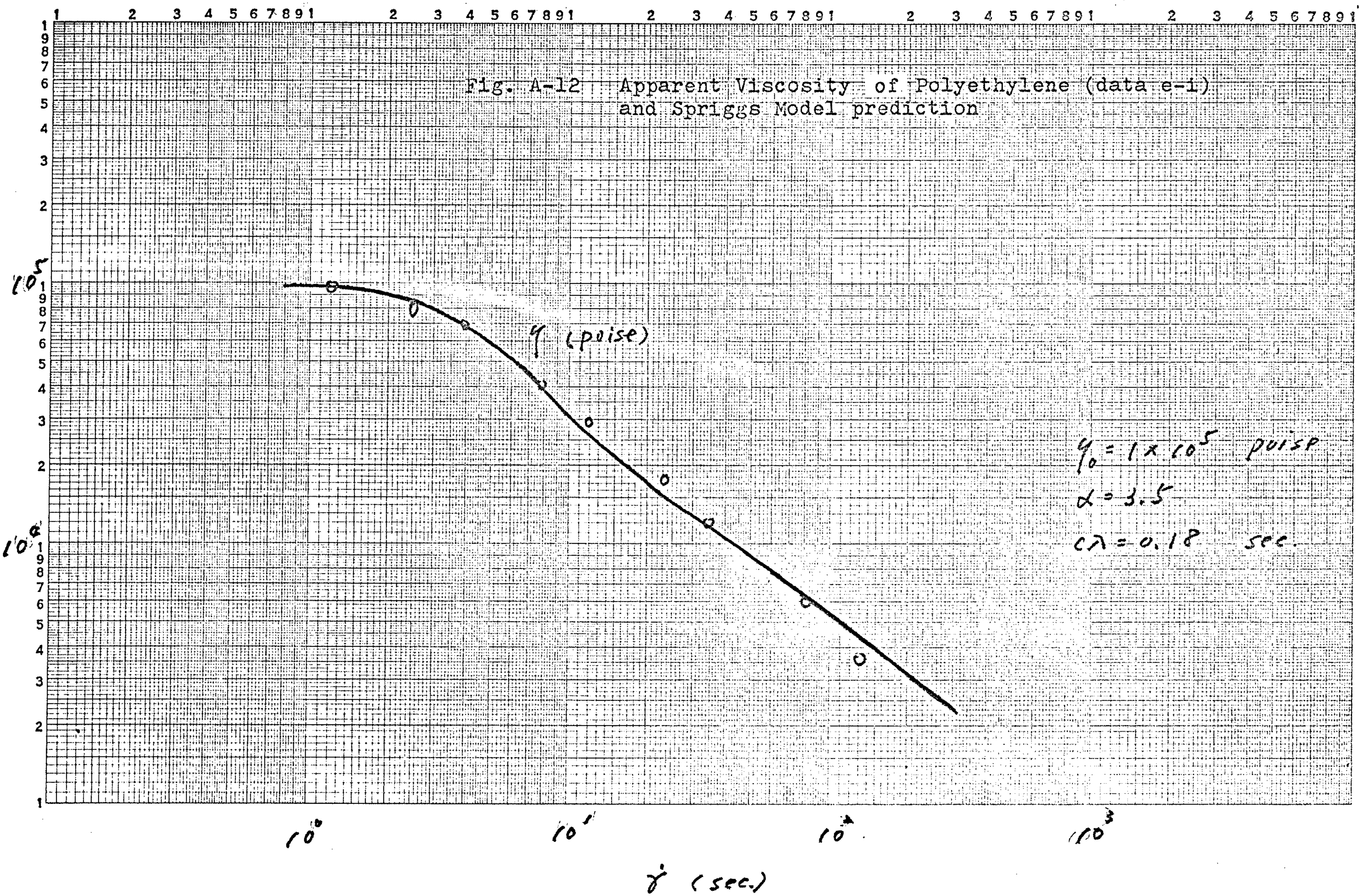


Fig. A-12 Apparent Viscosity of Polyethylene (data e-i) and Spriggs Model prediction

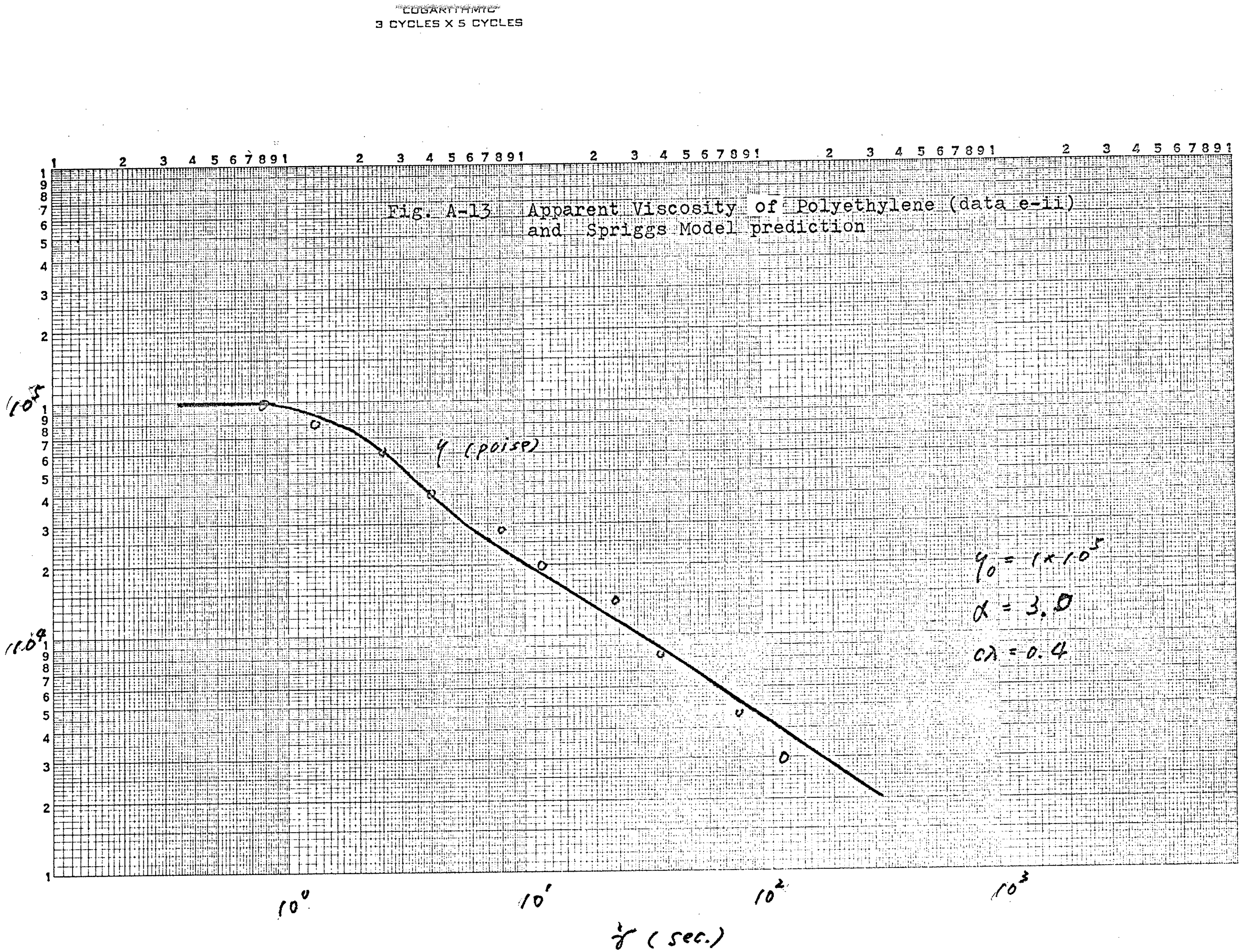


Fig. A-13 Apparent Viscosity of Polyethylene (data e-ii) and Spriggs Model prediction

<u>Discussion of Spriggs Model.</u> The parameters used in predicting the Spriggs Model and the deviations of model prediction are summarized on the next page.

From the table on the next page and the forgoing figures A-3 through A-13, we know that the Spriggs Model predicts polymer melts always with great deviations, in many cases it deviates more than 100%. Nevertheless, for most of the samples, it still predicts apparent viscosity fairly good for quite a long range and predicts the primary normal stress difference qualitatively correct. We know also that most of the deviation of the apparent viscosity happen to be in the intermediate range between power law region and zero shear rate viscosity region.

Table III The Parameters and Deviations of Spriggs Model for Various Samples

Sample	(poise) x10^{-5}		(sec.)	c	shear rate(angular velocity) range of deviation(10% or larger) (sec.) η or η'	$-(\pi_{11}-\pi_{22})$ or ωη''	largest percentage deviation η or η'	$-(\pi_{11}-\pi_{22})$ or ωη''
a-i	0.3	1.5	0.045	5.5	0.5-9	below 2	33	>100
a-ii	0.22	1.5	0.068	4.4	0.4-5, also above 20	below 1.5, also above 30	26	90
a-iii	0.18	1.5	0.068	4.1	1.5-6.5, also above 40	below 1.5	36	90
a-iv	1.29	1.5	20		————————	below 0.07	—	—
a-v	1.66	2.0	83		————————	below 0.2	—	—
b-i	3.8	1.5	3.51	0.97	0.05-1.5	below 0.2	>100	>100
b-i(alternative)	3.8	1.5	10.3	0.815	above 1	———————	>100	———
b-ii,iii	16.0	1.5	10.55	7.2	0.005-0.02, also above 1.5		>100	>100
c	1.2	1.5	2.62	0.65	0.2-0.7	above 2	12	
d-i	6.0	1.5	13/c		0.005-0.12		35 ~~>100~~	
d-ii	22.0	1.5	1.2/c		~~0.005-0.12~~		>100	
e-i	1.0	3.5	0.18/c		above 100		16	
e-ii	1.0	3.0	0.4/c		"		10	

<u>Evaluation of Bird and Carreau Model.</u>

This model takes the same form as WJFLMB Model but has a different memory function.

<u>The model.</u> (2)

$$\tau^{ij} = -\int_{-\infty}^{t} \mu(t-t', II(t'))\Big[\left(1+\frac{\epsilon}{2}\right)\left(\hat{g}^{ij}(t)-\hat{g}^{ij}(t')\right)$$

$$+\frac{\epsilon}{2}\,\hat{g}^{ir}(t)\,\hat{g}^{js}(t')\left(\hat{g}_{rs}(t)-\hat{g}_{rs}(t')\right)\Big]\,dt' \qquad \ldots\ldots\ldots(66)$$

the memory function μ is taken to be

$$\mu(t-t', II(t')) = \sum_{p=1}^{\infty} \frac{\eta_p}{\lambda_{2p}^2}\,\frac{e^{-\frac{t-t'}{\lambda_{2p}}}}{1+\frac{1}{2}\lambda_{1p}^2\,II(t')} \qquad \ldots\ldots\ldots(67)$$

the second invariant of the rate-of-strain tensor II(t') is

$$II(t') = \hat{g}_{ik}(t)\,\hat{g}_{jl}(t)\left(\frac{\partial \gamma^{ij}}{\partial t'}\right)\left(\frac{\partial \gamma^{kl}}{\partial t'}\right) \qquad \ldots\ldots\ldots(68)$$

$$\eta_p = \eta_0\,\frac{\lambda_{1p}}{\sum_p \lambda_{1p}} \qquad \ldots\ldots\ldots(69)$$

$$\lambda_{1p} = \lambda_1\left(\frac{1+n_1}{p+n_1}\right)^{\alpha_1} \qquad \ldots\ldots\ldots(70)$$

$$\lambda_{2p} = \lambda_2\left(\frac{1+n_2}{p+n_2}\right)^{\alpha_2} \qquad \ldots\ldots\ldots(71)$$

<u>The material functions.</u> (2) (34) For steady shear flow with velocity gradient $\dot{\gamma} = \frac{dv^1}{dx_2}$, one obtains for the material functions

$$\eta(\dot{\gamma}) = \sum_{p=1}^{\infty} \frac{\eta_p}{1+(\lambda_{1p}\dot{\gamma})^2} \qquad \ldots\ldots\ldots(72)$$

$$\Psi(\dot{\gamma}) = 2\sum_{p=1}^{\infty} \frac{\eta_p\,\lambda_{2p}}{1+(\lambda_{1p}\dot{\gamma})^2} \qquad \ldots\ldots\ldots(73)$$

$$\eta'(\omega) = \sum_{p=1}^{N} \frac{\eta_p}{1+(\lambda_p\omega)^2} \qquad \ldots\ldots.(74)$$

$$\frac{\eta''(\omega)}{\omega} = \sum_{p=1}^{N} \frac{\eta_p\lambda_p}{1+(\lambda_p\omega)^2} \qquad \ldots\ldots.(75)$$

For low shear rate or frequency, the series of the material functions given above can be rearranged into rapidly convergent series, in which usually only the first few terms are needed. After incorporating the expressions for the time constants we obtain:

$$\frac{\eta}{\eta_0} = 1 - \frac{(2^{\alpha_1}\lambda_1\dot\gamma)^2}{Z(\alpha_1)-1}\sum_{p=2}^{\infty}\frac{p^{-\alpha_1}}{p^{2\alpha_1}+(2^{\alpha_1}\lambda_1\dot\gamma)^2} \qquad \ldots\ldots.(76)$$

$$\frac{\theta}{\eta_0} = \frac{2^{\alpha_1+1}\lambda_1}{Z(\alpha_1)-1}\left[Z(2\alpha_1)-1-(2^{\alpha_1}\lambda_1\dot\gamma)^2\sum_{p=2}^{\infty}\frac{p^{-3\alpha_1}}{p^{2\alpha_1}+(2^{\alpha_1}\lambda_1\dot\gamma)^2}\right] \quad ..(77)$$

$$\frac{\eta'}{\eta_0} = 1 - \frac{(2^{\alpha_1}\lambda_1\omega)^2}{Z(\alpha_1)-1}\sum_{p=2}^{\infty}\frac{p^{-\alpha_1}}{p^{2\alpha_1}+(2^{\alpha_1}\lambda_1\omega)^2} \qquad \ldots\ldots.(78)$$

$$\frac{\eta''}{\eta_0} = \frac{2^{\alpha_1}\lambda_1\omega}{Z(\alpha_1)-1}\left[Z(2\alpha_1)-1-(2^{\alpha_1}\lambda_1\omega)^2\sum_{p=2}^{\infty}\frac{p^{-3\alpha_1}}{p^{2\alpha_1}+(2^{\alpha_1}\lambda_1\omega)^2}\right] \quad ..(79)$$

where $Z(\alpha)$ is the Riemann zeta function. For $\alpha_1 \geq 0.5$ the following relations hold:

$$0.97 \le \frac{\eta}{\eta_0} \le 1 \quad \text{for} \quad \dot\gamma \le \frac{1}{2^{\alpha_1+1}\lambda_1} \qquad \ldots\ldots.(80)$$

$$0.94 \le \frac{\eta'}{\eta_0} \le 1 \quad \text{for} \quad \omega \le \frac{1}{2^{\alpha_1+1}\lambda_1} \qquad \ldots\ldots.(81)$$

The material functions can be calculated within one percent error by summing the first N terms only of the rearranged series. The values of N for [illegible] and [illegible] are given in Fig. B-1. N is dependent on [illegible] (or [illegible]) and increases rapidly with dimensionless shear rate of frequency, however for large enough shear rate of frequency, asymptotic expressions can be used.

At high shear rate or frequency, the material functions can be approximated by simple analytical functions through the use of the Euler-Maclaurin sum formula:

$$\sum_{p=1}^{\infty} f(p) = \sum_{p=0}^{\infty} f(p) - f(0) = \int_1^{\infty} f(y)\,dy + \tfrac{1}{2}\left(f(\infty) - f(1)\right)$$

$$- f(0) - \sum_{k=1}^{n} \frac{B_{2k}}{[illegible]}\left(f^{[illegible]}(\infty) - f^{[illegible]}(1)\right) + E_n \qquad \text{.......(82)}$$

where [illegible] are Bernoulli numbers and En is the error . If we consider the function

$$f(y) = \frac{[illegible]}{[illegible]} \qquad [illegible]$$

equation (82) gives for n = 1

$$\sum_{p=1}^{\infty} \frac{[illegible]}{[illegible]} = \int_1^{\infty} \frac{[illegible]}{[illegible]}\,dy - \frac{1}{2}\,\frac{1}{[illegible]}$$

$$- \frac{B_2}{2!}\left(\frac{[illegible]}{[illegible]} - \frac{[illegible]}{[illegible]}\right) + E \qquad \text{.......(83)}$$

There is no way of calculating the magnitude of the error in equation (83), since the derivative $f''(y)$ changes sign in the interval $(1, \infty)$. However, the error should be of the order ([illegible]) and [illegible] rapidly as x becomes large. We evaluate the integral of equation (83) in two parts.

$$\int_1^{\infty} \frac{[illegible]}{[illegible]}\,dy = \int_{[illegible]}^{\infty} \frac{[illegible]}{[illegible]}\,dy - \int_{[illegible]}^{1} \frac{[illegible]}{[illegible]}\,dy = I_1 - I_2 \qquad \text{.......(84)}$$

From integral table I, becomes

$I_1 =$ [illegible] ....(85)

The second term can be rewritten as

$I_2 =$ [illegible] ....(86)

Neglecting all terms of order ([illegible]) and higher then equation (85) becomes

[illegible] ....(87)

The four material functions of equations (76)-(79) then in the limit of large rate or large frequency become

$\frac{\eta}{\eta_0} \to$ [illegible] ..(88)

[illegible] .(89)

[illegible] ..(90)

[illegible] ..(91)

For high enough values of shear rate or frequency, the second and third terms in the expressions are negligible and the model predicts power-law behavior as experimentally observed for most viscoelastic fluids.

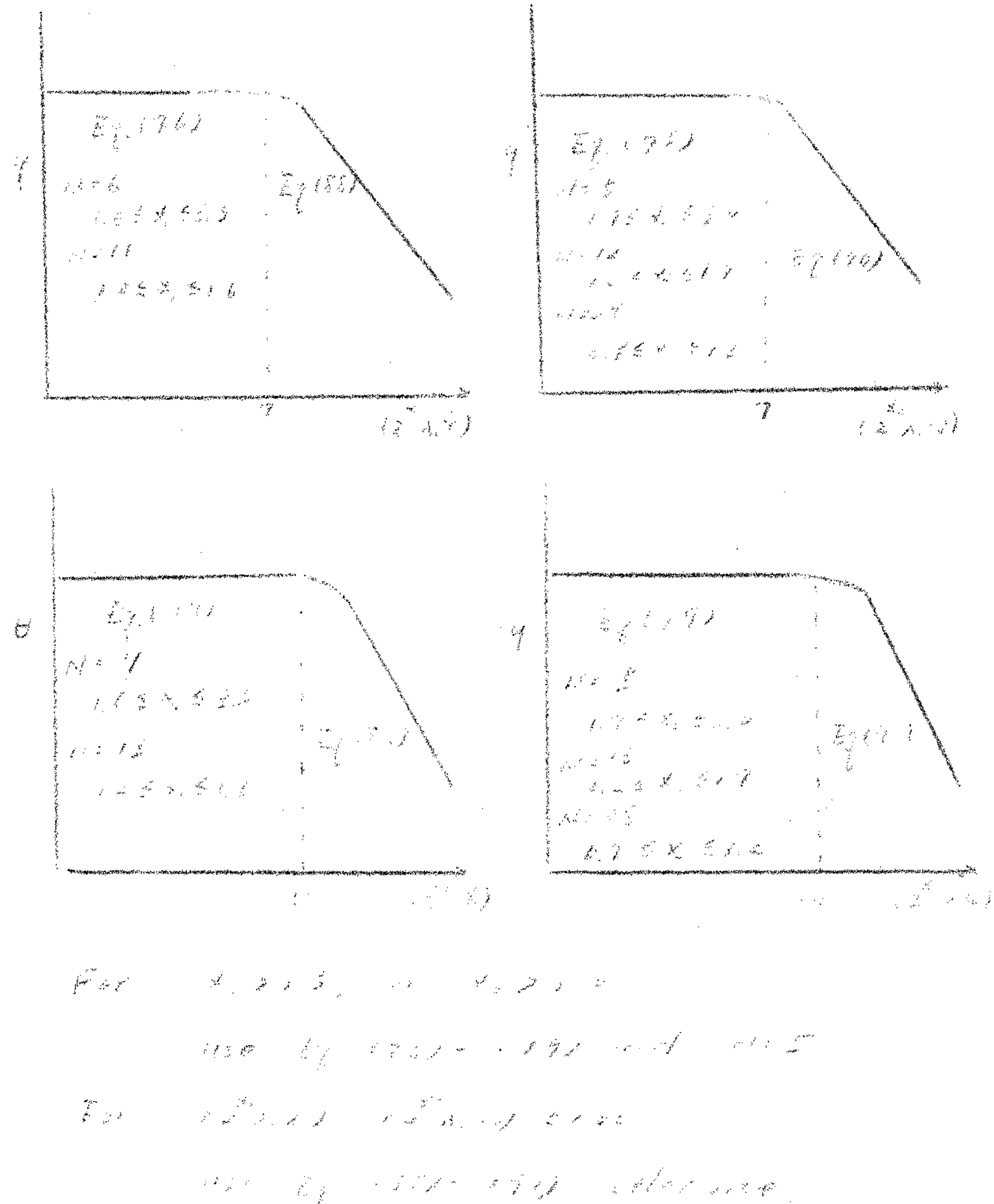


Fig. B-1 Graphical representation of the regions in which the low shear rate (or frequency) summation and the high shear rate (or frequency) asymptotes should be used. (prediction with less than 1% error)

<u>Comparison of data and model.</u> Similar procedures as in evaluating the Spriggs Model are used here. Use equations (76), (83) and Fig. B-1 to make the master curve set of apparent viscosity (Fig. B-2), then compare with data to get the first three constants η_0, α_1, λ_1. The Riemann Zeta function in equations (76), (83) etc. is calculated by using

$$Z(A)=\sum_{j=1}^{\infty} j^{-A}=\sum_{j=1}^{R-1} j^{-A}+\frac{1}{(A-1)R^{A-1}}+\frac{1}{2R^{A}}+E_0\left(\frac{1}{12R^{A+1}}\right)\ldots\ldots(92)$$

obtained from the Euler-Maclaurin sum formula equation (82). The error E is less than $A/12R^{A+1}$ and very good accuracy is obtained by taking $R = 10$.

The other two parameters α_2, λ_2 are obtained from primary normal stress difference data. Rearrange equations (77) and (89) as

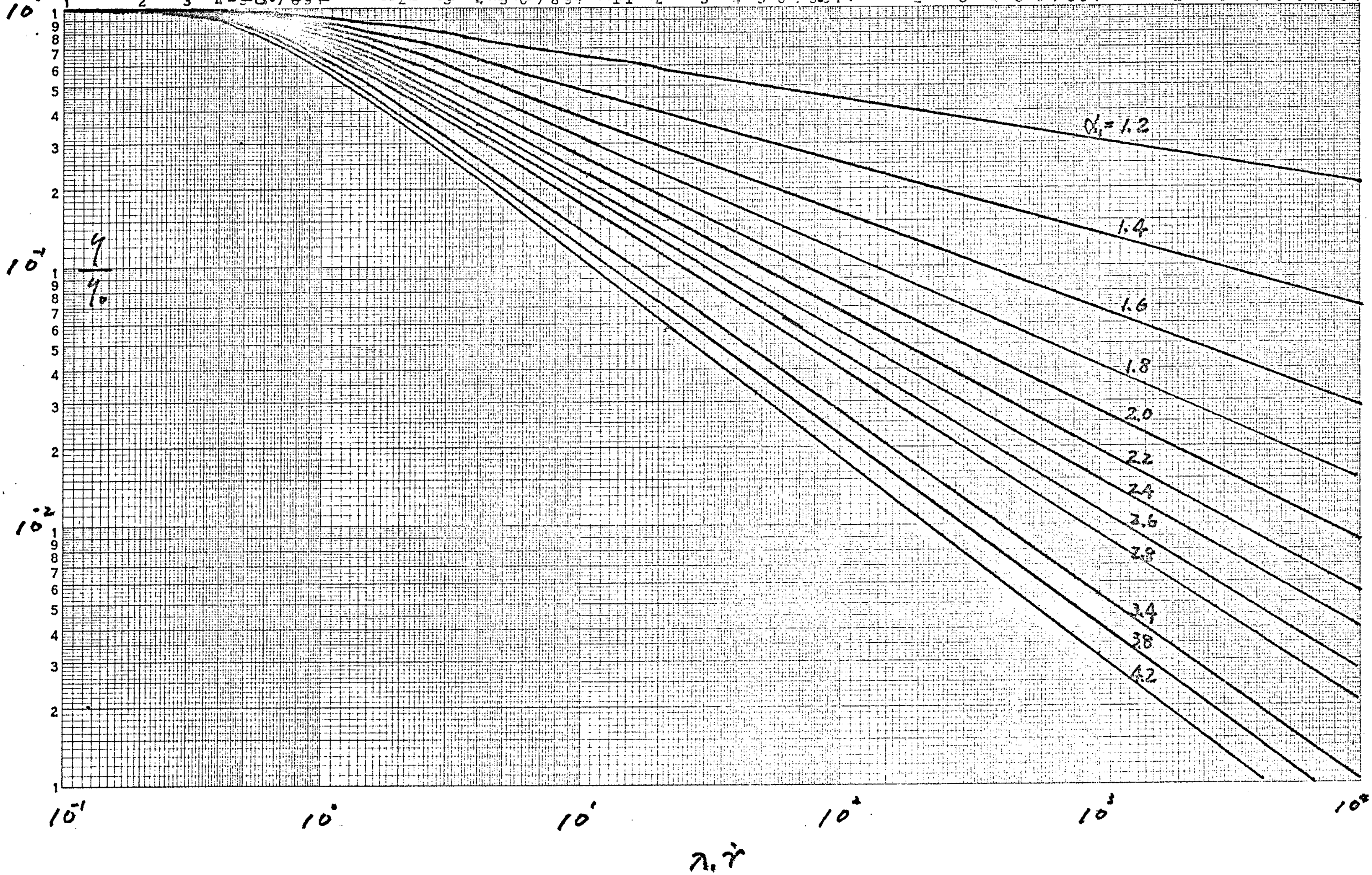
$$-\frac{(\tau_{11}-\tau_{22})}{\lambda_2}=\frac{2^{\alpha_2+1}\eta_0\dot{\gamma}^2}{Z(\alpha_1)-1}\left[Z(\alpha_1+\alpha_2)-1-(2^{\alpha_1}\lambda_1\dot{\gamma})^2\sum_{p=2}^{\infty}\frac{p^{-(\alpha_1+\alpha_2)}}{p^{2\alpha_1}+(2^{\alpha_1}\lambda_1\dot{\gamma})^2}\right] \quad (77')$$

$$\rightarrow\frac{2^{\alpha_1+1}\eta_0\dot{\gamma}^2}{Z(\alpha_1)-1}\left\{\frac{\pi(2^{\alpha_1}\lambda_1\dot{\gamma})^{\frac{1-\alpha_1-\alpha_2}{\alpha_1}}}{2\alpha_1\sin\left(\frac{1-\alpha_1-\alpha_2}{2\alpha_1}\pi\right)}-\frac{1}{(\alpha_1-\alpha_2+1)(2^{\alpha_1}\lambda_1\dot{\gamma})^2}-\frac{1+\frac{1}{2}(\alpha_1-\alpha_2)}{2(1+(2^{\alpha_1}\lambda_1\dot{\gamma})^2)}\right\} \quad (89')$$

From the above equations, use some appropriate values of to make a set of curves of $-\frac{(\tau_{11}-\tau_{22})}{\lambda_2}$ vs. $\dot{\gamma}$ for every set of parameters η_0, α_1, and λ_1 (Fig. B-3 to B-7). The value of α_2 differs little from α_1, so only limited number of these curves are needed. Compare these curves with normal stress data, the other two constants are easily solved.

LOGARITHMIC
3 CYCLES X 5 CYCLES

Fig. B-2 Master Curves of Apparent Viscosity (Careau's Model)



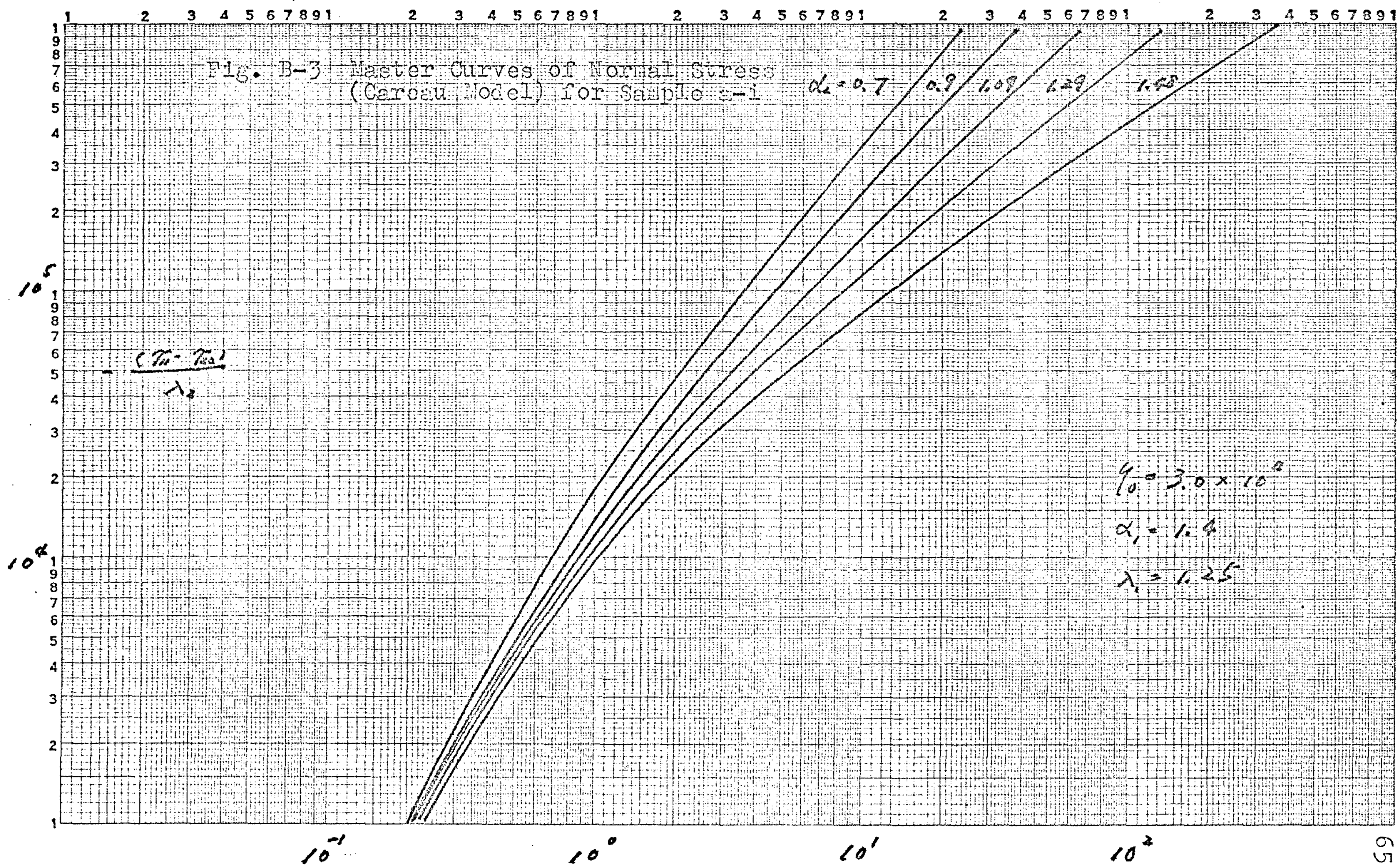


Fig. B-3 Master Curves of Normal Stress (Carreau Model) for Sample s-1

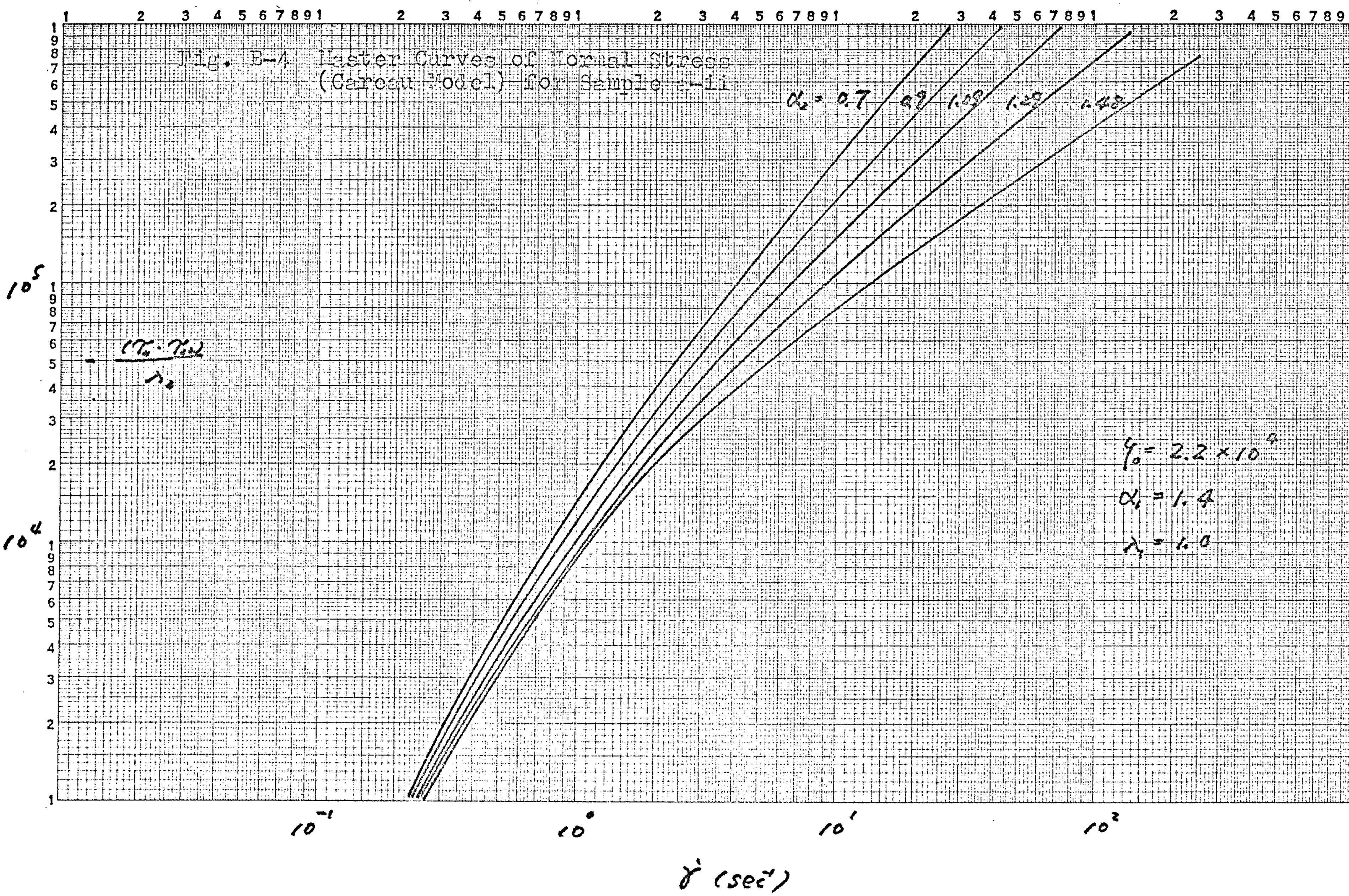


Fig. B-4 Master Curves of Normal Stress (Carreau Model) for Sample A-11

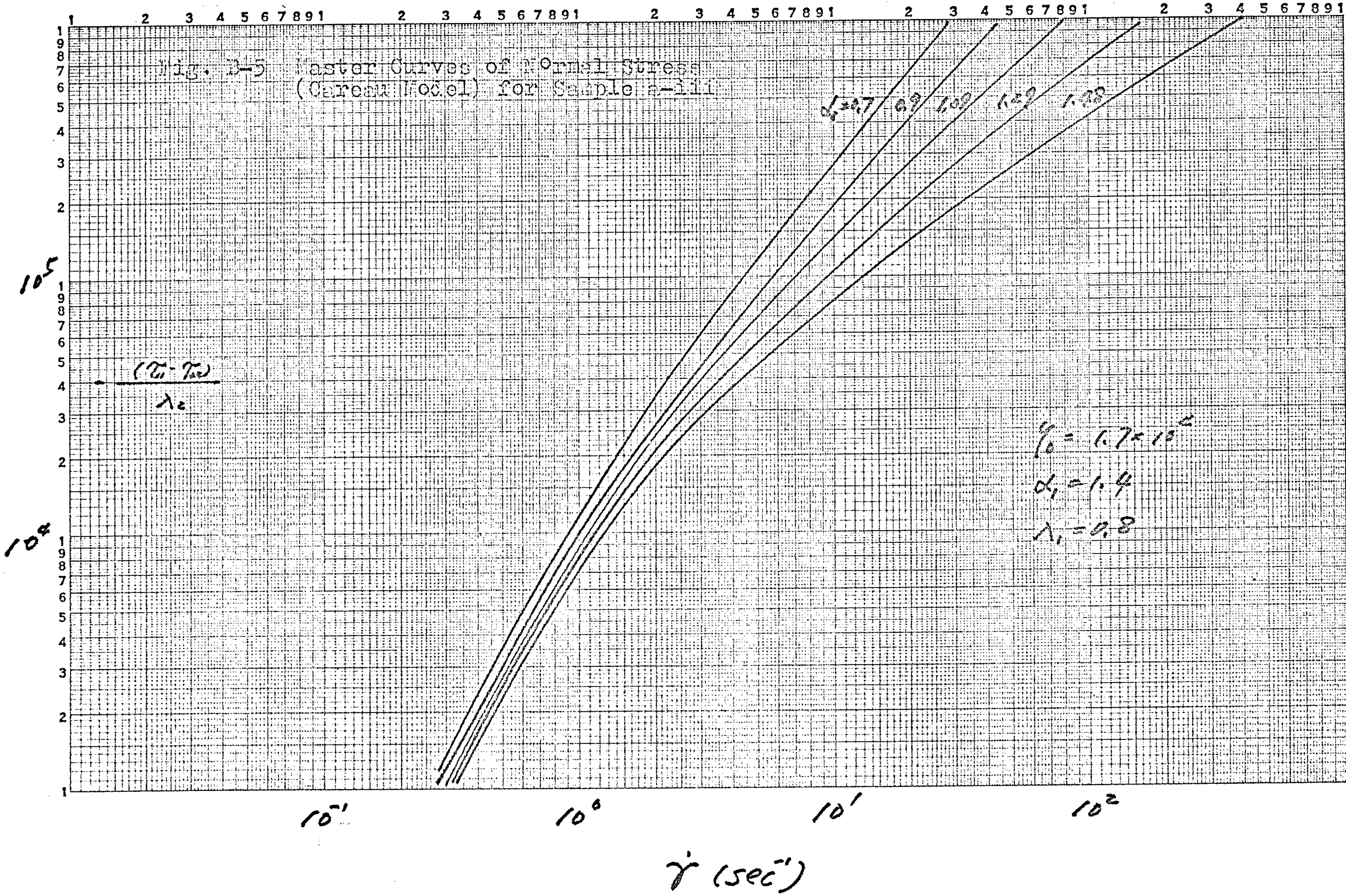


Fig. B-5 Master Curves of Normal Stress (Carreau Model) for Sample a-iii

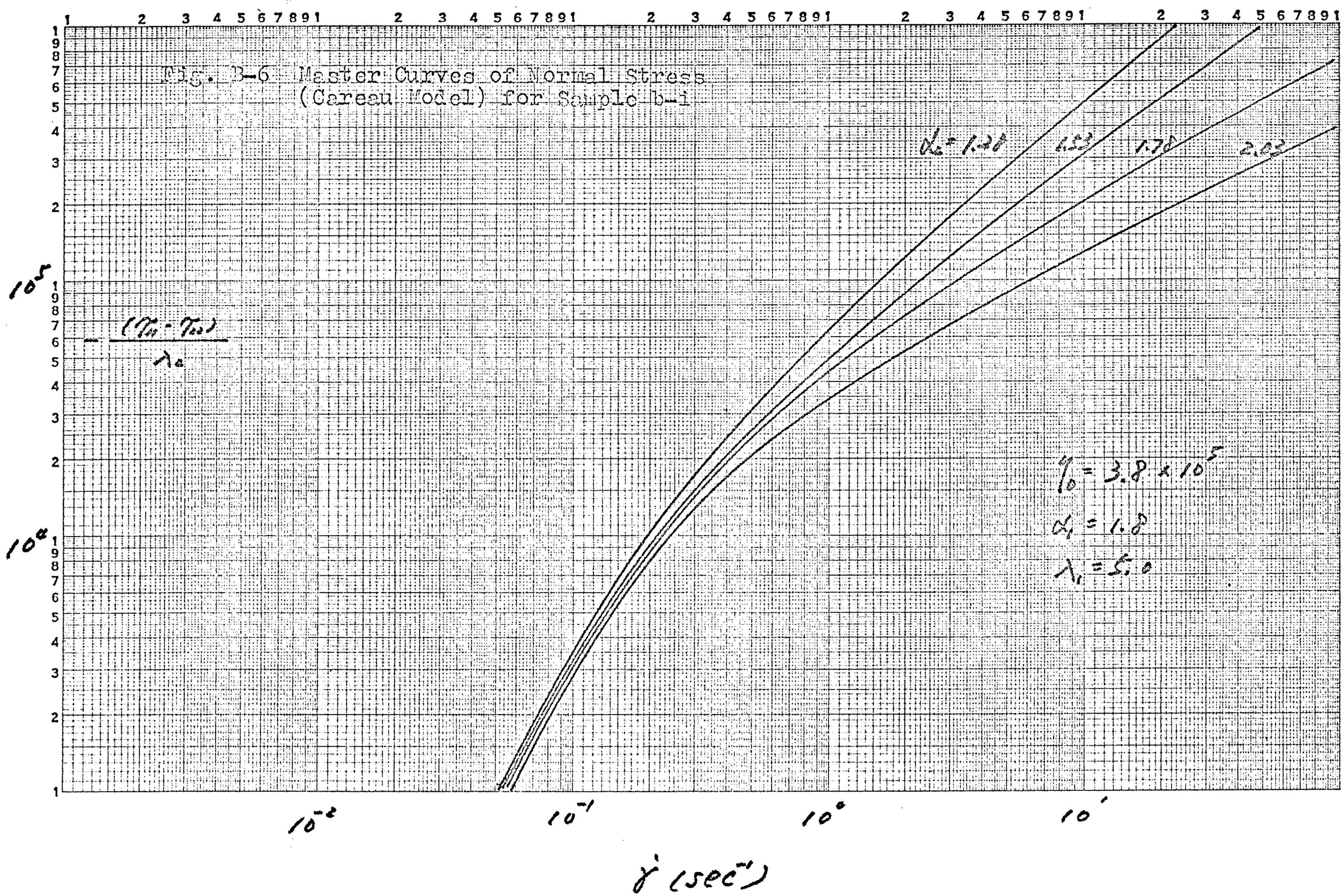
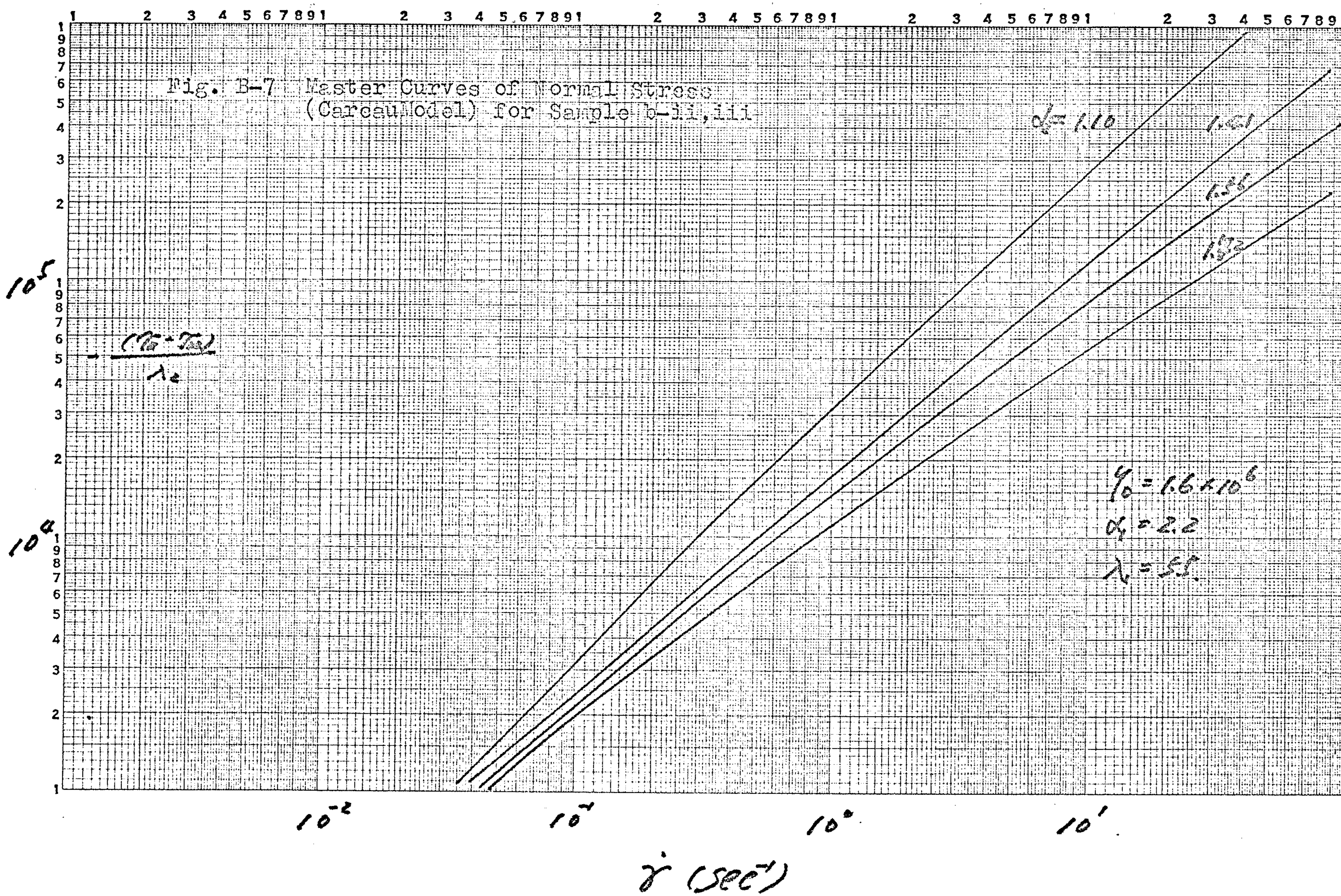


Fig. B-6 Master Curves of Normal Stress (Careau Model) for Sample b-i

3 CYCLES X 5 CYCLES



3 CYCLES X 5 CYCLES

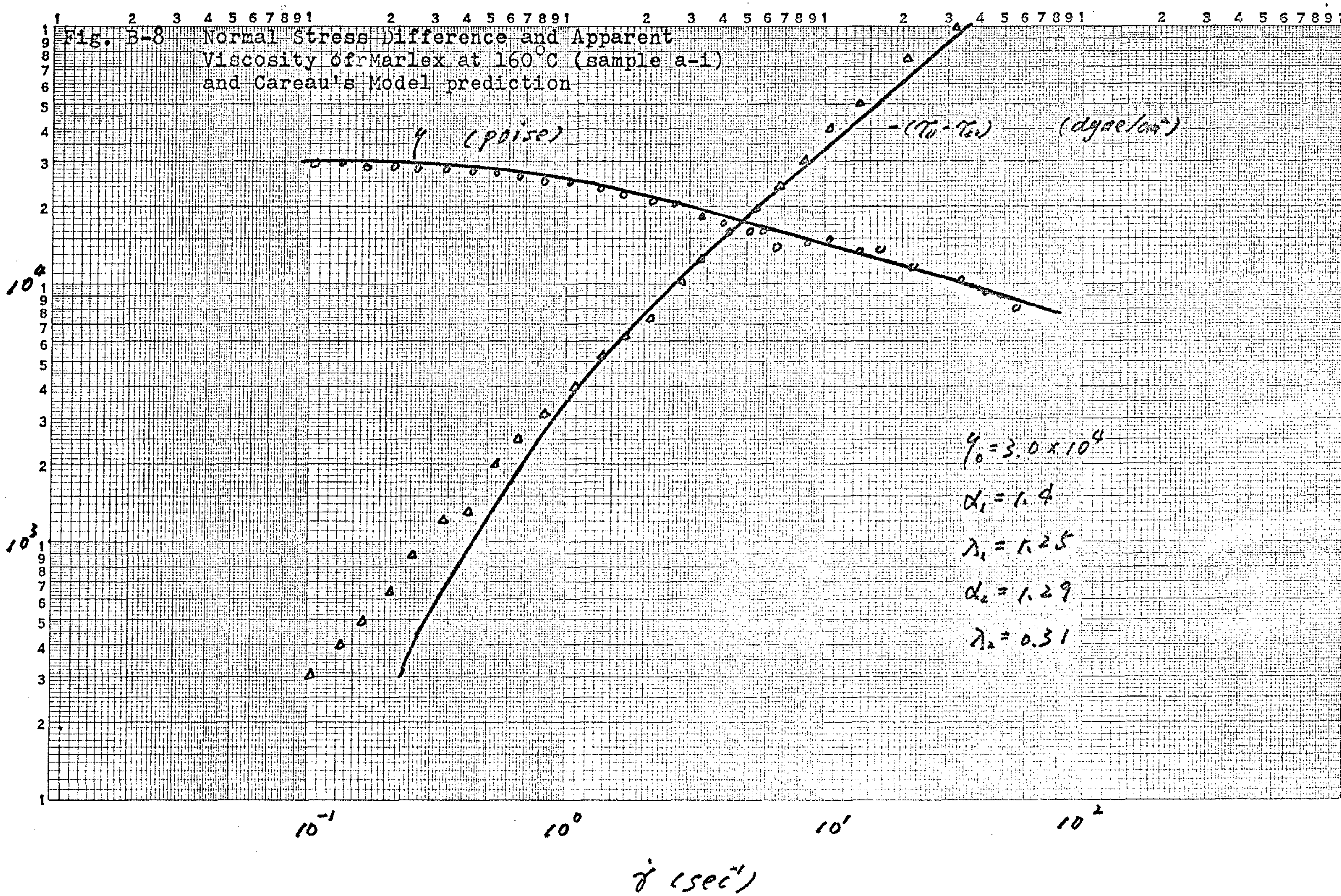
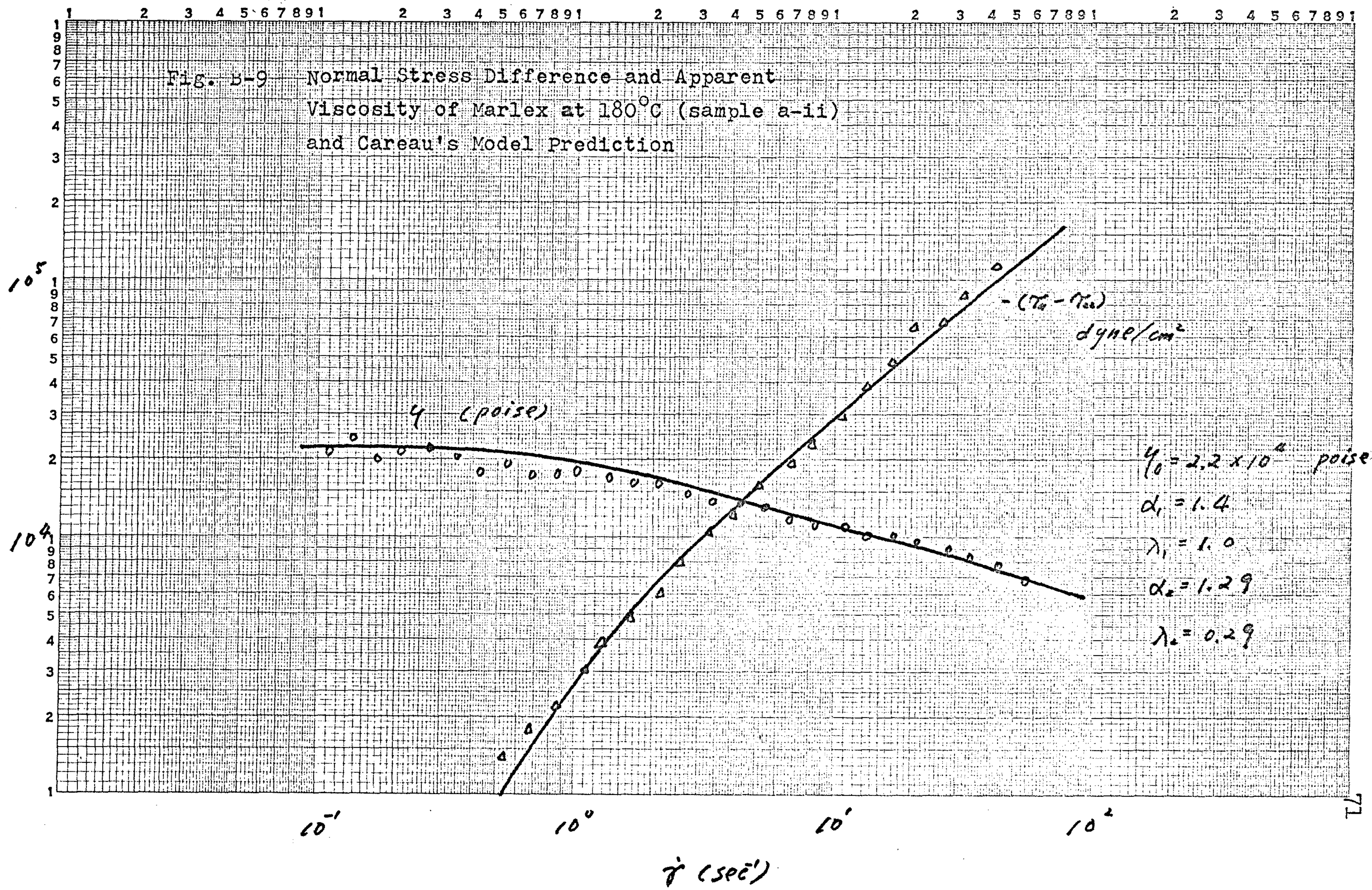


Fig. B-8 Normal Stress Difference and Apparent Viscosity of Marlex at 160°C (sample a-i) and Careau's Model prediction

Fig. B-9 Normal Stress Difference and Apparent Viscosity of Marlex at 180°C (sample a-ii) and Careau's Model Prediction



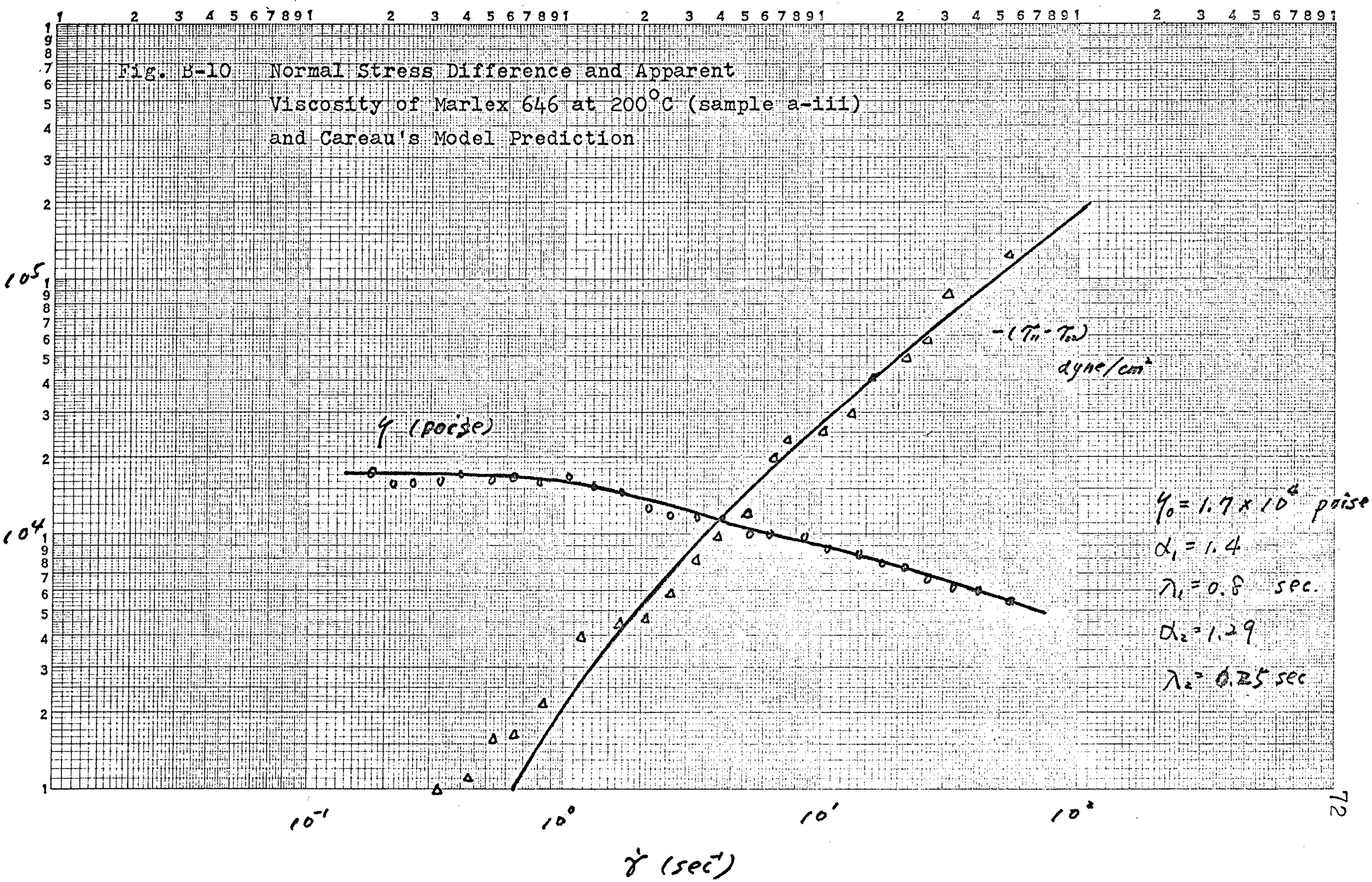


Fig. B-10 Normal Stress Difference and Apparent Viscosity of Marlex 646 at 200°C (sample a-iii) and Careau's Model Prediction

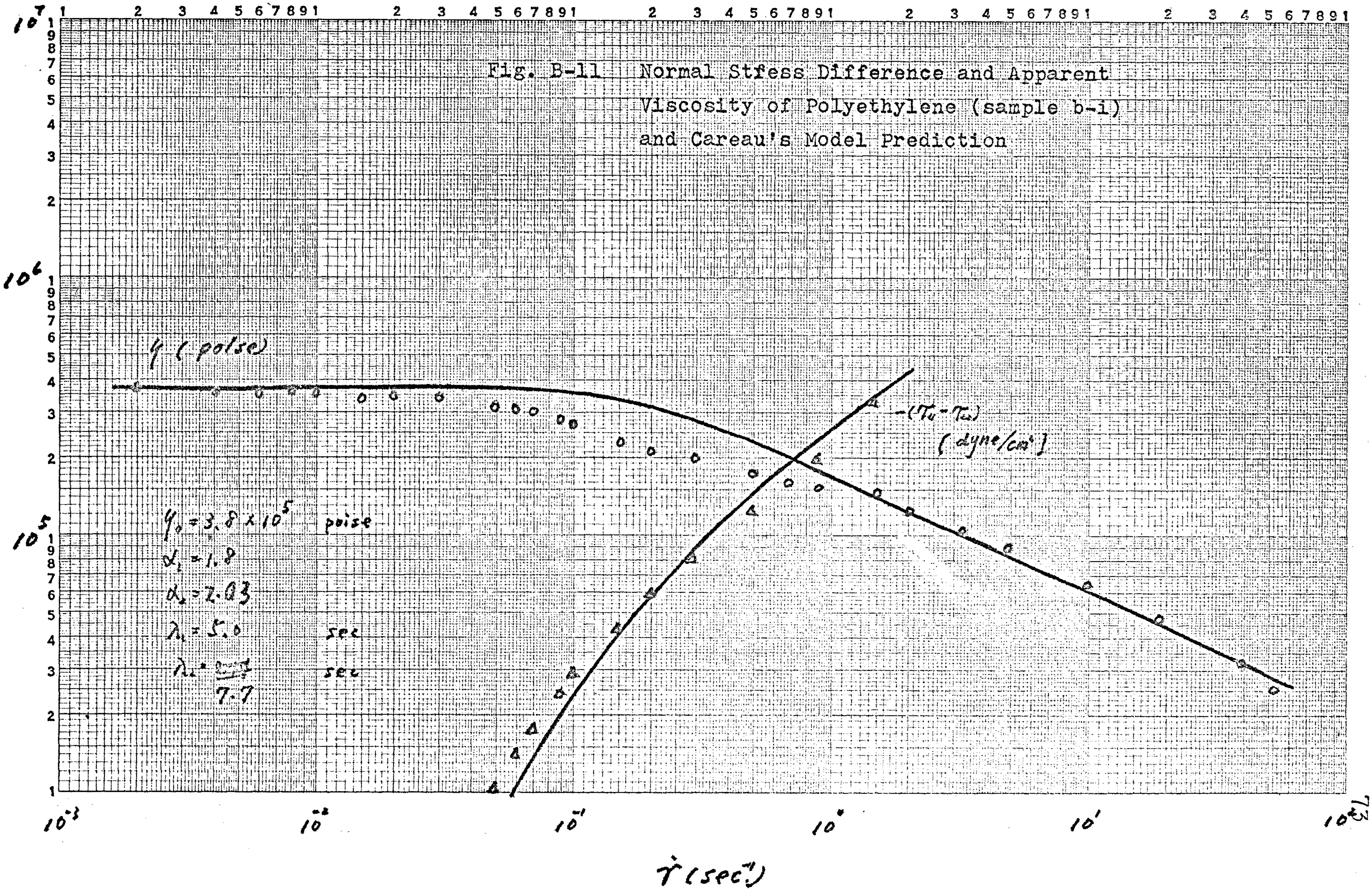


Fig. B-11 Normal Stfess Difference and Apparent Viscosity of Polyethylene (sample b-i) and Careau's Model Prediction

LOGARITHMIC
3 CYCLES X 5 CYCLES

MADE IN U. S. A.

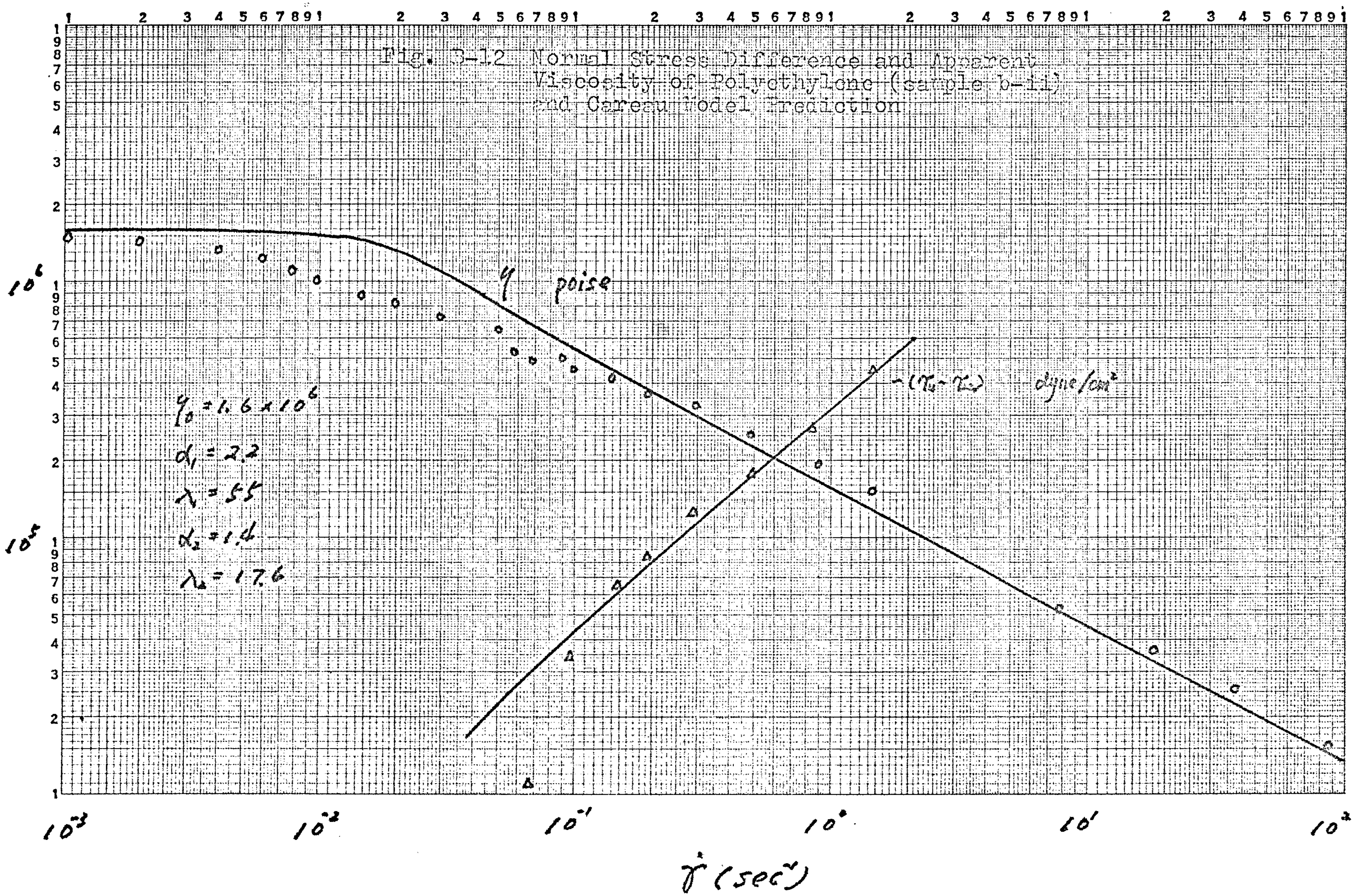
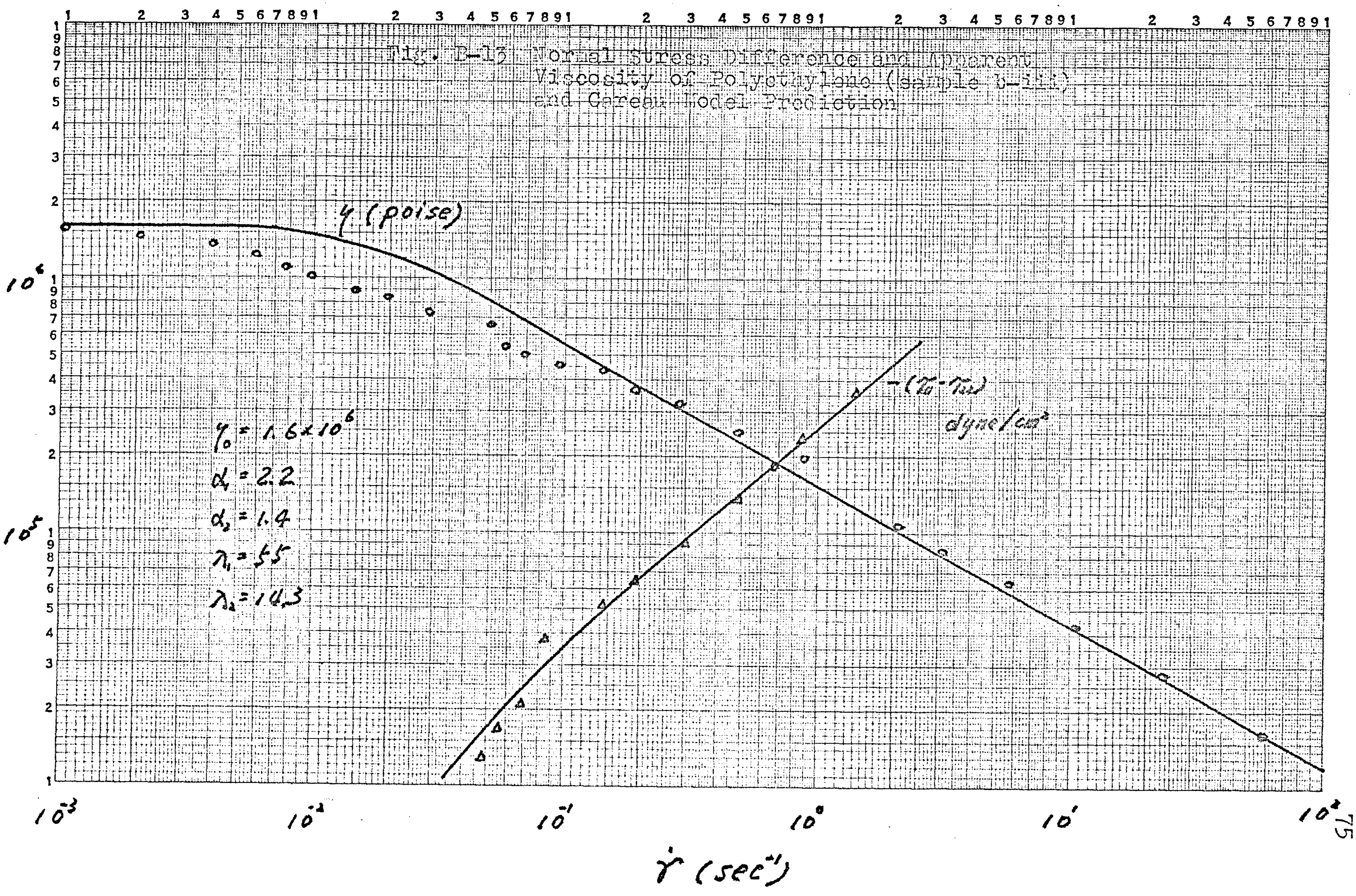


Fig. 3-12 Normal Stress Difference and Apparent Viscosity of Polyethylene (sample b-ii) and Careau Model Prediction

Fig. B-13 Normal Stress Difference and Apparent Viscosity of Polyethylene (sample B-iii) and Careau Model Prediction



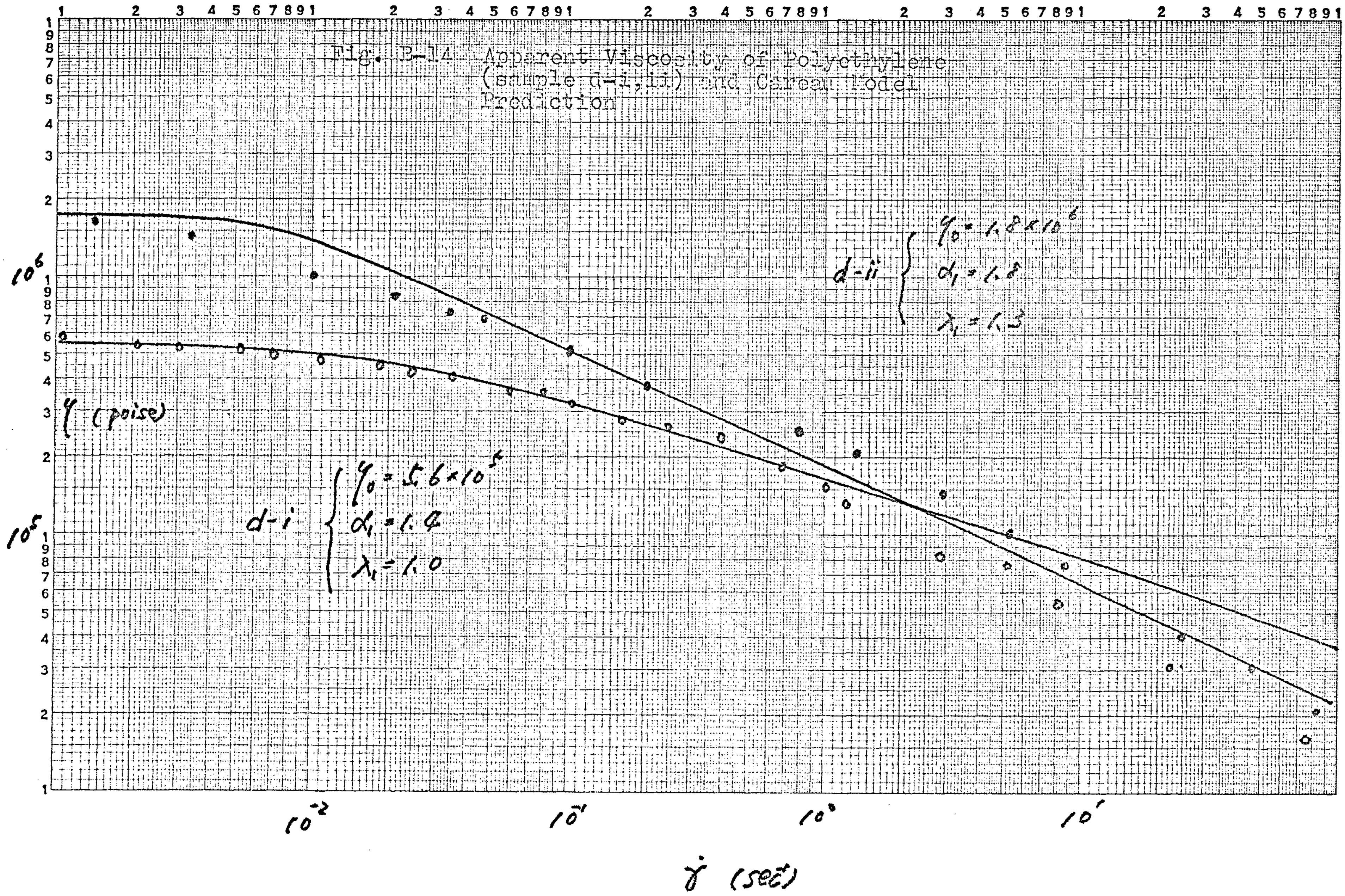


Fig. B-14 Apparent Viscosity of Polyethylene (sample d-i,ii) and Carreau Model Prediction

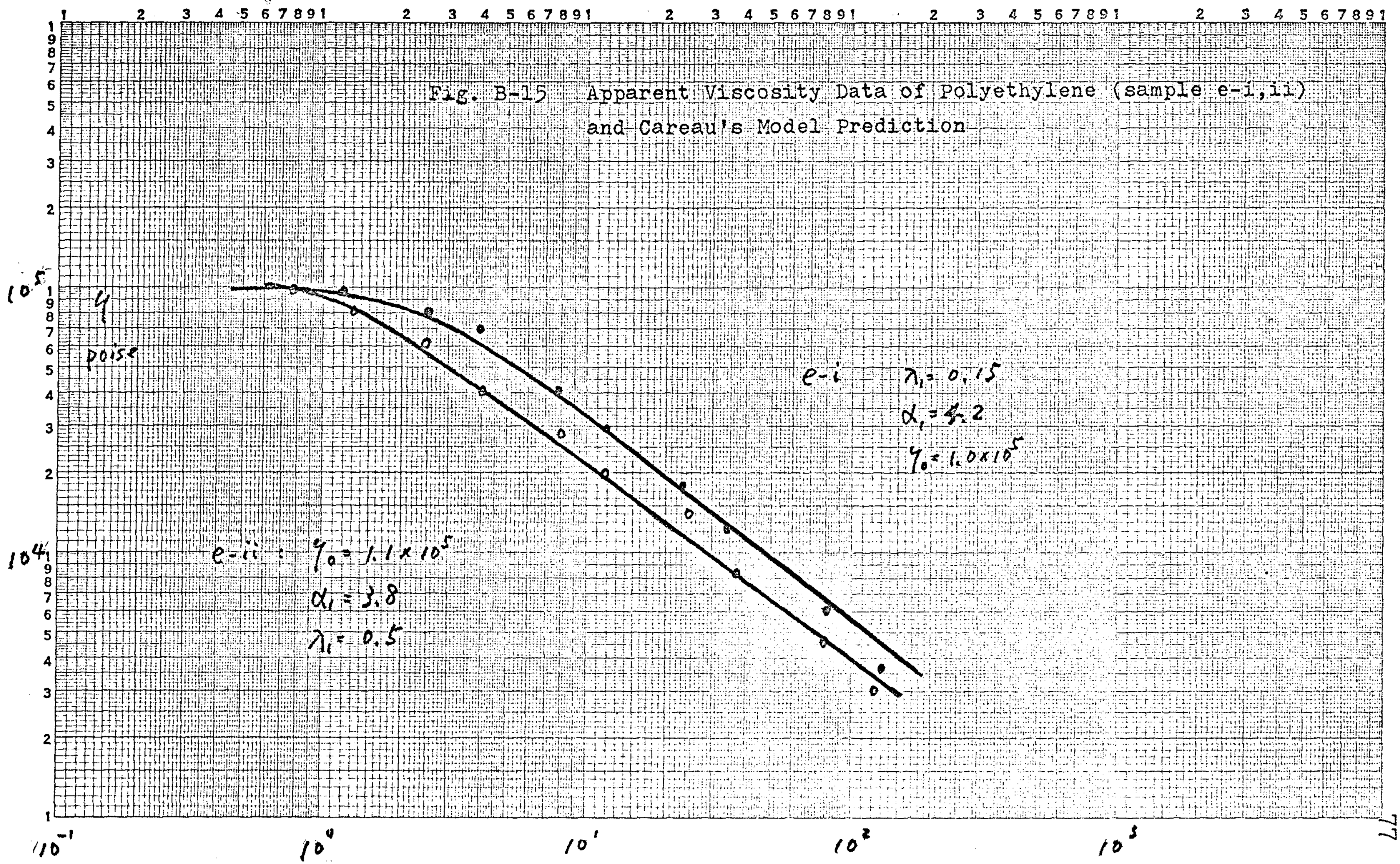


Fig. B-15 Apparent Viscosity Data of Polyethylene (sample e-i,ii) and Careau's Model Prediction

<u>Discussion.</u> This five-constant model is quite flexible, and gives fairly good prediction for both apparent viscosity and primary normal stress difference of some polymer melt samples as shown on the forgoing figures B-8 through B-15 and the table on the next page. However, the deviations for samples in certain ranges are very significant. For apparent viscosity the largest deviation usually occurs in the range right after constant viscosity, and the normal stress difference cannot more be predicted by this model below certain shear rate. This means that this model is reliable at high shear rate, but predicts either incorrect shear stress or normal stress at low to moderate shear rate.

Table IV The Parameters and Deviations of Careau's Model for Various Samples

Sample	η_0 (poise) $\times 10^{-5}$	α_1	α_2	λ_1(sec)	λ_2(sec)	shear rate range of deviation(10% or [illegible] larger) (sec^{-1}) η	shear rate range of deviation $-(\tau_{11}-\tau_{22})$	largest percentage deviation η	largest percentage deviation $-(\tau_{11}-\tau_{22})$
a-i	0.3	1.4	1.29	1.25	0.31	———	below 1	--	>100
a-ii	0.22	1.4	1.29	1.0	0.29	0.4-1.0	below 0.8	18	50
a-iii	0.17	1.4	1.29	0.8	0.25	———	below 1.3	--	>100
b-i	3.8	1.8	2.03	5.0	7.7	0.04-1	below 0.1	50	50
b-ii	16.0	2.2	1.4	55.	17.6	0.0035-0.1	below 0.13	65	>100
b-iii	16.0	2.2	1.4	55.	14.3	0.0035-0.1	below 0.09	65	30
c(Ref.34)	12.7	1.4	1.1	5.18	6.59	———	below 0.1	--	25
d-i	5.6	1.4	1.0			above 0.13		>100	
d-ii	18.0	1.8	1.3			0.003-6.0		>100	
e-i	1.0	4.2	0.15			———		--	
e-ii	1.1	3.8	0.5			———		--	

<u>Evaluation of an Empirical Equation for Apparent viscosity.</u>(30)

$$\log\left(\frac{\eta}{\eta_0}\right)=\left[\left(\frac{\eta}{\eta_0}\right)-a\right]\log\left[1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b\right] \quad ....(93)$$

This equation has the properties of being able to predict the power law region at large shear rate and constant viscosity at very low shear rate. When $\dot{\gamma}$ is very small

$$1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b \longrightarrow 1$$

$$\log\left(\frac{\eta}{\eta_0}\right) \longrightarrow 0 \quad \text{or} \quad \eta \to \eta_0 \quad ---(94)$$

and when $\dot{\gamma}$ is large $\left(\frac{\eta}{\eta_0}\right)$ becomes very small and

$$1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b \longrightarrow \left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b$$

$$\log\left(\frac{\eta}{\eta_0}\right) \to -a\log\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b = -ab\log\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right) \quad ....(95)$$

When plot in $\log\left(\frac{\eta}{\eta_0}\right)$ vs. $\log\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)$ scale, ab is the slope in the high shear rate region.

Equation(93) is not easy to solve for $\frac{\eta}{\eta_0}$ because both sides of the equation have this term. But if we reverse the process to take $\frac{\dot{\gamma}}{\dot{\gamma}_0}$ as dependent variable and $\frac{\eta}{\eta_0}$ as independent variable, it will be much easier to manipulate. Rewrite equation (93) as

$$\left(\frac{\eta}{\eta_0}\right)=\left[1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b\right]^{\left(\frac{\eta}{\eta_0}-a\right)}$$

$$\left(\frac{\eta}{\eta_0}\right)^{\frac{1}{\left(\frac{\eta}{\eta_0}-a\right)}} = 1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^b$$

or

$$\frac{\dot{\gamma}}{\dot{\gamma}_0}=\left[\left(\frac{\eta}{\eta_0}\right)^{\frac{1}{\left(\frac{\eta}{\eta_0}-a\right)}}-1\right] \quad ....(96)$$

then we get the explicit form for $\dot{\gamma}/\dot{\gamma}_0$.

Using a simple computer program (see appendix), we change the values of constants a and b while keep ab equal to the value determined from equation (95) at large shear rate, and we can prepare a set of curves. By comparing data and those curves, the constants are easily obtained, and then they are used to get the equation curve.

This four constants empirical equation is very flexible and proved to fit molten polymer data quite well (30). On the next page, four sets of data are used to show good fit of this equation.

3 CYCLES X 5 CYCLES

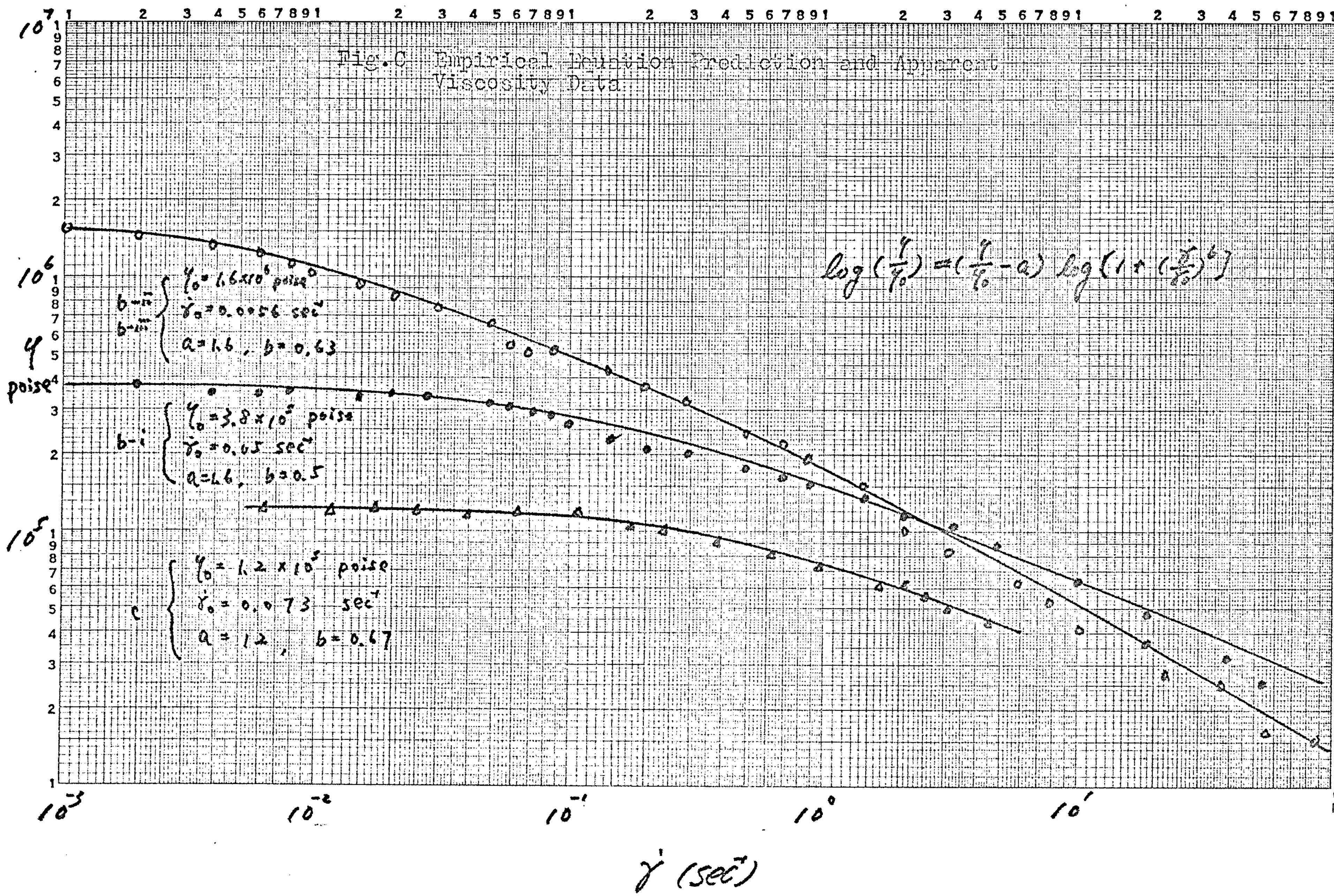


Fig. C Empirical Equation Prediction and Apparent Viscosity Data

Evaluation of an Empirical Equation for Normal Stress Difference.

$$\log[-(\tau_{11}-\tau_{22})] = a\dot{\gamma}^c + b \qquad \text{.......(97)}$$

where a, b, c are constants.

Let

$$y = -(\tau_{11}-\tau_{22})$$

$$x = \dot{\gamma}$$

$$Ly = \log y$$

then equation (97) becomes

$$Ly = ax^c + b \qquad \text{.......(98)}$$

If we take three particular points (x_1, y_1), (x_2, y_2) (x_3, y_3) from the curve, then

$$Ly_1 = ax_1^c + b_1 \qquad \text{.......(99)}$$

$$Ly_2 = ax_2^c + b_2 \qquad \text{.......(100)}$$

$$Ly_3 = ax_3^c + b_3 \qquad \text{.......(101)}$$

Eliminate a and b from these three equations

$$\frac{Ly_1 - Ly_2}{Ly_2 - Ly_3} = \frac{x_1^c - x_2^c}{x_2^c - x_3^c} \qquad \text{.......(102)}$$

If x_1, x_2, x_3 are chosen to have the relation

$$10x_1 = x_2 = 10^{-1}x_3 \qquad \text{.......(103)}$$

then equation (102) becomes

$$\frac{Ly_1 - Ly_2}{Ly_2 - Ly_3} = \frac{10^{-c} - 1}{1 - 10^{c}} = \frac{1 - 10^{c}}{10^{c} - 10^{2c}} \quad \text{.......(104)}$$

or

$$10^{2c} - \left(\frac{Ly_1 - Ly_3}{Ly_1 - Ly_2}\right)10^{c} + \left(\frac{Ly_2 - Ly_3}{Ly_1 - Ly_2}\right) = 0 \quad \text{.......(105)}$$

$$10^{c} = \frac{1}{2}\left\{\frac{Ly_1 - Ly_3}{Ly_1 - Ly_2} - \sqrt{\left(\frac{Ly_1 - Ly_3}{Ly_1 - Ly_2}\right)^2 - 4\left(\frac{Ly_2 - Ly_3}{Ly_1 - Ly_2}\right)}\right\} \quad \text{.......(106)}$$

Take logarithms on both sides.

$$c = \log \frac{1}{2}\left\{\frac{Ly_1 - Ly_3}{Ly_1 - Ly_2} - \sqrt{\left(\frac{Ly_1 - Ly_3}{Ly_1 - Ly_2}\right)^2 - 4\left(\frac{Ly_2 - Ly_3}{Ly_1 - Ly_2}\right)}\right\} \quad \text{.....(107)}$$

The constants a and b expressed in terms of c are:

$$a = \frac{Ly_1 - Ly_2}{x_1^{c} - x_2^{c}} \quad \text{.......(108)}$$

$$b = Ly_1 - a x_1^{c} \quad \text{.......(109)}$$

As an illustration, we plot data of sample b-1 on log-log scale (Fig B-4) and read three points (0.05, 11500), (0.5, 130000), (5.0, 630000). By using a simple computer program (see appendix), constant c is first calculated from equation (107), then a and b are got from equations (108) (109). Plug these constants into the equation, the curve is then drawn.

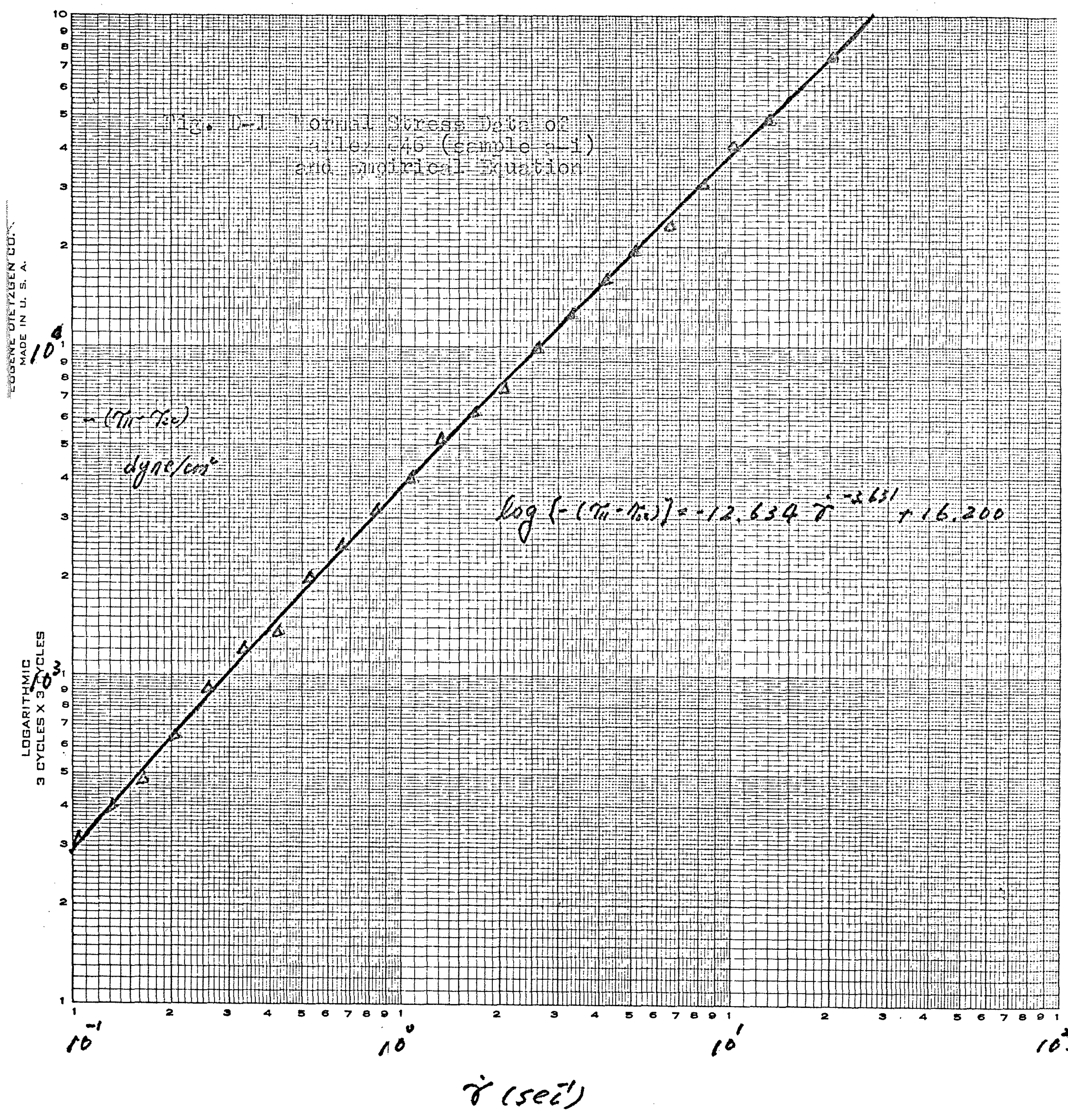


Fig. D-1 Normal Stress Data of [illegible] 46 (sample [illegible]-1) and Empirical Equation

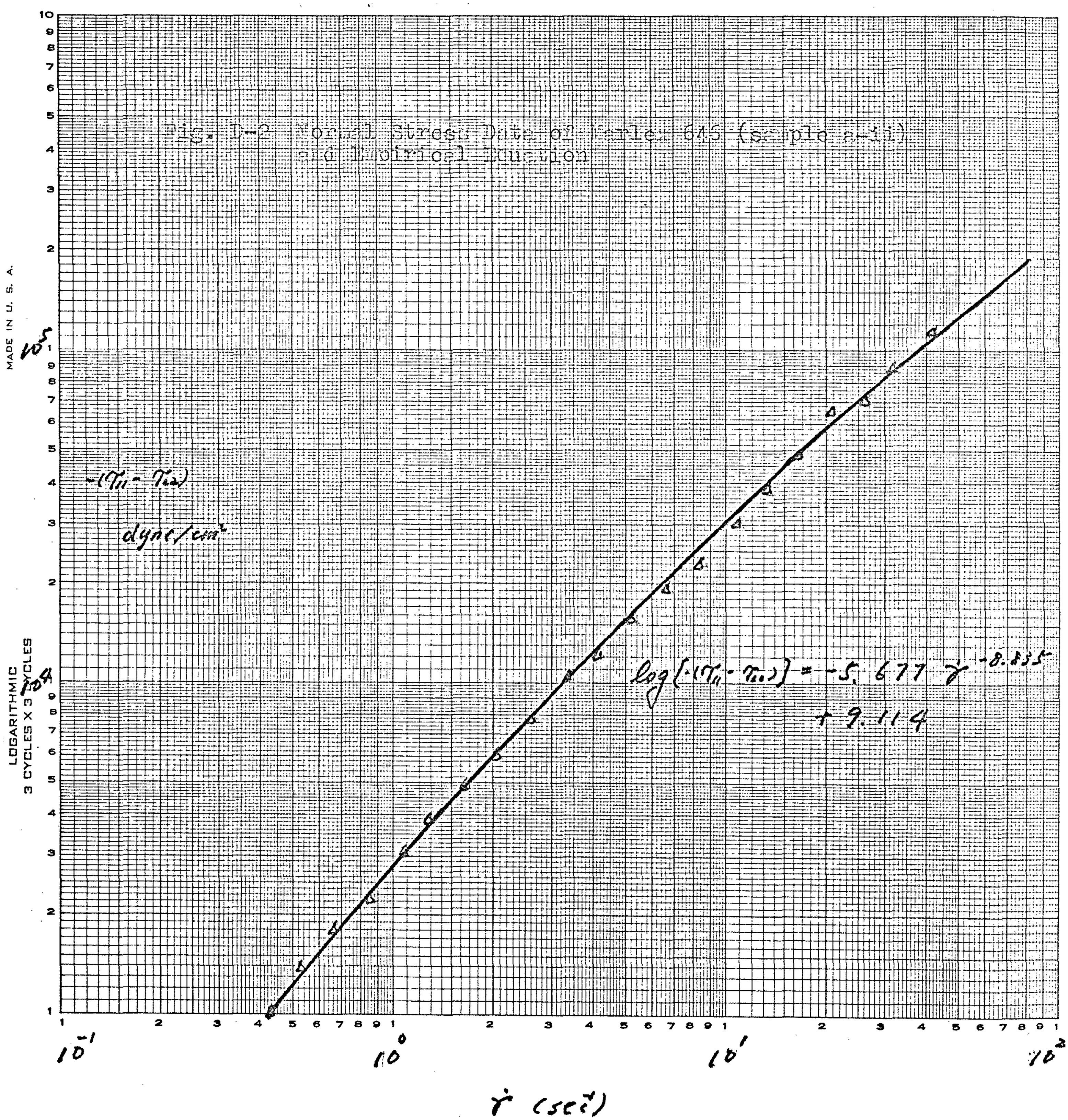


Fig. D-2 Normal Stress Data of Marlex 645 (sample A-11) and Empirical Equation

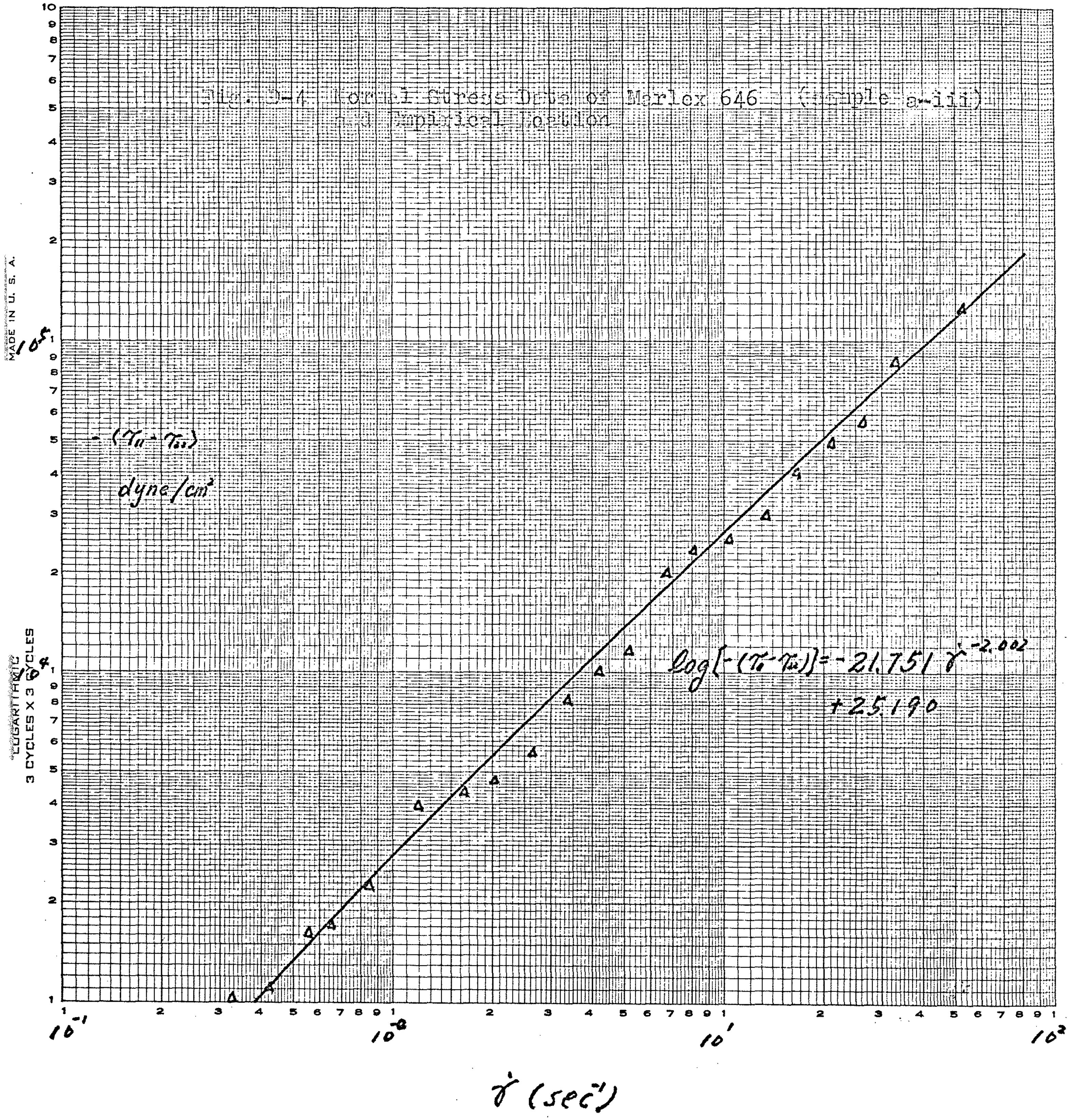


Fig. 5-4 Normal Stress Data of Marlex 646 (Sample a-iii) and Empirical Equation

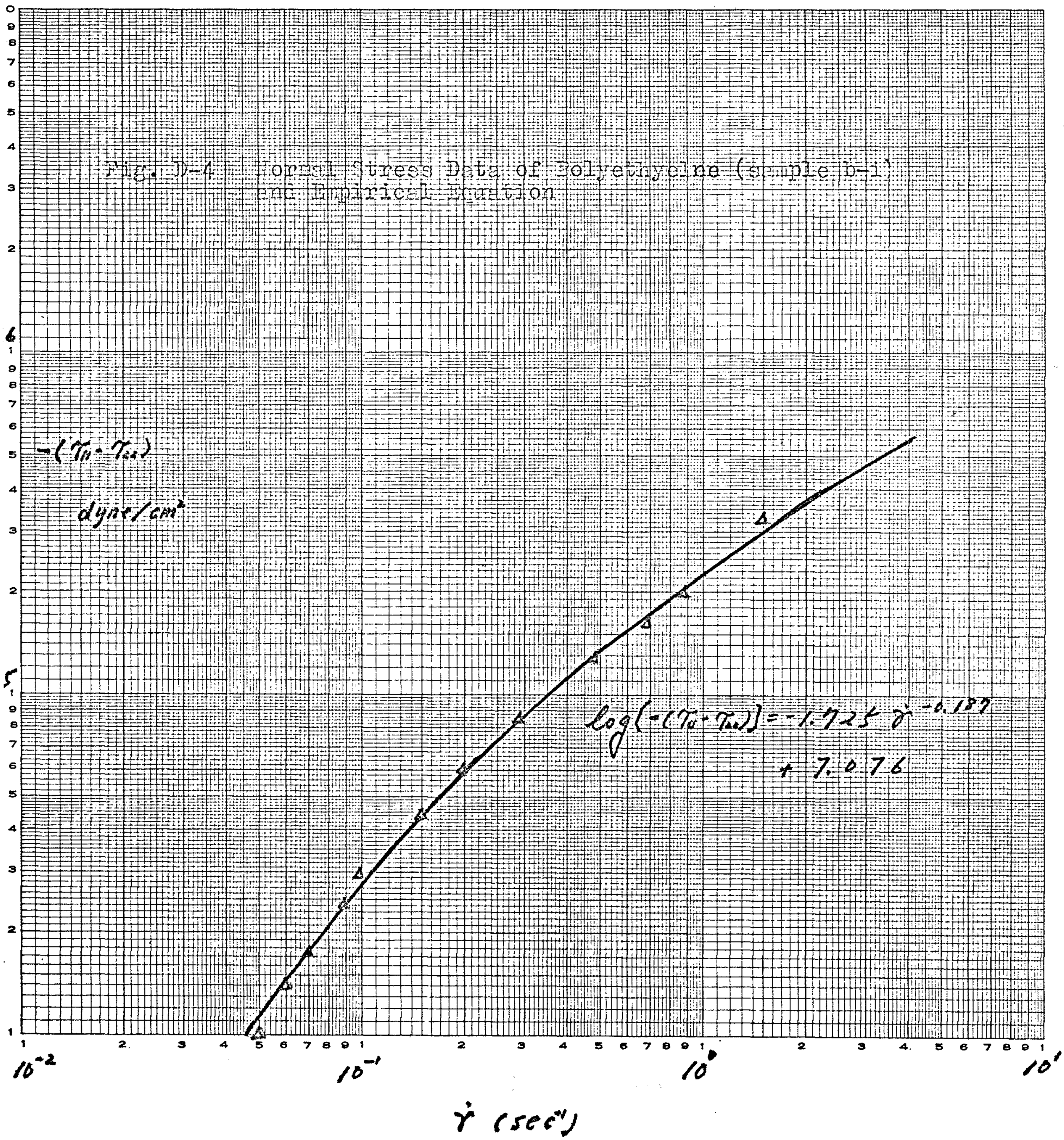


Fig. D-4 Normal Stress Data of Polyethylene (sample b-1) and Empirical Equation

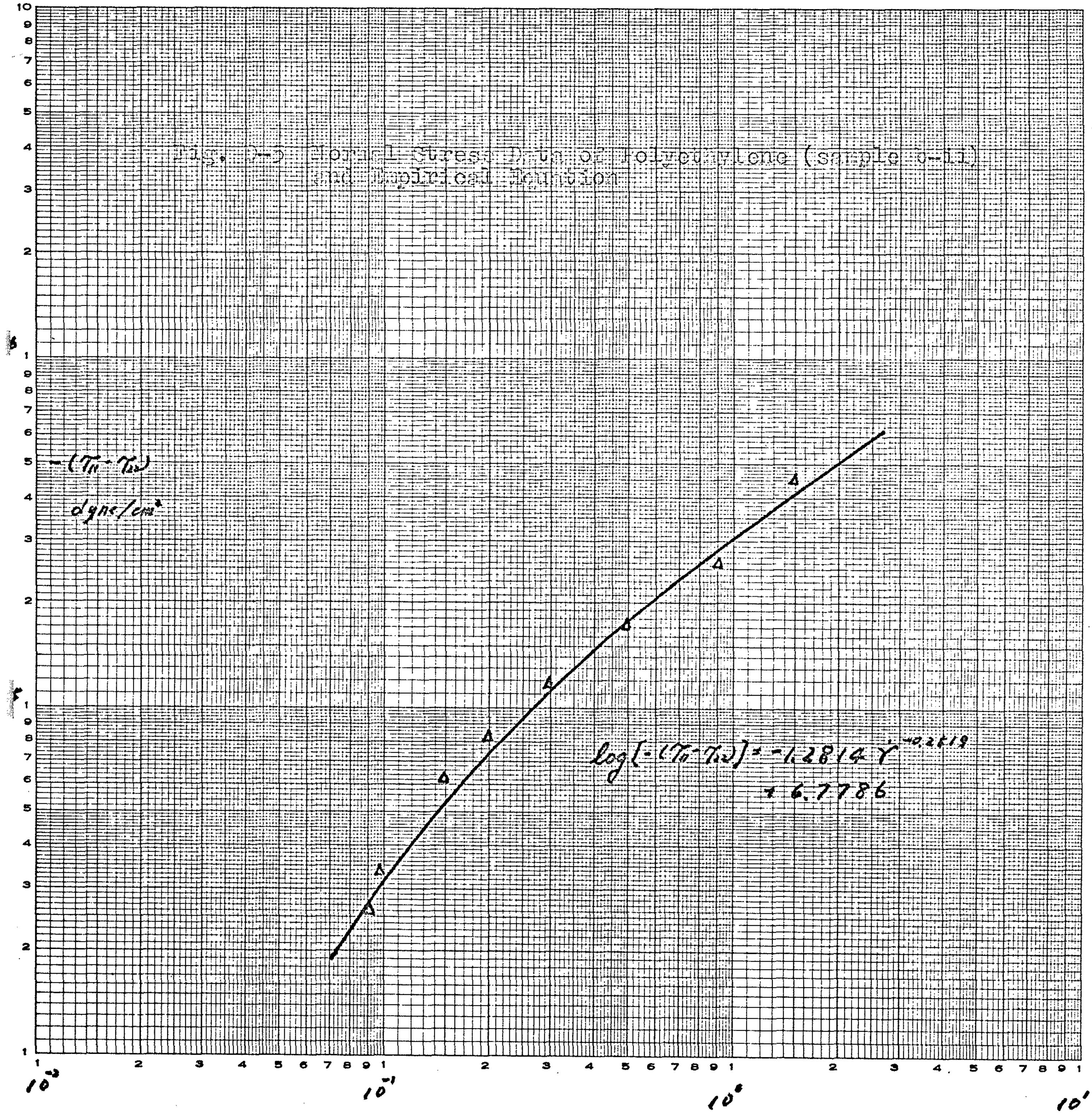


Fig. D-5 Normal Stress Data of Polyethylene (sample C-11) and Empirical Equation

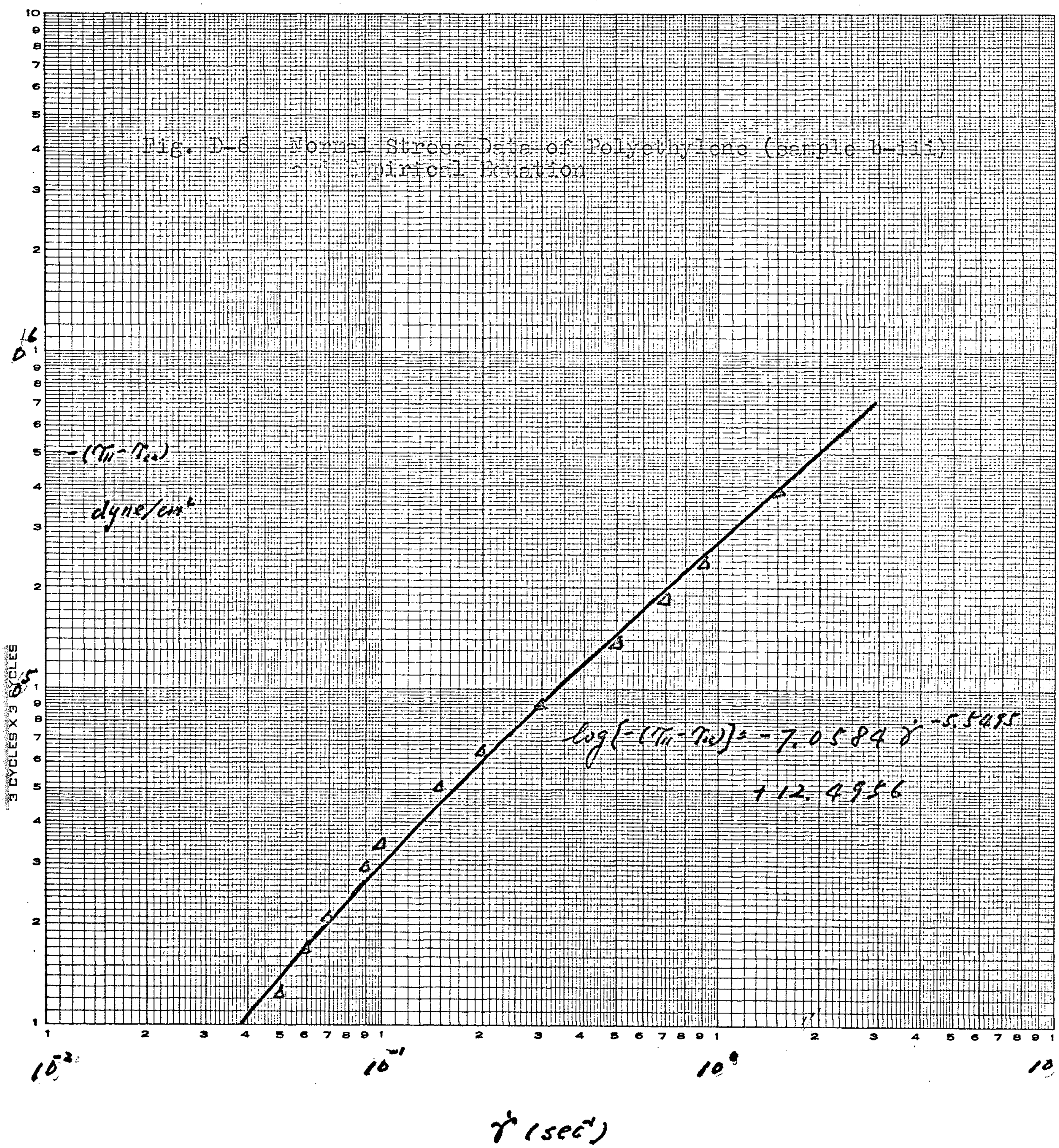


Fig. D-6 Normal Stress Data of Polyethylene (sample b-111) and Empirical Equation

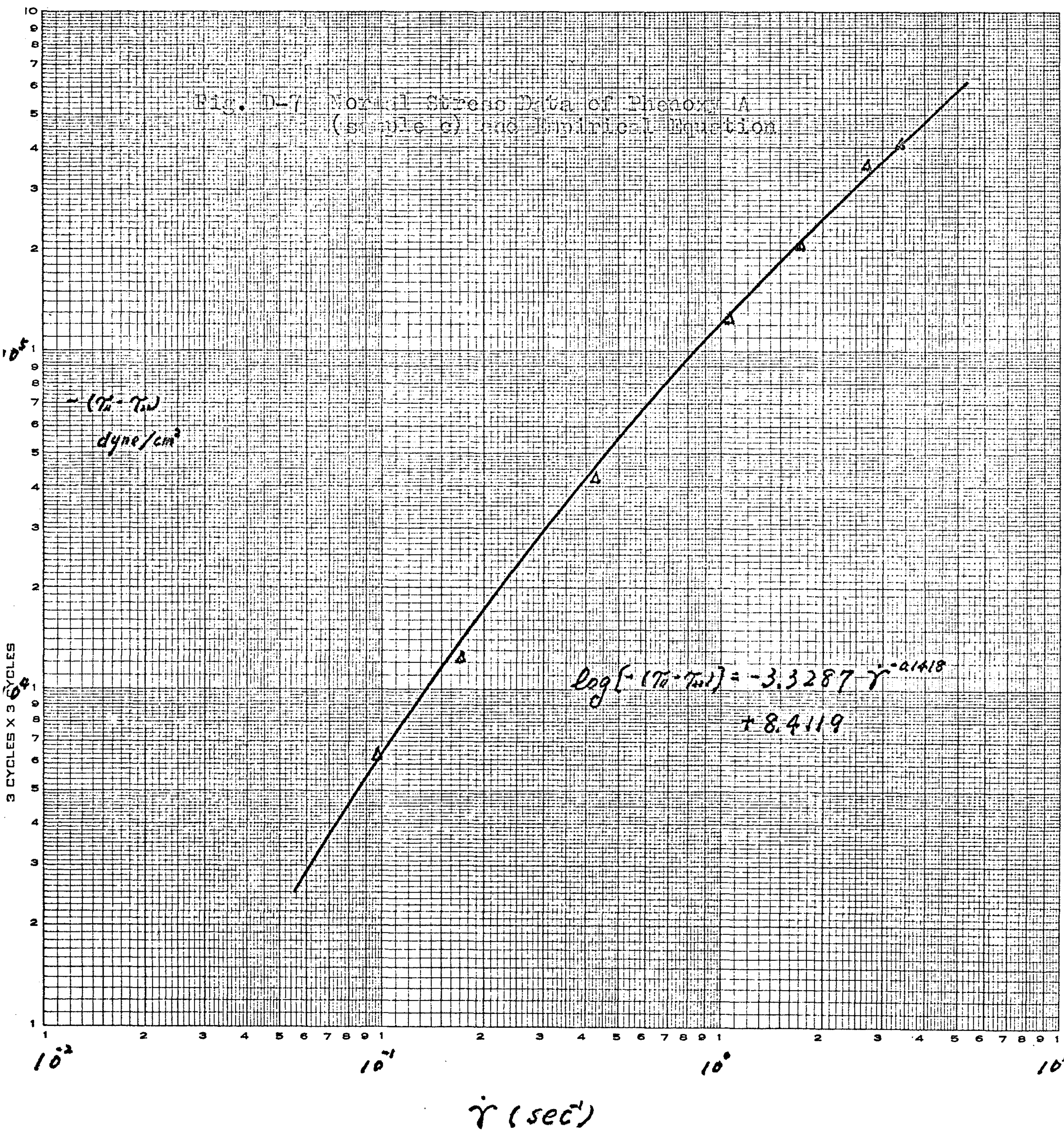


Fig. D-7 Normal Stress Data of Phenoxy A (sample c) and Empirical Equation

<u>Discussion.</u> The following table summarizes the constants of this empirical equation for several samples.

Table V Constants of the Empirical Normal Stress Equation

Sample	−a	b	−c
a-i	12.6344	16.2005	3.6513
a-ii	5.6770	9.1138	8.8350
a-iii	21.7510	25.1910	2.0020
b-i	1.7250	7.0760	0.1870
b-ii	1.2814	6.7786	0.2519
b-iii	7.0584	12.4956	5.5495
c	3.3237	8.4119	0.1418

This new equation is very easy to manipulate either by hand or by computer as illustrated before, and, from inspecting figures D-1 through D-7, it fits data excellently also.

V CONCLUSION AND RECOMMENDATION

The deviations of both Carreau and Spriggs Model in predicting molten polymers are compared in Table VI page 94.

The conclusions reached in the present work are as follows:

(1) The Spriggs Model was unsatisfactory in both representing apparent viscosity and normal stress data for molten polymers.

(2) The representation for normal stress data was particularly bad having deviations of over 100%. The result was that the Spriggs Model can give only qualitative representation for molten polymer normal stress data.

(3) Deviations for apparent viscosity data were lower but still ranged from 25% to 100%. For most samples the worst fit were in low shear rate ranges roughly from 0.1 to 1 sec^{-1}.

(4) The Carreau Model was somewhat better but still yielded large deviations.

(5) It predicted normal stress of molten polymer fairly well for a short range but gave bad representation in the ranges approximately below 0.1 sec^{-1}.

(6) Although this model was satisfactory for some samples in describing apparent viscosity, it was not flexible enough to represent other similar samples. In the worst condition the deviation was over 100%

(7) Empirical equations take simpler forms but should always be used carefully. Hajakawa & Wong's equation was satisfactory for representing apparent viscosity data.

(8) The new empirical equation derived in this work fitted normal stress data satisfactory, and could be handled easily.

A considerable amount of molten polymer rheological data was added to the open literature in the present work also.

It is suggested that a new model be developed for better description of molten polymers. As pointed out in chapter II, a good constitutive equation should not only be able to describe the apparent viscosity, the complex viscosity, and the normal stress data, which are the most commonly measured properties, but also be able to describe other properties, in order to get a good new model, the experiments for getting such data as recoil, relaxation, elongation flow etc. should be conducted.

Although Carreau Model was unsatisfactory as mentioned above, it showed promising for better description of polymer melts. This model could be modified by changing the memory function (equation 67, chapter IV); particularly changing the constants n_1 and n_2 in equation (70), chapter IV to other values larger than one, which would be expected to give better representation for apparent viscosity as inspecting equation (76) of chapter IV and the forgoing data, or, even making n_1 or n_2 be another parameter thus introducing another degree of flexibility.

Table VI Comparison of Deviations of Careau and Spriggs Models

Sample	shear rate range of deviation(10% or larger) (sec.$^{-1}$)				largest percentage deviation			
	η		$-(\tau_{11}-\tau_{22})$		η		$-(\tau_{11}-\tau_{22})$	
	Spriggs	Careau	Spriggs	Careau	Spriggs	Careau	Spriggs	Careau
a-i	0.5-9.0	-----	below 2	below 1	33	-----	100	100
a-ii	0.4-5.0 above 20	0.4-1.0	below 1.5 above 30	below 0.8	26	18	90	50
a-iii	1.5-6.5 above 40	-----	below 1.5	below 1.3	36	-----	90	100
b-i	0.05-1.5	0.04-1.	below 0.2	below 0.1	100	50	100	50
b-ii	0.005-0.02 above 1.5	0.0035-0.1	0.05-1.5	below 0.13	100	65	100	100
b-iii	"	"	0.05-1.5	below 0.09	100	65	100	30
c	0.2-0.7	-----	above 2 below 0.12	below 0.1	12	-----	25	25
d-i	0.005-0.12	above 0.13			35	100		
d-ii	0.001-100	0.003-6.			100	100		
e-i	above 100	-----			16	-----		
e-ii	above 100	-----			10	-----		

APPENDIX A CALCULATED DATA OF MARLEX 646 (SAMPLE a-i,ii,iii)

MARLEX 646 TEMPERATURE= 200

EXP. NO	SHEAR RATE	SHEAR STRESS	ELASTISITY	NORMAL STRESS	NS/P	VISCOSITY	T
65	0.8491E 01	0.7779E 05	0.7635E 05	0.1983E 05	0.2550E 00	0.9162E 04	0.1200E 00
65	0.8491E 01	0.7779E 05	0.6460E 05	0.2344E 05	0.3013E 00	0.9162E 04	0.1418E 00
65	0.8491E 01	0.8209E 05	0.7059E 05	0.2389E 05	0.2910E 00	0.9669E 04	0.1370E 00
66	0.8491E 01	0.8642E 05	0.5758E 05	0.3246E 05	0.3756E 00	0.1018E 05	0.1768E 00
67	0.1071E 02	0.9939E 05	0.9138E 05	0.2705E 05	0.2722E 00	0.9276E 04	0.1015E 00
68	0.1071E 02	0.9247E 05	0.9127E 05	0.2344E 05	0.2535E 00	0.8630E 04	0.9456E-01
69	0.1349E 02	0.1145E 06	0.1070E 06	0.3065E 05	0.2677E 00	0.8486E 04	0.7928E-01
70	0.1349E 02	0.1145E 06	0.1103E 06	0.2976E 05	0.2599E 00	0.8486E 04	0.7696E-01
71	0.1627E 02	0.1340E 06	0.1107E 06	0.4058E 05	0.3029E 00	0.8231E 04	0.7438E-01
72	0.1627E 02	0.1318E 06	0.1121E 06	0.3877E 05	0.2941E 00	0.8099E 04	0.7222E-01
73	0.2133E 02	0.1556E 06	0.1400E 06	0.4328E 05	0.2782E 00	0.7295E 04	0.5213E-01
74	0.2133E 02	0.1556E 06	0.1084E 06	0.5590E 05	0.3593E 00	0.7295E 04	0.6733E-01
75	0.2695E 02	0.1815E 06	0.1475E 06	0.5590E 05	0.3080E 00	0.6736E 04	0.4567E-01
76	0.2695E 02	0.1901E 06	0.1568E 06	0.5770E 05	0.3035E 00	0.7056E 04	0.4501E-01
77	0.3396E 02	0.2204E 06	0.1586E 06	0.7664E 05	0.3477E 00	0.6490E 04	0.4091E-01

APPENDIX A CALCULATED DATA OF MARLEX 646 (cont'd)

78	0.3396E 02	0.2226E 06	0.1571E 06	0.7889E 05	0.3545E 00	0.6553E 04	0.4171E-01
79	0.3396E 02	0.2550E 06	0.1604E 06	0.1014E 06	0.3978E 00	0.7507E 04	0.4681E-01
80	0.3396E 02	0.2723E 06	0.2352E 06	0.7888E 05	0.2897E 00	0.8017E 04	0.3409E-01
81	0.3396E 02	0.2614E 06	0.1404E 06	0.1217E 06	0.4657E 00	0.7696E 04	0.5480E-01
82	0.5357E 02	0.2917E 06	0.1615E 06	0.1319E 06	0.4521E 00	0.5445E 04	0.3372E-01
83	0.5357E 02	0.2863E 06	0.1685E 06	0.1217E 06	0.4252E 00	0.5344E 04	0.3172E-01
84	0.6767E 01	0.6807E 05	0.5653E 05	0.2051E 05	0.3013E 00	0.1006E 05	0.1779E 00
85	0.5357E 01	0.5565E 05	0.6487E 05	0.1195E 05	0.2147E 00	0.1039E 05	0.1601E 00
86	0.4265E 01	0.4807E 05	0.5653E 05	0.1023E 05	0.2128E 00	0.1127E 05	0.1994E 00
87	0.3396E 01	0.3944E 05	0.4797E 05	0.8115E 04	0.2058E 00	0.1161E 05	0.2421E 00
88	0.2695E 01	0.3241E 05	0.4668E 05	0.5632E 04	0.1738E 00	0.1203E 05	0.2577E 00
89	0.2133E 01	0.2699E 05	0.4046E 05	0.4507E 04	0.1670E 00	0.1266E 05	0.3128E 00
90	0.1698E 01	0.2419E 05	0.3250E 05	0.4507E 04	0.1863E 00	0.1425E 05	0.4384E 00
91	0.1349E 01	0.2010E 05	0.2548E 05	0.3966E 04	0.1973E 00	0.1489E 05	0.5844E 00
92	0.1073E 01	0.1793E 05	0.1942E 05	0.4144E 04	0.2311E 00	0.1672E 05	0.8609E 00
93	0.8491E 01	0.1338E 05	0.2070E 05	0.2164E 04	0.1617E 00	0.1576E 04	0.7612E-01
94	0.6767E 01	0.1123E 05	0.1842E 05	0.1713E 04	0.1526E 00	0.1659E 04	0.9009E-01
95	0.5357E 01	0.9076E 04	0.1270E 05	0.1623E 04	0.1788E 00	0.1694E 04	0.1334E 00
96	0.4265E 00	0.7546E 04	0.1317E 05	0.1082E 04	0.1434E 00	0.1769E 05	0.1343E 01

97	0.3346E 00	0.5393E 04	0.7353E 04	0.9900E 03	0.1836E 00	0.1612E 05	0.2193E 01
98	0.2695E 00	0.4304E 04	0.8570E 04	0.5410E 03	0.1257E 00	0.1597E 05	0.1864E 01
99	0.2133E 00	0.4304E 04	0.7652E 04	0.6059E 03	0.1408E 00	0.2018E 05	0.2638E 01
100	0.1698E 00	0.3241E 04	0.3654E 04	0.7195E 03	0.2220E 00	0.1909E 05	0.5224E 01
101	0.1349E 00	0.3023E 04	0.4228E 04	0.5410E 03	0.1789E 00	0.2241E 05	0.5299E 01

MARLEX 646 TEMPERATURE= 180

EXP. NO	SHEAR RATE	SHEAR STRESS	ELASTISITY	NORMAL STRESS	NS/P	VISCOSITY	T
104	0.1073E 00	0.2375E 04	0.7907E 04	0.1785E 03	0.7516E-01	0.2214E 05	0.2800E 01
102	0.6767E-01	0.1297E 04				0.1916E 05	
103	0.8491E-01	0.2204E 04				0.2596E 05	
105	0.1349E 00	0.3348E 04	0.7854E 04	0.3571E 03	0.1067E 00	0.2481E 05	0.3159E 01
106	0.1698E 00	0.3456E 04	0.6658E 04	0.4490E 03	0.1299E 00	0.2035E 05	0.3057E 01
107	0.2133E 00	0.4641E 04	0.9965E 04	0.5410E 03	0.1166E 00	0.2176E 05	0.2184E 01
108	0.2695E 00	0.6042E 04	0.1126E 05	0.8115E 03	0.1343E 00	0.2242E 05	0.1992E 01
109	0.3396E 00	0.6897E 04	0.1326E 05	0.8981E 03	0.1302E 00	0.2031E 05	0.1532E 01
110	0.4265E 00	0.7779E 04	0.1400E 05	0.1082E 04	0.1391E 00	0.1824E 05	0.1303E 01
111	0.5357E 00	0.1015E 05	0.1789E 05	0.1442E 04	0.1420E 00	0.1895E 05	0.1060E 01
112	0.6767E 00	0.1210E 05	0.2031E 05	0.1803E 04	0.1490E 00	0.1788E 05	0.8801E 00
113	0.8491E 00	0.1512E 05	0.2537E 05	0.2254E 04	0.1491E 00	0.1780E 05	0.7017E 00

APPENDIX A CALCULATED DATA OF MARLEX 646 (cont'd)

114	0.1073E 01	0.1945E 05	0.3091E 05	0.3062E 04	0.1575E 00	0.1813E 05	0.5866E 00
115	0.1349E 01	0.2334E 05	0.3599E 05	0.3787E 04	0.1623E 00	0.1730E 05	0.4806E 00
116	0.1698E 01	0.2764E 05	0.3927E 05	0.4869E 04	0.1761E 00	0.1628E 05	0.4145E 00
117	0.2133E 01	0.3371E 05	0.4710E 05	0.6038E 04	0.1791E 00	0.1581E 05	0.3356E 00
118	0.2695E 01	0.3931E 05	0.4876E 05	0.7931E 04	0.2018E 00	0.1459E 05	0.2992E 00
119	0.1698E 01	0.2754E 05	0.3897E 05	0.4869E 04	0.1768E 00	0.1622E 05	0.4161E 00
120	0.2133E 01	0.3348E 05	0.4645E 05	0.6038E 04	0.1804E 00	0.1570E 05	0.3379E 00
121	0.2695E 01	0.4105E 05	0.5345E 05	0.7888E 04	0.1922E 00	0.1523E 05	0.2850E 00
122	0.3396E 01	0.4968E 05	0.5959E 05	0.1037E 05	0.2086E 00	0.1463E 05	0.2455E 00
123	0.4265E 01	0.5834E 05	0.6997E 05	0.1217E 05	0.2086E 00	0.1368E 05	0.1955E 00
124	0.5357E 01	0.6913E 05	0.7920E 05	0.1510E 05	0.2184E 00	0.1290E 05	0.1629E 00
125	0.6767E 01	0.7561E 05	0.7468E 05	0.1916E 05	0.2534E 00	0.1117E 05	0.1496E 00
126	0.5357E 01	0.6807E 05	0.7349E 05	0.1578E 05	0.2318E 00	0.1271E 05	0.1729E 00
127	0.6767E 01	0.8103E 05	0.8577E 05	0.1916E 05	0.2364E 00	0.1197E 05	0.1396E 00
128	0.8491E 01	0.9506E 05	0.9646E 05	0.2344E 05	0.2466E 00	0.1120E 05	0.1161E 00
129	0.1071E 02	0.1167E 06	0.1145E 06	0.2976E 05	0.2550E 00	0.1089E 05	0.9511E-01
130	0.1349E 02	0.1426E 06	0.1344E 06	0.3787E 05	0.2655E 00	0.1057E 05	0.7864E-01
131	0.1698E 02	0.1685E 06	0.1488E 06	0.4779E 05	0.2835E 00	0.9925E 04	0.6672E-01
132	0.2133E 02	0.2074E 06	0.1687E 06	0.6384E 05	0.3077E 00	0.9727E 04	0.5766E-01
133	0.2695E 02	0.2463E 06	0.2159E 06	0.7033E 05	0.2855E 00	0.9142E 04	0.4234E-01

134	0.3396E 02	0.2826E 06	0.2239E 06	0.8927E 05	0.3158E 00	0.8322E 04	0.3716E-01
135	0.4265E 02	0.3348E 06	0.2439E 06	0.1150E 06	0.3434E 00	0.7848E 04	0.3217E-01
136	0.5357E 02	0.3620E 06				0.6757E 04	

MARLEX 646 TEMPERATURE= 160

EXP. NO	SHEAR RATE	SHEAR STRESS	ELASTISITY	NORMAL STRESS	NS/P	VISCOSITY	T
138	0.6767E-01	0.2160E 04	0.6480E 04	0.1802E 03	0.8341E-01	0.3192E 05	0.4926E 01
137	0.5357E-01	0.1945E 04				0.3630E 05	
139	0.8491E-01	0.2808E 04	0.1095E 05	0.1802E 03	0.6415E-01	0.3307E 05	0.3019E 01
140	0.1073E 00	0.3241E 04	0.9719E 04	0.2705E 03	0.8346E-01	0.3022E 05	0.3109E 01
141	0.1349E 00	0.4105E 04	0.1170E 05	0.3603E 03	0.8778E-01	0.3042E 05	0.2600E 01
142	0.1698E 00	0.5186E 04				0.3054E 05	
143	0.2133E 00	0.6265E 04	0.1452E 05	0.6763E 03	0.1079E 00	0.2937E 05	0.2023E 01
144	0.2695E 00	0.7779E 04	0.1866E 05	0.8115E 03	0.1043E 00	0.2887E 05	0.1547E 01
145	0.3396E 00	0.9724E 04	0.1877E 05	0.1261E 04	0.1296E 00	0.2863E 05	0.1525E 01
146	0.4265E 00	0.1208E 05	0.2539E 05	0.1439E 04	0.1191E 00	0.2833E 05	0.1116E 01
147	0.5357E 00	0.1468E 05	0.2491E 05	0.2164E 04	0.1474E 00	0.2740E 05	0.1100E 01
148	0.6767E 00	0.1727E 05	0.2856E 05	0.2613E 04	0.1513E 00	0.2552E 05	0.8936E 00
149	0.8491E 00	0.2160E 05	0.3702E 05	0.3154E 04	0.1460E 00	0.2544E 05	0.6873E 00
150	0.1073E 01	0.2593E 05	0.4147E 05	0.4058E 04	0.1565E 00	0.2417E 05	0.5829E 00

APPENDIX A CALCULATED DATA OF MARLEX 646 (cont'd)

151	0.1349E 01	0.3112E 05	0.4636E 05	0.5226E 04	0.1680E 00	0.2306E 05	0.4974E 00
152	0.1676E 01	0.3890E 05	0.6001E 05	0.6308E 04	0.1622E 00	0.2321E 05	0.3867E 00
153	0.2133E 01	0.4538E 05	0.6350E 05	0.8115E 04	0.1788E 00	0.2128E 05	0.3351E 00
154	0.2719E 01	0.5510E 05	0.7330E 05	0.1037E 05	0.1881E 00	0.2027E 05	0.2765E 00
155	0.3396E 01	0.6483E 05	0.8184E 05	0.1285E 05	0.1982E 00	0.1909E 05	0.2332E 00
156	0.4265E 01	0.7616E 05	0.9069E 05	0.1600E 05	0.2101E 00	0.1785E 05	0.1969E 00
157	0.5357E 01	0.8912E 05	0.1002E 06	0.1983E 05	0.2225E 00	0.1664E 05	0.1660E 00
158	0.3396E-01	0.1079E 04				0.3176E 05	
159	0.4265E-01	0.1297E 04				0.3040E 05	
160	0.5357E-01	0.1457E 04	0.2977E 04	0.1785E 03	0.1225E 00	0.2720E 05	0.9139E 01
161	0.6767E-01	0.1945E 04	0.3499E 04	0.2705E 03	0.1391E 00	0.2874E 05	0.8214E 01
162	0.8491E-01	0.2645E 04	0.4858E 04	0.3603E 03	0.1362E 00	0.3115E 05	0.6412E 01
163	0.1073E 00	0.3348E 04	0.7783E 04	0.3603E 03	0.1076E 00	0.3121E 05	0.4010E 01
164	0.1349E 00	0.4105E 04	0.9356E 04	0.4507E 03	0.1098E 00	0.3042E 05	0.3252E 01
165	0.1698E 01	0.4753E 04	0.1141E 05	0.4956E 03	0.1043E 00	0.2799E 04	0.2454E 00
166	0.2133E 00	0.6042E 04	0.1448E 05	0.6308E 03	0.1044E 00	0.2833E 05	0.1956E 01
167	0.2616E 00	0.7237E 04	0.1211E 05	0.1082E 04	0.1495E 00	0.2766E 05	0.2284E 01
168	0.3396E 00	0.9490E 04	0.2003E 05	0.1125E 04	0.1186E 00	0.2794E 05	0.1395E 01
169	0.4265E 00	0.1145E 05	0.2426E 05	0.1353E 04	0.1181E 00	0.2685E 05	0.1107E 01
170	0.5357E 00	0.1468E 05	0.2992E 05	0.1802E 04	0.1228E 00	0.2740E 05	0.9157E 00
171	0.6767E 00	0.1727E 05	0.3186E 05	0.2343E 04	0.1356E 00	0.2552E 05	0.8011E 00

APPENDIX A CALCULATED DATA OF MARLEX 646 (cont'd)

172	0.8491E 00	0.2096E 05	0.3387E 05	0.3246E 04	0.1549E 00	0.2469E 05	0.7289E 00
173	0.1073E 01	0.2593E 05	0.4344E 05	0.3874E 04	0.1494E 00	0.2417E 05	0.5565E 00
174	0.1349E 01	0.3112E 05	0.4842E 05	0.5004E 04	0.1608E 00	0.2306E 05	0.4763E 00
175	0.1698E 01	0.3673E 05	0.5311E 05	0.6357E 04	0.1731E 00	0.2163E 05	0.4073E 00
176	0.2133E 01	0.4320E 05	0.5920E 05	0.7888E 04	0.1826E 00	0.2026E 05	0.3421E 00
177	0.2695E 01	0.5186E 05	0.6635E 05	0.1014E 05	0.1956E 00	0.1925E 05	0.2901E 00
178	0.3396E 01	0.6049E 05	0.7389E 05	0.1239E 05	0.2049E 00	0.1781E 05	0.2411E 00
179	0.4265E 01	0.6752E 05	0.7232E 05	0.1578E 05	0.2336E 00	0.1583E 05	0.2189E 00
180	0.5357E 01	0.7994E 05	0.8250E 05	0.1938E 05	0.2425E 00	0.1492E 05	0.1809E 00
181	0.6767E 01	0.9291E 05	0.9214E 05	0.2344E 05	0.2523E 00	0.1373E 05	0.1490E 00
182	0.8491E 01	0.1124E 06	0.1095E 06	0.2885E 05	0.2568E 00	0.1323E 05	0.1209E 00
183	0.6767E 01	0.1102E 06	0.1087E 06	0.2795E 05	0.2536E 00	0.1629E 05	0.1498E 00
184	0.8491E 01	0.1318E 06	0.1252E 06	0.3471E 05	0.2634E 00	0.1552E 05	0.1240E 00
185	0.1071E 02	0.1599E 06	0.1577E 06	0.4058E 05	0.2538E 00	0.1492E 05	0.9465E-01
186	0.1349E 02	0.1707E 06	0.1470E 06	0.4959E 05	0.2905E 00	0.1265E 05	0.8604E-01
187	0.1349E 02	0.1772E 06	0.1584E 06	0.4959E 05	0.2799E 00	0.1313E 05	0.8289E-01
188	0.1698E 02	0.2117E 06	0.1338E 06	0.8386E 05	0.3960E 00	0.1247E 05	0.9320E-01
189	0.2133E 02	0.2463E 06	0.2029E 06	0.7484E 05	0.3038E 00	0.1155E 05	0.5693E-01
191	0.3396E 02	0.3457E 06	0.2602E 06	0.1150E 06	0.3325E 00	0.1018E 05	0.3913E-01
192	0.4265E 02	0.3835E 06	0.2634E 06	0.1397E 06	0.3644E 00	0.8992E 04	0.3414E-01
193	0.5357E 02	0.4268E 06	0.2735E 06	0.1666E 06	0.3905E 00	0.7966E 04	0.2913E-01

APPENDIX D   DYNAMIC VISCOSITY OF ALATHON 10
(sample a-IV)

ϕ	$\sin\phi$	$\cot\phi$	f(cps)	$\omega = 2\pi f$	$\eta_F \times 10^{-4}$	$\eta' \times 10^{-4} = \sin^2\phi\, \eta_F \times 10^{-4}$	$\omega\eta'' \times 10^{-4} = \omega \cot\phi\, \eta'$
0.6729	.623	1.255	2.38	14.94	1.710	0.703	13.90
0.6804	.629	1.235	2.38	14.94	1.694	0.672	12.40
0.7556	.693	1.040	0.952	5.97	2.543	1.22	7.60
0.8510	.752	0.8765	0.379	2.38	3.641	2.05	4.26
0.9208	.795	0.763	0.151	0.941	5.03	3.18	2.28
0.9538	.815	0.7111	0.06	0.377	7.177	4.77	1.61
0.9810	.831	0.669	0.0238	0.1495	0.864	0.596	0.0597
1.0390	.862	0.588	0.00948	0.0595	13.70	10.20	0.360
0.6280	.588	1.380	6.0	37.7	1.032	0.375	19.20
0.6490	.604	1.320	3.8	23.8	1.45	0.530	16.70
0.7000	.645	1.185	2.4	14.95	1.718	0.716	12.70
0.7370	.673	1.099	1.512	9.42	2.152	0.975	10.10
0.7764	.701	1.017	0.952	5.97	2.605	1.28	7.42
0.8170	.729	0.939	0.6	3.77	3.102	1.65	5.85
0.8400	.745	0.895	0.38	2.38	3.692	2.05	4.37
0.8870	.775	0.816	0.24	1.495	4.320	2.59	3.16
0.9120	.790	0.776	0.1512	0.941	6.488	4.06	2.95
0.9420	.809	0.727	0.0952	0.597	6.156	4.03	1.75
0.9820	.832	0.667	0.060	0.377	6.867	4.75	1.20
0.9550	.818	0.703	0.038	0.238	8.446	5.66	0.948
0.9550	.818	0.703	0.038	0.238	8.572	5.73	0.94
1.091	.858	0.598	0.024	0.1495	9.412	6.94	0.62

APPENDIX C DYNAMIC VISCOSITY OF CELANESE
(sample c-V)

ϕ	$\sin\phi$	$\cot\phi$	f	$\omega=2\pi f$	$\eta_F\times10^{-4}$	$\eta'\times10^{-4}$	$\omega\eta''\times10^{-4}$
0.627	0.587	1.38	6.0	37.7	3.674	1.26	69.4
0.632	0.591	1.36	3.79	23.8	4.828	1.68	54.5
0.675	0.626	1.24	2.38	14.95	5.947	2.32	43.0
0.696	0.641	1.19	1.50	9.41	7.305	2.93	34.5
0.714	0.655	1.15	0.948	5.95	9.424	4.04	27.7
0.747	0.679	1.07	0.60	3.77	11.68	5.34	21.7
0.753	0.684	1.06	0.379	2.38	14.97	7.02	17.7
0.748	0.680	1.07	0.238	1.495	19.13	8.83	14.1
0.759	0.688	1.05	0.151	0.941	23.66	11.22	11.1
0.752	0.683	1.07	0.0948	0.595	31.35	14.63	9.25
0.754	0.685	1.06	0.060	0.377	38.31	17.00	7.13
0.753	0.684	1.07	0.0379	0.238	51.22	23.90	6.09
0.738	0.673	1.09	0.0238	0.1495	70.67	32.10	5.23
0.747	0.680	1.08	0.0151	0.0941	92.07	42.50	4.32
0.716	0.656	1.13	0.00948	0.0595	123.4	53.20	3.64
0.689	0.636	1.21	0.0060	0.0377	182.9	74.00	3.48
0.737	0.673	1.09	0.00379	0.0238	235.6	107.0	2.77
0.653	0.607	1.30	0.60	3.77	15.39	5.67	27.70
0.554	0.527	1.61	6.0	37.7	4.499	1.83	74.7
0.532	0.508	1.70	9.48	59.5	3.598	0.93	94.1
0.531	0.506	1.70	15.10	94.1	2.576	0.66	142.0

APPENDIX D PROGRAM DNCE (MARLEX 646 DATA CALCULATION PROGRAM) AND EXPERIMENTAL DATA

```
// JOB W.S.LEE/CC78
      PROGRAM DNCE
      MEM=0
    1 READ 10,NO,SEC,MEMP,DT,DN
   10 FORMAT(I4,F11.2,I7,2F12.2)
      X=90./SEC
      P=2593.*DT
      Y=P/X
      IF(DN-0.)5,6,5
    6 PRINT 50,NO,X,P,Y
   50 FORMAT(/2XI4,2F14.4,42XF14.4)
      GO TO 100
    5 P=3110.*DT**2/DN
      SN=541.*DN
      RE=SN/P
      T=Y/R
      IF(MEM-MEMP)2,3,2
    2 PRINT 20,MEMP
   20 FORMAT(///11H MARLEX 646,5X12HTEMPERATURE=,I4)
      MEM=MEMP
      PRINT 30
   30 FORMAT(//8H EXP. NO,2X10HSHEAR RATE,2X12HSHEAR STRESS,
     12X10HELASTICITY,2X13HNORMAL STRESS,6X4HN/P,
     27X9HVISCOSITY,10X1HT)
    3 PRINT 40,NO,X,P,R,SN,RE,Y,T
   40 FORMAT(/2XI4,7F14.4)
  100 IF(193-NO)1,70,1
   70 STOP
      END
// EXEC
   65         10.6        200         30.              36.66
   65         10.6        200         30.              43.33
   65         10.6        200         31.66            44.16
   66         10.6        200         33.33            60.
   67          8.4        200         38.33            50.
   68          8.4        200         35.66            43.33
   69          6.67       200         44.16            56.66
   70          6.67       200         44.16            55.
   71          5.33       200         51.66            75.
   72          5.33       200         50.83            71.65
   73          4.22       200         60.              80.
   74          4.22       200         60.             103.33
   75          3.34       200         70.             103.33
   76          3.34       200         73.33           106.66
   77          2.65       200         85.             141.66
   78          2.65       200         85.83           145.83
   79          2.65       200         98.33           187.5
   80          2.65       200        105.             145.8
   81          2.65       200        100.8            225.
   82          1.68       200        112.5            242.77
   83          1.68       200        110.4            225.
   84         13.3        200         26.25            37.91
   85         16.8        200         21.46            28.08
   86         21.1        200         18.54            19.91
   87         26.5        200         15.21            17.
   88         33.4        200         12.5             10.41
   89         42.2        200         10.41             8.33
   90         53.         200          9.33             5.33
```

APPENDIX D PROGRAM DNCE AND EXP'T DATA (cont'd)

91	66.7	200	7.75	7.33
92	83.9	200	6.916	7.66
93	10.6	200	5.16	4.
94	13.3	200	4.33	3.166
95	16.8	200	3.5	3.
96	211.	200	2.91	2.
97	269.	200	2.08	1.83
98	334.	200	1.66	1.
99	422.	200	1.66	1.12
100	530.	200	1.25	1.33
101	667.	200	1.166	1.
104	839.	180	.916	.33
102	1330.	180	.50	0.
103	1060.	180	.85	.0
105	667.	180	1.291	.66
106	530.	180	1.333	.83
107	422.	180	1.79	1.
108	334.	180	2.33	1.50
109	265.	180	2.66	1.66
110	211.	180	3.	2.
111	168.	180	3.916	2.666
112	133.	180	4.666	3.333
113	106.	180	5.83	4.166
114	83.9	180	7.50	5.66
115	66.7	180	9.	7.
116	53.	180	10.66	9.
117	42.2	180	13.	11.16
118	33.4	180	15.16	14.66
119	53.	180	10.62	9.
120	42.2	180	12.91	11.16
121	33.4	180	15.83	14.58
122	26.5	180	19.16	19.16
123	21.1	180	22.5	22.5
124	16.8	180	26.66	27.91
125	13.3	180	29.16	30.41
126	16.8	180	26.25	28.16
127	13.3	180	31.25	35.41
128	10.6	180	36.66	43.33
129	8.4	180	45.	55.
130	6.67	180	55.	70.
131	5.3	180	65.	88.33
132	4.22	180	80.	118.
133	3.34	180	95.	130.
134	2.65	180	100.	165.
135	2.11	180	120.1	212.5
136	1.68	180	130.6	.0
138	1330.	160	.833	.333
137	1680.	160	.75	.0
139	1060.	160	1.083	.333
140	839.	160	1.25	.5
141	667.	160	1.583	.666
142	530.	160	2.	.0
143	422.	160	2.416	1.25

APPENDIX D PROGRAM DNCE A'D EXP'T DATA (cont'd)

144	324.	160	3.	1.5
145	265.	160	3.75	2.33
146	211.	160	4.66	2.66
147	168.	160	5.66	4.
148	133.	160	6.66	4.83
149	106.	160	8.33	5.83
150	83.9	160	10.	7.5
151	66.7	160	12.	9.66
152	53.7	160	15.	11.66
153	42.20	160	17.5	15.
154	33.1	160	21.25	19.16
155	26.5	160	25.	23.75
156	21.1	160	29.37	29.58
157	16.8	160	34.37	36.66
158	2650.	160	.416	[illegible]
159	2110.	160	.5	[illegible]
160	1680.00	160	.562	.33
161	1330.	160	.75	.50
162	1060.	160	1.02	.666
163	839.	160	1.291	.666
164	667.	160	1.583	.833
165	532.	160	1.833	.916
166	422.	160	2.33	1.166
167	344.	160	2.791	2.
168	265.0	160	3.66	2.08
169	211.0	160	4.416	2.50
170	168.	160	5.66	3.33
171	133.	160	6.66	4.33
172	106.	160	8.083	6.
173	83.9	160	10.	7.16
174	66.7	160	12.	9.25
175	53.	160	14.166	11.75
176	42.2	160	16.66	14.58
177	33.4	160	20.	18.75
178	26.5	160	23.33	22.91
179	21.1	160	26.04	29.16
180	16.8	160	30.83	35.83
181	13.3	160	35.83	43.33
182	10.6	160	43.33	53.33
183	13.3	160	42.50	51.66
184	10.6	160	50.83	64.16
185	8.4	160	61.66	75.
186	6.67	160	65.83	91.66
187	6.67	160	68.33	91.66
188	5.30	160	81.66	155.
189	4.22	160	95.	133.33
191	2.65	160	133.33	212.5
192	2.11	160	147.91	258.3
193	1.68	160	164.58	308.

APPENDIX E PROGRAM MAA (VISCOSITY MASTER CURVE OF SPRIGGS MODEL)

```
 1 READ 2,A
 2 FORMAT(F3.1)
   PRINT 2,A
 8 E=1.
   R1=E**(-A)
 5 E=E&1.
   R2=R1&E**(-A)
   R=ABS((R2-R1)/R2)
   IF(R-.005)3,3,11
11 R1=R2
   GO TO 5
 3 DO 12 N=1,6
   DO 12 I=1,9,2
   D=I
   CTX=D*10.**(N-2)
   F=1.
   S1=1./(F**A&(CTX**2)/(F**A))
 4 F=F&1.
   S2=S1&1./(F**A&(CTX**2)/(F**A))
   S=ABS(S1/S2)
   IF(S-.005)10,10,9
 9 S1=S2
   GO TO 4
10 Y=S2/R2
   PRINT 15, CTX,Y,F,E
15 FORMAT(5x2E9.3,5X2F5.1)
12 CONTINUE
   END
```

APPENDIX F PROGRAM MAB (NORMAL STRESS DIFFERENCE MASTER CURVE OF SPRIGGS MODEL)

```
 1 READ,A
   PUNCH,A
 8 E=1.
   R1=E**(-A)
 5 E=E+1.
   R2=R1+E**(-A)
   R=ABS((R2-R1)/R2)
   IF(R-0.01)3,3,11
11 R1=R2
   GO TO 5
 3 DO 12 N=2,4
   DO 12 I=2,10,2
   D=I
   CTX=D*(1.E-4)*10.**N
   F=1.
   S1=1./(F**(A+A)+CTX**2)
 4 F=F+1.
   S2=S1+1./(F**(A+A)+CTX**2)
   S=ABS((S2-S1)/S2)
   IF(S-0.01)10,10,9
 9 S1=S2
   GO TO 4
10 Y=CTX**2*(S2+S")/R2
   PUNCH,CTX,Y,F,E
12 CONTINUE
   END
```

APPENDIX G PROGRAM DAA (SPRIGGS MODEL PREDICTION FOR APPARENT VISCOSITY)

```
    1  READ,A
       PUNCH,A
    8  E=1.
       R1=E**(-A)
    5  E=E+1.
       R2=R1+E**(-A)
       R=ABS((R2-R1)/R2)
       IF(R-0.01)3,3,11
   11  R1=R2
       GO TO 5
    3  DO 12 N=2,6
       DO 12 I=2,10,2
       D=I
       X=D*(1.E-4)*10.**N
       CT=1.1 9.6
       CTX=CT*X
       F=1.
       S1=F**A/(F**(A+A)+CTX**2)
    4  F=F+1.0
       S2=S1+F**A/(F**(A+A)+CTX**2)
       S=ABS((S2-S1)/S2)
       IF(S-0.01)10,10,9
    9  S1=S2
       GO TO 4
   10  Y=S2/R2
       Z=Y*1600000.
       PUNCH,X,Z,F,E
   12  CONTINUE
       END
  1.5000000
```

APPENDIX H PROGRAM DAB (SPRIGGS MODEL PREDICTION FOR NORMAL STRESS DIFFERENCE)

```
    1 READ,A
      PUNCH,A
    8 E=1.
      R1=E**(-A)
    5 E=E+1.
      R2=R1+E**(-A)
      R=ABS((R2-R1)/R2)
      IF(R-0.01)3,3,11
   11 R1=R2
      GO TO 5
    3 DO 12 N=2,4
      DO 12 I=2,10,2
      D=I
      X=D*(1.E-4)*10.**N
      CT=8.4
      CTX=CT*X
      F=1.
      S1=1./(F**(A+A)+CTX**2)
    4 F=F+1.0
      S2=S1+1./(F**(A+A)+CTX**2)
      S=ABS((S2-S1)/S2)
      IF(S-0.01)10,10,9
    9 S1=S2
      GO TO 4
   10 Y=CTX**2*(S2+S2)/R2
      Z=Y*3.9E5/(8.4*.88)
      PUNCH,X,Z,F,E
   12 CONTINUE
      END
      1.5
```

APPENDIX I PROGRAM MBA (VISCOSITY MASTER CURVE OF CAREAU MODEL)

```
      PROGRAM MBA
C   MASTER CURVES OF APPARENT VISCOSITY
  100 READ 1,A,N
    1 FORMAT%F3.1,I4<
      IF%N-50<20,30,20
   20 PRINT 50,A,N
   50 FORMAT%//5X4HA # ,F3.1,5X4HN # ,I2/<
      PRINT 60
   60 FORMAT%10X38HREDUSED SHEAR RATE   REDUSED VISCOSITY<
     0Z#1.&2.**%-A<&3.**%-A<&4.**%-A<&5.**%-A<&6.**%-A<&7.**%-A<
     1&8.**%-A<&9.**%-A<&1./%%A-1.<*10.**%A-1.<<&1./%2.*10.**%A<<
      DO 11 I#1,6
      DO 11 J#2,10,2
      D#J
      X#D*10.**%I-3<
      IF%N-12<16,15,16
   15 X#X*A
   16 X2#%2.**A*X<**2
      Y2#0.
      IF%X2-49.<3,3,4
    3 DO 5 K#2,N
      E#K
      Y1#E**%-A</%E**%2.*A<&X2<
    5 Y2#Y2&Y1
      Y#1.-%X2/%Z-1.<<*Y2
      IF%N-12<17,18,17
   18 Y#Y*126940.
   17 GO TO 10
    40Y#%3.142*X2**%%1.-A</%2.*A<</%2.*A*SIN%3.142*%1.&A</%2.*A<
     1-1./%%A&1.<*X2<-%1.&A/6.</%2.*%1.&X2<<</%Z-1.<
   10 PRINT 12,X,Y
   12 FORMAT%15XE8.2,10XE8.2<
   11 CONTINUE
      GO TO 100
   30 STOP
      END
```

APPENDIX J   PROGRAM MBB (NORMAL STRESS DIFFERENCE MASTER CURVE OF CAREAU MODEL)

```
      PROGRAM MBB
  100 READ 1,A,N,YO,T1
    1 FORMAT(F3.1,I2,F6.1,F5.2)
      IF(N-50)20,20,20
   20 PRINT 50,A,YO,T1,N
   50 FORMAT(//5X4HA = ,F3.1,5X5HYO = ,F8.2,5X5HT1 = ,F4.1,5X4HN = ,I2/)
     0Z=1.+2.**(-A)+3.**(-A)+4.**(-A)+5.**(-A)+6.**(-A)+7.**(-A)
     1+8.**(-A)+9.**(-A)+1./((A-1.)*10.**(A-1.))+1./(2.*10.**(A))
   22 DO 11 M=1,10
      G=M
      R=.43+.07*G
   44 B=A*R
      PRINT 55,B,R
   55 FORMAT(10X4HB = ,F4.2,5X4HR = ,F4.2)
      PRINT 60
   60 FORMAT(/14X29HSHEAR RATE        NORMAL STRESS)
      C=-A-B
     0Z2=1.+2.**C+3.**C+4.**C+5.**C+6.**C+7.**C
     1+8.**C+9.**C+1./((-C-1.)*10.**(-C-1.))+1./(2.*10.**(-C))
      DO 11 I=1,4
      DO 11 J=2,10,2
      D=J
      X=D*10.**(I-3)
      X2=(2.**A*T1*X)**2
      IF(X2-100.)2,2,4
    2 Y2=0.
      DO 25 K=2,N
      E=K
      Y1=E**C/(E**(2.*A)+X2)
    5 Y2=Y2+Y1
   25 CONTINUE
      Y=YO*2.**(B+1.)*(Z2-1.-X2*Y2)/(Z-1.)
      Y=Y*X**2
   17 GO TO 10
    40Y=(YO*2.**(B+1.)/(Z-1.))*((3.142*X2**((1.+C)*.5/A))/(2.*A*SIN((1.
     1+A-B)*3.142/(2.*A)))-1./((A-B+1.)*X2)-(1.+(A-B)/6.)/(2.*(1.+X2)))
      Y=Y*(X**2)
   10 PRINT 12,X,Y
   12 FORMAT(15XF8.2,10XF8.2)
   11 CONTINUE
      GO TO 100
   30 STOP
      END
// EXEC
 1.4153.0E 4  1.25
 1.4152.2E 4  1.00
 1.4151.7E 4  0.80
 1.8 73.9E 5  4.80
 2.2 71.6E 655.00
 1.0501.0E 1  1.00
```

APPENDIX K PROGRAM DBA (CAREAU MODEL PREDICTION FOR APPARENT VISCOSITY)

```
      PROGRAM DBA
  100 READ 1,A,N,YO,T1
    1 FORMAT%F3.1,I2,E6.1,F4.1<
      IF%N-50<20,30,20
   20 PRINT 50,A,YO,T1,N
   50 FORMAT%//5X4HA # ,F3.1,5X5HYO # ,E8.2,5X5HT1 # ,F4.1,5X4HN # ,I2/
      PRINT 60
   60 FORMAT%14X27HSHEAR RATE         VISCOSITY<
     0Z#1.&2.**%-A<&3.**%-A<&4.**%-A<&5.**%-A<&6.**%-A<&7.**%-A<
     1&8.**%-A<&9.**%-A<&1./%%A-1.<*10.**%A-1.<<&1./%2.*10.**%A<<
      DO 11 I#2,7
      DO 11 J#2,10,2
      D#J
      X#D*10.**%I-5<
      XT#X*T1
   16 X2#%2.**A*XT<**2
      Y2#0.
      IF%X2-49.<3,3,4
    3 DO 5 K#2,N
      E#K
      Y1#E**%-A</%E**%2.*A<&X2<
    5 Y2#Y2&Y1
      Y#1.-%X2/%Z-1.<<*Y2
      Y#Y*YO
   17 GO TO 10
    40Y#%3.142*X2**%%1.-A</%2.*A<</%2.*A*SIN%3.142*%1.&A</%2.*A<<<
     1-1./%%A&1.<*X2<-%1.&A/6.</%2.*%1.&X2<<</%Z-1.<
      Y#Y*YO
   10 PRINT 12,X,Y
   12 FORMAT%15XE8.2,10XE8.2<
   11 CONTINUE
      GO TO 100
   30 STOP
      END
```

APPENDIX L PROGRAM DBB(CAREAU MODEL PREDICTION FOR NORMAL STRESS DIFFERENCE)

```
      PROGRAM DBB
  100 READ 1,A,B,N,Y0,T1,T2
    1 FORMAT(2F4.2,I3,F6.1,2F5.2)
      IF(N-50)20,30,20
   20 PRINT 50,A,B,Y0,T1,T2,N
   50 FORMAT(//5X4HA = ,F3.1,5X4HB = ,F3.1,5X5HY0 = ,F8.2,5X5HT1 = ,
     1F4.1,5X5HT2 = ,F4.1,5X4HN = ,I3)
      Z=1.+2.**(-A)+3.**(-A)+4.**(-A)+5.**(-A)+6.**(-A)+7.**(-A)
     1+8.**(-A)+9.**(-A)+1./((A-1.)*10.**(A-1.))+1./(2.*10.**(A))
      PRINT 60
   60 FORMAT(/14X29HSHEAR RATE          NORMAL STRESS)
      C=-A-B
      Z2=1.+2.**C+3.**C+4.**C+5.**C+6.**C+7.**C
     1+8.**C+9.**C+1./((-C-1.)*10.**(-C-1.))+1./(2.*10.**(-C))
      DO 11 I=1,4
      DO 11 J=2,10,2
      D=J
      X=D*10.**(I-3)
      X2=(2.**A*T1*X)**2
      IF(X2-100.)2,2,4
    2 Y2=0.
    3 DO 25 K=2,N
      E=K
      Y1=E**C/(E**(2.*A)+X2)
    5 Y2=Y2+Y1
   25 CONTINUE
      Y=Y0*2.**(B+1.)*(Z2-1.-X2*Y2)/(Z-1.)
      Y=Y*X**2
   17 GO TO 10
    4 Y=(Y0*2.**(B+1.)/(Z-1.))*((3.142*X2**((1.+C)*.5/A))/(2.*A*SIN((1.
     1+A-B)*3.142/(2.*A)))-1./((A-B+1.)*X2)-(1.+(A-B)/6.)/(2.*(1.+X2)))
      Y=Y*(X**2)
      Y=Y*B
   10 PRINT 12,X,Y
   12 FORMAT(15XE8.2,10XE8.2)
   11 CONTINUE
      GO TO 100
   30 STOP
      END
// EXEC
```

APPENDIX M PROGRAM MCA (VISCOSITY EMPIRICAL EQUATION MASTER CURVE)

```
      DO 11 M=4,12
      ABM=M
      AB=ABM/10.
      DO 11 N=12,44,4
      AN=N
A     A=AN/10.
      B=AB/A
      PRINT 1,AB,A,B
    1 FORMAT(//5XF3.1,5XF3.1,5XF3.1//)
      PRINT 2
    2 FORMAT(5X41HREDUCED SHEAR STRESS     REDUCED SHEAR RATE)
      DO 11 I=1,3
      DO 11 J=2,10
      D=J
      Y=(10.-1.*(D-1.))/(10.**I)
      X=(10.**((LOG(Y))/(Y-A))-1.)**(1./B)
      PRINT 40,Y,X
   40 FORMAT(10XE8.2,15E8.2)
   11 CONTINUE
      STOP
      END
```

APPENDIX N PROGRAM DDB (EMPIRICAL NORMAL STRESS EQUATION PREDICTION)

```
C EMPIRICAL EQUATION, LOG(Y)=A*X**C+B ,
   10. READ 1,X1,Y1,X2,Y2,X3,Y3
       GY1=(LOG(Y1))/2.303
       GY2=(LOG(Y2))/2.303
       GY3=(LOG(Y3))/2.303
       T1=(GY1-GY3)/(GY1-GY2)
       T=T1-(T1**2-4.*(GY2-GY3)/(GY1-GY2))**.5
       C=(LOG(.5*T))/2.303
       A=(GY1-GY2)/(X1**C-X2**C)
       B=GY1-A*X1**C
 PUNCH,A,B,C
       DO 10 I=1,3
       DO 10 J=2,10,2
       B=J
       X=B*10.**(I-3)
       Y=10.**(A*X**C+B)
 PUNCH,Y,Y
    10 CONTINUE
       STOP
 98     END
 0.05 011500.  0.50 130000.  5.00 630000.
```

A	B	C
-1.7245029	7.0755776	-.18655333

X	Y
2.0000000E-02	5146.3521
4.0000000E-02	8546.3783
6.0000000E-02	14491.388
8.0000000E-02	20564.426
.10000000	26653.373
.20000000	55868.779
.40000000	107053.17
.60000000	150886.62
.80000000	189570.82
1.0000000	224426.60
2.0000000	362239.02
4.0000000	554699.05
6.0000000	632521.13
8.0000000	824577.03
10.000000	887003.40

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