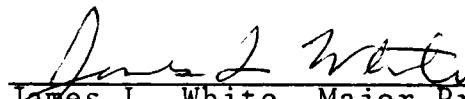
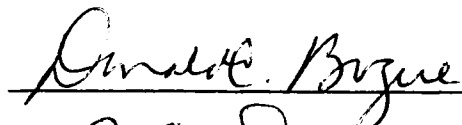
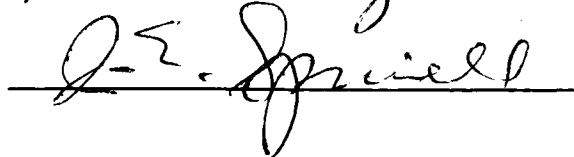


To the Graduate Council:

I am submitting herewith a thesis written by Yoshiyuki Suetsugu entitled "Basic Study of the Rheological Properties of Particle Filled Polymer Melts." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


James L. White, Major Professor

We have read this thesis and
recommend its acceptance:

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Vice Chancellor
Graduate Studies and Research

BASIC STUDY OF THE RHEOLOGICAL PROPERTIES
OF PARTICLE FILLED POLYMER MELTS

A Thesis

Presented for the
Master of Science

Degree

The University of Tennessee, Knoxville

Yoshiyuki Suetsugu

August 1982

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ABSTRACT

Basic rheological studies in steady shear and elongational flow were carried out for small particle filled molten state polymer compounds.

Polystyrene has been chosen as a matrix polymer. Polystyrene is one of the most widely used polymers and exhibits little thermal and mechanical degradation. Calcium carbonate particles having average particle diameters of 17 μm to 0.07 μm were used as fillers both in the untreated and stearic acid surface treated states. Carbon black with basic particle diameters of 0.045 μm was also used for comparison.

The influences of particle size, surface treatment and loading level were discussed. The yield stresses of these systems were estimated graphically both in steady shear and elongational flow experiments. It was found that the yield stresses of the systems decrease roughly inversely with increasing average particle diameter. The stearic acid surface coating was observed to substantially reduce the yield stress and viscosity in both shear and elongational flow. The addition of untreated calcium carbonate and carbon black particles makes the shear stress or viscosity overshoot phenomenon more striking in the transient state of steady shear flow. Stearic acid surface coating reduces the overshoot phenomenon.

A phenomenological plastic viscoelastic constitutive equation was applied to filled systems with time dependent yield values. Theoretical predictions give satisfactory agreement with experimental data. Comparison was made for both transient and steady state shear and elongational flow.

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CHAPTER I

INTRODUCTION

In the polymer industry, reinforcement with small particles, such as carbon black, calcium carbonate, talc, etc., is often used to improve the properties and performance of polymeric materials.

It is well known that the addition of fillers to polymeric phases changes its rheological properties drastically in the molten state as well as in solid state. Many investigations have appeared which characterize the rheological behavior of small particle filled polymer melts. However, most earlier investigations are limited to the rheological effects of volume loading level of filler in steady shear flow experiments. In order to understand the rheological effects of particle size and surface characteristics of filler, more systematic studies are required. It is one of the purposes of the present work to fill this need. The earlier researches were mainly limited to studies of rheological behavior at the steady state. Although the transient behavior of particle filled Newtonian fluid has been studied widely, that of particle filled polymer melt was not investigated. This present study includes the characterization of transient behavior of filled systems.

Phenomenological models for particle filled systems have been developed by earlier investigators from these laboratories. We have developed new phenomenological models for filled systems which include yield values with time-deformation rate dependent characteristics. Such yield values allow the prediction of thixotropic phenomena found in time dependent experiments.

CHAPTER II

LITERATURE SURVEY

A. Experimental Studies on Rheological Properties of Suspension

A.1 Suspensions of Particles in Newtonian Fluids

Unique rheological properties of suspensions which clearly differ from conventional Newtonian fluids were first reported by Reynolds (134) in 1885. Reynolds found that rigid particle suspensions in water increased their volume (volumetric dilatation) during shearing deformation. Reynolds introduced the term "dilatancy" to represent this newly observed phenomenon.

Bingham and Green (12) and Bingham (11) reported yield stress in shear flow of paints. Bingham introduced the term "plasticity" to represent this behavior. Following Bingham (11) the term "Bingham plastic" implies the constitutive equation

$$\sigma_{12} = Y + \eta_B \dot{\gamma} \quad [\text{II.1}]$$

Similar phenomena were observed on other concentrated suspensions in succeeding years. However, the authors in a later period (32, 36, 124) showed that Bingham's attempt to maintain linearity was not generally true for non-Newtonian systems. The phenomenon of a viscosity

decreasing with shear rate has been called "pseudo-plasticity" by Williamson (180).

Freundlich (40, 41) found that the apparent viscosity of certain colloidal systems decreases with an increasing extent of deformation of initially virgin materials, and the apparent viscosity recovers to its initial value when the deformation is discontinued. Freundlich called this time dependent phenomenon "thixotropy."

Later Freundlich and Juliusberger (43) found what seemed an opposite phenomenon in other colloidal systems, that is, the apparent viscosity increases with an increasing extent of deformation. They denoted this phenomenon "rheopexy." Both of these phenomena, thixotropy and rheopexy, were dependent upon the history of the deformation.

Freundlich and Roder (44) associated Reynold's dilatancy (volumetric dilatation) to their observation of rheopexy. They sometimes seemed to observe a steady state viscosity which increased with shear rate. Freundlich et al. (40, 41, 43, 44) have studied the relationships among thixotropy, rheopexy and dilatancy and their occurrences. They considered dilatancy is the opposite of thixotropy and differs from rheopexy in which the equilibrium state of the former is a fluid and the latter a gel. Other aspects of these phenomena have been described by Green (53) and Reiner (130, 131).

In the 1950's, extensive studies of the viscosity of latices investigating particle size, volume fraction and shear rate dependence were carried out by Maron and Krieger and their coworkers (96, 97, 98) and Mooney (110). Mooney developed a useful semiempirical equation for the influence of volume fraction on viscosity. Other investigators studied suspensions of inorganic particles confirming the existence of yield values (129). Metzner and Whitlock (104) experimentally compared the occurrence of the Reynolds' and Freundlich-Roder's dilatant effects and reported that both dilatant effects do not necessarily occur with the same materials. In systems which show both phenomena, the Reynolds' effect occurs at lower shear stresses. It would seem that most authors in recent years have defined dilatancy in terms of the Freundlich-Roder's dilatant effect despite the original meaning of the term "dilation."

In 1959, Casson (23) proposed a viscosity equation for suspensions exhibiting yield stresses of the form

$$\sigma_{12}^{1/2} = Y^{1/2} + \eta_{\infty} \dot{\gamma}^{1/2} \quad [II.2]$$

where η_{∞} is a constant coefficient, and Y is the yield stress. A plot of $\sigma_{12}^{1/2}$ against $\dot{\gamma}^{1/2}$ gives $Y^{1/2}$ as an intercept.

Fryling (45) pointed out that the addition and removal of salts from rubber latices made enormous differences in viscosity resulting from the concentration of ions.

Brodnyan et al. (18, 19) reported that the addition of an electrolyte diminishes non-Newtonian properties of latices, and the viscosity of suspensions may obey Mooney's equation (110) independent of particle size, in the Newtonian region. Thomas (152), in 1965, summarized experimental data for viscosity as a function of volume fraction. He noted that the deviation mainly resulted from particle size distribution, and that colloidal forces are dominant in systems which have small particles with diameters less than 1 to 10 μm . Thomas pointed out that, in such cases, the viscosity increases with decreasing particle size and also depends on the shear rate.

In the 1970's, several important papers on concentrated suspensions have appeared. Hoffman (67, 68) investigated the flow of suspension of monodisperse polyvinyl chloride spheres in diotyl phthalate and suspensions of poly(styrene-coacrylonitrile) spheres in ethylene glycol. The particle sizes of polymeric sphere were about 1 μm or less. He investigated the structure of polymeric spheres in simple shear flow with the diffraction of light. He reported that the discontinuous viscosity behavior which occurs at solid concentrations above 0.50 is caused by a flow instability in which surfaces of spheres, packed in two-dimensional hexagonal packing at low shear rates, break up into less ordered arrays.

The effect of Brownian motion on the viscosity of concentrated suspensions has been pointed out by Krieger (84) in 1972 from experimental studies on latices of monodisperse particles without electroviscous effects. Krieger and Equiluz (85) reported the same results as Fryling (45) and Brodnyan (18, 19) about electroviscous effects on the non-Newtonian character of latices. They reported that latices show yield stresses which increase with increasing particle concentration and with decreasing electrolyte concentration.

Umeya and his coworkers (79, 156, 163, 164, 165), in the 1970's, have studied extensively the rheological behavior of suspensions of various particles in Newtonian fluids. They reported that the dilatant behavior was observed in a high shear rate range and thixotropic and rheopectic behavior were observed in a low shear rate range. More recently, they investigated the effect of flocculation on dilatant flow of aqueous suspensions of titanium dioxide powders with different particle sizes and with varying amounts of dispersing agent (161). They pointed out that the onset of dilatancy was observed at higher shear rates and the extent of dilatancy decreased with an increase in dispersion stability and varied with the amount of dispersing agent. A suspension with large particles showed dilatant behavior similar to that of the stable suspension.

In 1980, Gadala-Maria and Acrivos (47) studied suspensions of polystyrene sphere in silicone oils. They reported when the volume fraction of particles is larger than 0.3, the shear stress showed a memory for direction of the previous shear deformation. They argued that highly concentrated two-phase systems cannot be modeled as isotropic fluids having a scalar effective viscosity.

Lapasin et al. (86) investigated zinc dust suspensions in lithium-sodium silicate solution systems employing zinc dusts which have different mean particle diameters and different particle diameter distributions. Summarizing their experimental data with Bingham's equation, they found that yield stresses increase with decreasing particle size. Both yield stresses and ultimate viscosities (in Bingham's equation) increase with increasing periods of time after mixing.

Bullivant and Jones (20) studied the effect of concentration of china clay suspensions on the rheological properties. They reported that with increasing concentration, an initial shear thinning region is followed by a shear thickening one.

A.2 Suspensions of Particles in Polymer Solutions

In the 1970's, Matsumoto, Onogi et al. (99, 101, 120, 121) and Umeya et al. (158, 159, 160) investigated various kinds of suspensions (carbon black, crosslinked polymer beads, glass beads, clay, etc.) in polymer solutions. They

pointed out the existence of yield stresses in both dynamic measurements and in steady shear flow. In other words, the storage modulus shows a second plateau at low frequencies below the so-called rubbery region and the dynamic viscosity becomes infinite at finite shear stress levels. They reported that yield stresses increase with increasing particle concentration, with decreasing particle size and with increasing polymer concentration in medium. In these cases, the systems become more thixotropic. In addition, they studied the temperature dependence of the yield stress. It was also found that dynamic properties have a strong amplitude dependency, decreasing at larger amplitudes. They attempted to interpret small strain behavior in terms of linear viscoelasticity. Onogi et al. (100), studying a suspension of styrene-divinylbenzene copolymer particles in a polystyrene solution at volume contents of 0.1 to 0.3, an average particle diameter of 0.12 μm , found there was no yield stress. Onogi et al. consider the system to form a pseudo-gel which has a higher maximum relaxation time causing a long memory, but it still flows at very low stresses.

Nicodemo and Nicolais (114, 115) also investigated the suspensions of particles in polymer solutions. They considered that increasing the tendency of viscosity with decreasing shear rate to be due to aggregate formation of the particles in the suspension. This effect is indistinct in glass bead suspensions.

Hutton and his coworkers (10, 70, 71) reported that greases (frequently carbon black in polymer solutions) possess yield stresses. They mentioned problems in normal stress measurement in systems with yield stresses because of interactions between the instrument and the yield stress property, as well as shear fracture of samples. The zero of normal stress measurement was uncertain to within an amount proportional to the yield stress and normal stress measurements had less accuracy. They discussed the procedures for minimizing inaccuracies.

Matsumoto et al. (121) have modified Casson's equation for non-Newtonian media,

$$\sigma_{12}^{1/2} = Y^{1/2} + \eta_{\infty} \left[\frac{\eta_a}{\eta_0} \dot{\gamma} \right]^{1/2} \quad [II.3]$$

where η_a and η_0 are apparent and zero shear viscosity respectively. They obtained yield stresses of small particle suspensions in polymer solutions with the above equation.

In 1980, Umeya and Otsubo (166) studied the time-dependent behavior of a suspension of 1 μm glass beads in a polystyrene solution. They applied a pulse strain of the cosine type and analyzed the resultant stress with Fourier transformation. They pointed out that the imaginary part of a Fourier transformation could be employed as a parameter which characterizes structure. They noted that

the raised cosine pulse method provides useful information on the relaxation process of time-dependent materials which could not be obtained by a conventional dynamic method.

Shalopalkina et al. (140) studied TiO_2 filled saturated polyester resin with various solvents. Their system had a larger content of polymer in solvent (70%) in comparison with Umeya, Onogi et al. (20%). They observed remarkable stress overshoot phenomenon and yield stresses. They compared two different types of shear histories: in one case, structure was broken completely before each experiment; in another case, structure was broken completely only before the first experiment. They concluded that beginning with a nearly complete dispersion of the suspension, a thixotropic structure gradually forms in the suspension. They reported that the solvent type has a comparatively small effect on the structure of the system.

Fiber filled polymer solution systems have been investigated by Mikami, Matsumoto and Onogi (106, 122). They reported that suspensions of powdered glass fibers and titanate fibers in polystyrene solutions possess yield stresses, and suspensions of titanate fibers have a tendency to show remarkable rheopectic behavior at low shear rates after being sheared at high shear rates (122).

A.3 Rigid Particle Filled Polymer Melts

The Rheological properties of rigid particle filled polymer melts have been extensively investigated by many

authors. Carbon black, calcium carbonate, titanium dioxide, glass bead and glass fiber have been generally used as the fillers.

It has been well recognized that the loading of rigid particles into polymer melts increases the shear viscosity. Many papers report that small rigid particles increase the viscosity of filled systems to the greatest extent at the low shear rate region. This is often related to the existence of yield stresses. The yield stresses of rigid particle filled polymer melt systems have been investigated by many rheologists.

In 1962, Zakharenko et al. (183) studied the rheological properties of pure and carbon black filled polyisobutylene. They observed the existence of Newtonian region for pure polyisobutylene but not for carbon black filled ones. They pointed out that deviations from Newtonian flow increases with the content of filler. Chapman and Lee (25), in 1970, investigated talc filled polypropylene melts. They pointed out that the viscosity of talc filled polypropylene is almost identical to that of pure polypropylene at the high shear rate region ($\dot{\gamma} > 10^0 \text{ sec}^{-1}$), and that the viscosity of talc filled polypropylene increases with increasing loading level and decreasing particle diameter in the low shear rate region. In 1972, Vinogradov et al. (168) investigated acetylene black filled low-molecular polyisobutylenes. They

concluded that acetylene black can form a three-dimensional structure which causes yield stresses.

Yield stresses have been found for rod-shaped particle-filled systems (31, 174), small disc-shaped particle-filled systems (14) as well as for small spherical particle-filled systems. White et al. (150, 174) summarized the effect of particle size on the rheological properties of filled systems. They pointed out that the yield stresses in shear and elongational flow are observed when particle size is smaller than 0.5μ , and Newtonian viscosities are observed at low deformation rates when particle size is larger than 10μ . The magnitude of yield stress tends to increase with decreasing diameters of particles. However, the yield stress seems related to the other factors such as inter-particle forces since calcium carbonate filled systems have a larger yield stress than other filled systems which have smaller particle sizes at the same loading level: It has been reported that the surface treatment of calcium carbonate decreases shear and elongational viscosities and yield stress of these systems (150).

The effect of loading level of filler has been investigated on various combinations of filler and matrix polymer, by White et al. (91, 107, 150). They denoted that with increasing loading level of filler in polymer melt, the shear and elongational viscosity at low deformation rates, yield stress and first normal stress difference at fixed

shear rate increase. They concluded that the system takes on the characteristics of a gel at the volume loadings between 10 and 20%. Kataoka et al. (80, 83) obtained the yield stresses from Casson's plot and reported that the yield stress increases with increasing loading level of filler.

It has been reported that small particles reduces the first normal stress difference in shear flow at constant shear stress (56, 91, 150, 174). Lobe, Tanaka and White (91, 150) indicated that the first normal stress difference at the fixed shear stress decreases with increasing loading level of filler. Although generally addition of fiber tends to increase the first normal stress difference (24, 31, 173, 174), a very small diameter fiber has been found to decrease it (174).

It has been pointed out that the addition of small particles may reduce the elastic recovery of polymer melts following flow. Many investigators pointed out that the addition of small particles decreases extrudate swell (175, 107). Bagch and Sirkar (2) have related extrudate swell to the free rubber volume fraction.

Elongational measurements of filled materials have been reported by a few authors. Cotten and Thiele (30) measured transient elongational viscosity; however, they did not obtain the steady state values. Lobe and White (91) and Tanaka and White (150) reported the elongational

viscosity at a constant elongational rate, and obtained yield stresses for carbon black and calcium carbonate-filled polystyrene melts. White and Tanaka (177) suggested that the existence of yield stress in elongational viscosity leads to enhanced instability of uniaxial stretching and melt spinning. Instabilities are found in both simple stretching and melt spinning, that is, necking and low elongation to break in simple stretching and draw resonance at low draw down ratios.

Few authors have been reported the small strain viscoelastic properties of filled polymer melts. Payne (125, 126) found that the dynamic moduli of carbon black filled rubber vulcanizates are strongly dependent on amplitude. It suggests the existence of a gel. He suggested that the system may behave almost elastically at low strains with the modulus independent of strain because of the formation of a gel by carbon black-carbon black structure. Lobe and White (91) have studied dynamic and stress relaxation properties for carbon black filled polystyrene melts. They reported that the addition of carbon black reduces the rate of stress relaxation and makes the low frequency storage modulus, $G'(W)$, tend to a finite value and dynamic viscosity tend to infinity.

The effect of the addition of titanate coupling agent has been reported by Han et al. (58). They pointed out that the addition of coupling agents to calcium carbonate

filled polypropyrene melt reduces the shear viscosity and increases the first normal stress difference at fixed shear stress. The effect of coupling agents on glass bead filled polypropyrene is not simple. The shear viscosity and the first normal difference show opposite tendencies to the case of the calcium carbonate filled system. They reported that the spinability of a calcium carbonate filled system is enhanced considerably by the introduction of coupling agents, and that the tensile strength of the melt-spun fibers were also improved by their addition.

It has been reported that the surface treatment of filler reduces the viscosity of its composites (14, 25, 57, 150). Tanaka and White (150) show the reduction of the first normal stress difference at fixed shear stress by surface treatment of calcium carbonate. Zolotor (186) suggested that the extrudate swell of polymer melts may increase slightly by surface treatment of particles.

The transient stress or viscosity data of the steady shear experiments for rigid particle filled polymer melt systems has been considered in the literature. Mullins (111) has noted large time dependent overshoots in rubber-carbon black compounds. Trapeznikov and Frolova (155) have reported time dependent shear stress data on 40.7 vol% zinc oxide filled polydimethylsiloxane with 1.3 wt% of decyl alcohol as a surfactant. They observed a stress overshoot phenomenon which depends on the previous shear history and

temperature and deformation rate. However, there is no comparison between the transient stress data of a filled system and an unfilled system. They conclude that the shear modulus and thixotropic recovery velocity increase with an increase in temperature, and thixotropy may be evaluated using the shear modulus, ultimate strength, and fracture energy.

B. Rheological Theories

B.1 Phenomenological Theory for Unfilled Materials

B.1.a General (Newtonian fluid). The most fundamental and the simplest concept of fluid was proposed by Newton (113).

$$\sigma = \eta \dot{\gamma} \quad [\text{II.4}]$$

This Newtonian law of viscosity has been generalized into a three-dimensional constitutive equation by Stokes (147).

$$\underline{\sigma} = -p\underline{I} + 2\eta\underline{\dot{\gamma}} \quad [\text{II.5}]$$

where $\underline{I}$ is a unit tensor and $\underline{\dot{\gamma}}$ is the rate of deformation tensor defined by

$$\underline{\dot{\gamma}} = \frac{1}{2}[\nabla \underline{V} + (\nabla \underline{V})^T] \quad [\text{II.6}]$$

Generally, the total stress $\underline{\sigma}$ is divided into two parts for convenience.

$$\underline{\sigma} = -p\underline{I} + \underline{P} \quad [\text{II.7}]$$

where p is identified as the hydrodynamic pressure. During flow, p should be considered as a scalar value to be determined by boundary conditions in case of incompressible fluids. $\underline{P}$ is the deviatoric stress tensor associated with deformation.

$$\underline{\sigma} = \left(\frac{1}{3}\text{tr}\underline{\sigma}\right) \cdot \underline{I} + \underline{P} \quad [\text{II.8}]$$

B.1.b Viscoelastic fluid. Polymer melts show elastic or memory effects in the sense that the present stress depends on the previous history of deformation. The theory of viscoelasticity was originated in one-dimensional linear models for small strains. It has since been generalized to three-dimensional large strain models. There are two kinds of formulations: differential type models and integral type models.

B.1.b.1 Differential model. Differential type constitutive equations are based on Maxwell's equation (103).

$$\sigma + \tau \frac{d\sigma}{dt} = G\tau \frac{d\gamma}{dt} \quad [\text{II.9}]$$

$$G\tau = \eta$$

where σ is the stress, γ is the strain, G is the elastic modulus, and τ is the relaxation time. This is the simplest one-dimensional linear viscoelastic fluid model.

This one-dimensional equation has been generalized to three-dimensional large deformations and to be independent of a coordinate system. Zaremba (185) in 1903, first generalized Equation II.9 with a rigid embedded coordinate system which translates and rotates with a material point.

$$\frac{\partial \underline{T}}{\partial t} = 2G\dot{\underline{d}} - \frac{1}{\tau}\underline{T} \quad [\text{II.10}]$$

where

$$\frac{\partial T_{ij}}{\partial t} = \frac{\partial T_{ij}}{\partial t} + V_m \frac{\partial T_{ij}}{\partial x_m} - T_{im}w_{mj} - T_{mj}w_{im} \quad [\text{II.11}]$$

$$w_{ij} = \frac{1}{2} \frac{\partial V_i}{\partial x_j} - \frac{\partial V_j}{\partial x_i} = \text{vorticity tensor}$$

with summation notation. Here $\underline{T}$ is an extra stress tensor. This equation predicts non-Newtonian viscosity and normal stresses in simple shear flow. In 1950 Oldroyd (118) utilized a convected deforming coordinate system which was first introduced by Hencky (64) and which translates, rotates and deforms with the fluid. Since that time, various generalizations have been proposed by several authors (33, 116, 144, 145, 176, 179).

The expression developed by White and Metzner (176) is the simplest form among them and still describes many important features of non-linear viscoelasticity.

$$\frac{\delta \underline{P}}{\delta t} = 2G\dot{\underline{d}} - \frac{1}{\tau}\underline{P} \quad [\text{II.12}]$$

where

$$\frac{\delta P_{ij}}{\delta t} = \frac{\partial P_{ij}}{\partial t} + V_m \frac{\partial P_{ij}}{\partial x_m} - \frac{\partial V_j}{\partial x_m} P_{mj} - \frac{\partial V_i}{\partial x_m} P_{im} \quad [\text{II.13}]$$

White and Metzner (176) proposed that the relaxation time τ is a function of the second invariant of deformation rate tensor $\underline{d}$.

$$\tau = \tau(\text{II}_{\underline{d}}) = \tau(\text{tr} \underline{d}^2) \quad [\text{II.14}]$$

Equation II.12 is often called the convected Maxwell model or White-Metzner model. There have been numerous applications of this model in the literature.

B.1.b.2 Integral model. Integral type constitutive equations are based on Boltzmann's superposition principle (17) which represents the stress response to infinitesimal strains of linear-viscoelasticity. This is a three-dimensional heredity functional theory.

$$P(t) = \int_{-\infty}^t G(t-s) \frac{d\gamma}{dt} ds \quad [\text{II.15}]$$

or

$$P(t) = \int_0^{\infty} G(z) \frac{d\gamma}{dt} dz \quad [\text{II.16}]$$

where $z = t - s$ and $G(t)$ is a relaxation modulus at time t . Equation II.15 can be integrated by parts and rewritten as

$$P(t) = \int_{-\infty}^t \phi(t-s) \gamma(s) ds \quad [\text{II.17}]$$

where

$$\phi(t) = - \frac{dG(t)}{dt} \quad [\text{II.18}]$$

is the relaxation function. The linear Maxwell equation is a special case of the Boltzmann's superposition principle for which

$$G(t) = G_0 e^{-t/\tau} \quad [\text{II.19}]$$

$$\phi(t) = \frac{G_0}{\tau} e^{-t/\tau} \quad [\text{II.20}]$$

More generally $G(t)$ are often written by

$$G(t) = \sum_i G_i e^{-t/\tau_i} = \int_{-\infty}^t H(\tau) e^{-t/\tau} \frac{d\tau}{\tau} \quad [\text{II.21}]$$

where $H(\tau)$ is called the relaxation spectrum.

The Boltzmann's superposition principle which is for small deformation linear-viscoelasticity has been generalized to large deformation non-linear-viscoelasticity by various authors beginning with Oldroyd (118) and Lodge (93, 94). Lodge (93) first reported possible generalizations to large deformations with derivation in a Hencky-Oldroyd convected coordinate system. Yamamoto (181, 182) and Lodge (94) developed a non-linear generalization of Boltzmann's equation based on network theories of flexible polymer

chains. Lodge's equation is

$$\underline{\sigma} = -p\mathbf{I} + \int_{-\infty}^t \phi(t-s) \underline{c}^{-1}(s) ds \quad [\text{II.22}]$$

where $\underline{c}^{-1}$ is the Finger deformation tensor, and $\phi(t)$ is a relaxation function interpretable by the junction density at time t .

Green and Rivlin (54), in 1957, presented a completely general three-dimensional form of the hereditary functional constitutive equation for the stress tensor.

$$\underline{P} = \underline{F}[\underline{e}(t-s)] \quad \begin{matrix} -s = +t \\ -s = -\infty \end{matrix} \quad [\text{II.23}]$$

The stress is a hereditary function of the strain history. This function may be written as a Frechet expansion of integrals:

$$\begin{aligned} \underline{P} = & \int_{-\infty}^t \Phi(t-s) \underline{e}(s) ds \\ & + \int_{-\infty}^t \int_{-\infty}^t \psi(t-s_1, t-s_2) \underline{e}(s_1) \underline{e}(s_2) ds_1 ds_2 \\ & + \int_{-\infty}^t \int_{-\infty}^t \beta(t-s_1, t-s_2) [\text{tr } \underline{e}(s_1)] \underline{e}(s_2) ds_1 ds_2 \\ & + \dots \dots \dots \end{aligned} \quad [\text{II.24}]$$

where $\Phi(s)$, $\psi(s_1, s_2)$, $\beta(s_1, s_2)$, ... are relaxation

moduli, and $\mathbf{e}(s)$ is a suitable non-linear strain tensor referred to as the instantaneous state. The strain tensor $\mathbf{e}$ in terms of Finger deformation tensor $\mathbf{c}^{-1}$, that is,

$$e_{ij} = \frac{1}{2}[\mathbf{c}_{ij}^{-1} - \delta_{ij}] = \frac{1}{2}\left(\sum \frac{\partial x_i}{\partial X_A} \frac{\partial x_j}{\partial X_A} - \delta_{ij}\right) \quad [\text{II.25}]$$

$$\mathbf{e} = \frac{1}{2}[\mathbf{c}^{-1} - \mathbf{I}] \quad (\text{II.26})$$

Here x is the instantaneous fixed state cartesian components of a point, and X is components at some past time s .

Investigations of the relaxation moduli in Equation II.24 have been carried out by many authors. The linear viscoelastic relaxation modulus $\Phi(s)$ [or $G(s)$] has been studied by Tobolsky (153) and Ferry (37) and others. Higher relaxation moduli such as $\psi(s_1, s_2)$, $\beta(s_1, s_2)$ have been investigated by Lockett (92) and a series of experiments to evaluate relaxation moduli have been proposed.

Zapas and Craft (184) have reported that a hereditary function which is composed of a single integral is more appropriate than a hereditary function containing multiple integrals on the basis of multistep large deformation stress relaxation experiments on polyisobutylene. The hereditary function proposed can be written as

$$\begin{aligned} \mathbf{p} = & \int_{-\infty}^t \{m_1[(t-s), \mathbf{I}_C^{-1}, \mathbf{II}_C^{-1}] \mathbf{c}^{-1} \\ & - m_2[(t-s), \mathbf{I}_C^{-1}, \mathbf{II}_C^{-1}] \mathbf{c}\} ds \end{aligned} \quad [\text{II.27}]$$

where m_1 and m_2 are memory functions and $\underline{c}$ is a Cauchy deformation tensor, and

$$I_C^{-1} = \text{tr } \underline{c}^{-1}, \quad II_C^{-1} = \text{tr}(\underline{c}^{-1})^2 \quad [II.28]$$

This single integral model can be compared with the Lodge liquid (Equation II.22), where $m_2 = 0$. Many of the rheologists of the 1960's used this type of single integral model for large deformations of polymer fluids. Various memory functions were proposed to represent the response of viscoelastic materials to as many different types of applied strains as possible.

White and Tokita (178) simplified Green and Rivlin's Equation (II.24) to a single integral form using the Cayley-Hamilton theorem for the case when a single memory function is involved.

$$\begin{aligned} \underline{p} = & \int_{-\infty}^t [a_1(t-s, I_e, II_e) \underline{e}(s) \\ & + a_2(t-s, I_e, II_e) \underline{e}^2(s)] ds \end{aligned} \quad [II.29]$$

where $a_1(t-s, I_e, II_e)$ and $a_2(t-s, I_e, II_e)$ are the relaxation moduli which are the function of time and the first and second invariants of strain tensor.

Bernstein, Kearsley and Zapas (8, 9) suggested that the memory functions in a single integral theory (Equation II.27) can be represented by

$$m_1 = 2 \frac{\partial U}{\partial I_C^{-1}}$$

[II.30]

$$m_2 = 2 \frac{\partial U}{\partial II_C^{-1}}$$

Here, U is an empirical relation which can be interpreted as the stored energy. It is suggested that non-linearity of viscoelastic properties are due to the deformation invariants in their formulation.

Bird and his coworkers (13, 22, 146) proposed the memory functions in terms of the invariants of the rate of deformation $\dot{d}$.

Bogue (15) considered time average integrals of invariants of $\dot{d}$ as the memory functions. Bogue and White (16) suggested the memory functions by

$$m_1(t - s) = (1 + \frac{\epsilon}{2}) \sum_{i=1}^n \frac{G_i}{\tau_{i \text{ eff}}} e^{-(t - s)/\tau_{i \text{ eff}}}$$

[II.31]

$$m_2(t - s) = \frac{\frac{\epsilon}{2}}{1 + \frac{\epsilon}{2}} m_1(t - s)$$

where

$$\tau_{i \text{ eff}} = \frac{\tau_i}{1 + a\tau_i < II_d >^{1/2}}$$

[II.32]

$$< II_d >^{1/2} = \frac{1}{z} \int_0^z 2(\text{tr} \dot{d}^2)^{1/2} dz$$

[II.33]

where $z = t - s$ is time running back from present. The

experimental data both of steady shear flow (26, 39) and elongational flow (27, 72) on polymer melts have supported this model. The Bogue-White model has been perhaps the most widely applied constitutive equation to polymer melt systems. It is suggested that non-linearity is due to the deformation rate invariants in contrast to the BKZ formulation.

Wagner (169, 170) proposed a memory function

$$m(t - s, I_C^{-1}, II_C^{-1}) = m_0(t - s) h(I_C^{-1}, II_C^{-1}) \quad [II.34]$$

where $m_0(t - s)$ is a memory function for the linear behavior and $h(I_C^{-1}, II_C^{-1})$ is a so-called damping function depending on the first and second invariants of the Finger deformation tensor. Laun (87) has determined the damping function $h(I_C^{-1}, II_C^{-1})$ directly from the shear relaxation modulus measurements. His steady shear experimental data support Wagner's model.

B.2 Phenomenological Theory for Filled Materials with Yield Stress

B.2.a Bingham plastic fluid. On the basis of investigations of the flow of paints, Bingham (11) and Bingham and Green (12) have proposed a constitutive equation

$$\begin{aligned} \sigma < Y, \quad \dot{\gamma} &= 0 \quad \text{or} \quad \sigma = G\gamma \\ \sigma \geq Y, \quad \sigma &= Y + \eta_B \dot{\gamma} \end{aligned} \quad [II.35]$$

for the concentrated suspensions of small particles of Newtonian fluid. Here η_B is a constant viscosity and Y is the yield value. When shear stress σ is below the yield value Y , the material behaves like a solid. When shear stress is greater than the yield value, the material flows with a constant differential viscosity.

Hohenemser and Prager (69) in 1932 generalized the one-dimensional equation into a three-dimensional form using invariants. Here

$$\begin{aligned} \text{II}_P^{1/2} < Y & \quad d = 0 \\ \text{II}_P^{1/2} \geq Y & \quad 2\eta_B d = \left(\frac{\text{II}_P^{1/2} - Y}{\text{II}_P^{1/2}} \right) \cdot \dot{P} \end{aligned} \quad [\text{II.36}]$$

where II_P is the second invariant of the stress deviator

$$\text{II}_P = \frac{1}{2} \text{tr } P^2 \quad [\text{II.37}]$$

Their representation of yielding is the same as that of von Mises (108).

Oldroyd (117) in 1947 developed an equivalent three-dimensional constitutive equation.

B.2.b Viscoelastic plastic fluid. Schwedoff proposed the one-dimensional mechanical models, which are called Schwedoff bodies, for the viscoelastic plastic materials (95, 128, 132). The three-dimensional equations which represent Schwedoff bodies were derived by White and Lobe (91) and White (172). The one-dimensional form is

$$\sigma < Y \quad \frac{dY}{dt} = 0 \quad [II.38]$$

$$\sigma > Y \quad \frac{d\sigma}{dt} = G \frac{dY}{dt} - \frac{(\sigma - Y)}{\tau}$$

and

$$\sigma < Y \quad \sigma = G_1 \gamma_1$$

$$\sigma > Y \quad \frac{d\sigma}{dt} = G_2 \frac{d\gamma_2}{dt} - \frac{(\sigma - Y)}{\tau} \quad [II.39]$$

Solving Equations II.38 and II.39, we obtain

$$\sigma = Y + \int_0^\infty G e^{-z/\tau} \frac{dY}{dt} dz \quad [II.40]$$

and

$$\sigma = Y + \int_0^\infty G_2 e^{-t/\tau} \frac{d\gamma_2}{dt} dz \quad [II.41]$$

Equation II.41 is, however, an incomplete form as only strain γ_2 is included. The total strain, γ , is given by

$$\begin{aligned} \gamma &= \gamma_1 + \gamma_2 \\ &= \frac{\sigma}{G_1} + \frac{(\sigma - Y)}{G_2} + \int \frac{(\sigma - Y)}{\eta} dt \end{aligned} \quad [II.42]$$

and, then, solving this equation

$$\sigma = Y + \int_0^\infty \frac{G_2}{1 + G_2/G_1} e^{-t/\tau} \frac{dY}{dt} dz \quad [II.43]$$

was obtained. In this equation, relaxation time, τ , is given by

$$\tau = \frac{\frac{1}{G_1} + \frac{1}{G_2}}{\frac{1}{\eta}} \sim \frac{\eta}{G_2} \quad [\text{II.44}]$$

Three-dimensional large strain theory for the viscoelastic plastic fluid was considered by Lobe and White (91) and White (172). They generalized the mathematical procedure developed by Hohenemser and Prager (69) to a system which responds as non-linear viscoelastic fluid above the yield value.

$$\begin{aligned} \text{II}_P^{1/2} < Y & \quad P = G_{11} \mathfrak{C}^{-1} - G_{12} \mathfrak{C} \\ \text{II}_P^{1/2} \geq Y & \quad P \left(\frac{\text{II}_P^{1/2} - Y}{\text{II}_P^{1/2}} \right) = H \end{aligned} \quad [\text{II.45}]$$

where G_{11} and G_{12} are elongational and shear modulus respectively, and

$$H = H(\text{deformation history})$$

White (172) suggested a single integral equation in terms of deviatoric Finger and Cauchy deformation tensors.

$$\begin{aligned} \underline{\underline{H}} = \int_{-\infty}^t \{ m_1(t-s) [\mathfrak{C}^{-1} - \frac{1}{3}(\text{tr } \mathfrak{C}^{-1}) \underline{\underline{I}}] \\ - m_2(t-s) [\mathfrak{C} - \frac{1}{3}(\text{tr } \mathfrak{C}) \underline{\underline{I}}] \} ds \end{aligned} \quad [\text{II.46}]$$

This form of $\underline{H}$ satisfies

$$\text{tr } \underline{H} = 0 \quad [\text{II.47}]$$

White (172) rewrote Equation II.45 in the convenient form:

$$\underline{P} = \left[1 + \frac{Y}{\sqrt{\frac{1}{2} \text{tr } \underline{H}^2}} \right] \underline{H} \quad [\text{II.48}]$$

If we represent the memory functions as

$$m_1(t - s) = \frac{G}{\tau_{\text{eff}}} e^{-t/\tau_{\text{eff}}} \quad [\text{II.49}]$$

$$m_2(t - s) = 0$$

where

$$\tau_{\text{eff}} = \frac{\tau_0}{1 + a\tau_0 \bar{I} \bar{I}_d^{1/2}} \quad [\text{II.50}]$$

and where τ_0 is zero shear relaxation time. The Finger deformation tensor and hereditary functional $\underline{H}$ in simple shear flow are

$$\underline{C}^{-1} = \begin{vmatrix} 1 + \dot{\gamma}^2 z^2 & \dot{\gamma} z & 0 \\ \dot{\gamma} z & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad [\text{II.51}]$$

$$\underline{H} = G \cdot \begin{vmatrix} \frac{4}{3} \tau^2 \dot{\gamma}^2 & \tau \dot{\gamma} & 0 \\ \tau \dot{\gamma} & -\frac{2}{3} \tau^2 \dot{\gamma}^2 & 0 \\ 0 & 0 & -\frac{2}{3} \tau^2 \dot{\gamma}^2 \end{vmatrix} \quad [\text{II.52}]$$

where $z = t - s$. The shear viscosity has the forms

$$\eta_{\text{shear}} = \left(1 + \frac{Y}{[G^2 (\tau^2 \dot{\gamma}^2) + 4/3 \tau^4 \dot{\gamma}^4]^{1/2}}\right) G\tau \quad [\text{II.53}]$$

In elongational flow

$$\underline{c}^{-1} = \begin{vmatrix} \exp(2Ez) & 0 & 0 \\ 0 & \exp(-Ez) & 0 \\ 0 & 0 & \exp(-Ez) \end{vmatrix} \quad [\text{II.54}]$$

$$\underline{H} = G \cdot \begin{vmatrix} \frac{2\tau E}{(1+\tau E)(1-2\tau E)} & 0 & 0 \\ 0 & \frac{-\tau E}{(1+\tau E)(1-2\tau E)} & 0 \\ 0 & 0 & \frac{-\tau E}{(1+\tau E)(1-2\tau E)} \end{vmatrix} \quad [\text{II.55}]$$

The elongational viscosity is

$$\chi_{\text{elong}} = \frac{\sqrt{3} \cdot Y}{E} \frac{3G\tau}{(1 + \tau E)(1 - 2\tau E)} \quad [\text{II.56}]$$

when

$$E < \frac{1}{2\tau} \quad [\text{II.57}]$$

is satisfied. At $E = 1/2\tau$, elongational viscosity goes to infinity.

B.2.c Thixotropic fluid. Slibar and Paslay (142)

rewrote the generalized Bingham's constitutive equation of Hohenemser and Prager (69), for the materials which possess the property of gelling when in a state of rest for a certain period, what they called retarded Bingham flow.

$$\begin{aligned} II_P^{1/2} < Y_1 & \quad \dot{d} = 0 \\ II_P^{1/2} \geq Y_1 & \quad 2\eta\dot{d} = \left(\frac{II_P^{1/2} - Y_0}{II_P^{1/2}} \right) \dot{P} \end{aligned} \quad [II.58]$$

Here Y_0 is the yield stress for post initial loading and Y_1 is that for initial loading. When Y_1 is initially exceeded, the transition from Y_1 to Y_0 is assumed to occur instantaneously. The above-mentioned set of equations are suitable for materials in which "break down" of the yield stress occurs almost instantaneously after deformation sets in.

Slibar and Paslay (145) proposed another set of constitutive equations for the Bingham plastic thixotropic materials in which "break down" occurs too gradually to permit the above-mentioned equations in 1964.

$$\begin{aligned} II_P^{1/2} < Y_{crit} & \quad \dot{d} = 0 \\ II_P^{1/2} \geq Y_{crit} & \quad 2\eta\dot{d} = \left(\frac{II_P^{1/2} - Y_{crit}}{II_P^{1/2}} \right) \dot{P} \end{aligned} \quad [II.59]$$

Here the yield stress is

$$Y_{\text{crit}} = Y_0 - \frac{\int_{-\infty}^t II_T^{1/2} e^{-\alpha(t-s)} ds}{\beta + \int_{-\infty}^t II_T^{1/2} e^{-\alpha(t-s)} ds} (Y_0 - Y_1) \quad [II.60]$$

Here α , β , and Y_0 and Y_1 are material constants. Because Y_{crit} equals Y_0 before the deformation begins, the materials ought to obey

$$II_T^{1/2} < Y_0 \quad \dot{d} = 0 \quad [II.61]$$

After deformation sets in, Y_{crit} gradually decreases from Y_0 . When deformation is set to zero, Y_{crit} begins to increase to Y_0 .

Slibar and Paslay (143) compared their theoretical predictions with experimental data of Jones and Babson (78). Their theoretical predictions are in satisfactory agreement with experimental data. The maximum deviation between them occurred for completely gelled material. Slibar and Paslay expected this deviation due to the different mechanisms introduced in the final stage of gelling. Their equations were the first three-dimensional constitutive equations predicting both thixotropy and pseudoplastic viscosity.

Harris proposed a one-dimensional constitutive equation for thixotropic fluid (63)

$$II_P^{1/2} \geq Y \quad \underline{P}(t) = 2\eta(II_d, III_d) \underline{d}(t) \quad [II.62]$$

He presented the simplest form of integral equation for the viscosity

$$\eta_1 - \eta(t) = \int_{-\infty}^t f_1 [II_d(s), III_d(s)] M(t - s) ds \quad [II.63]$$

$$Y_1 - Y(t) = \int_{-\infty}^t f_2 [I_d(s) N(t - s)] ds \quad [II.64]$$

where η_1 is the undisturbed viscosity, $\eta(t)$ viscosity at current time t , Y_1 initial undisturbed yield stress, $Y(t)$ yield stress at t . Memory functions $M(t - s)$ and $N(t - s)$ are defined by

$$M(t - s) \equiv \int_0^{\infty} \frac{H(\tau)}{\tau} e^{-\frac{t-s}{\tau}} d\tau \quad [II.65]$$

$$N(t - s) \equiv \int_0^{\infty} \frac{S(\lambda)}{\lambda} e^{-\frac{t-s}{\lambda}} d\lambda \quad [II.66]$$

where $H(\tau)$ and $S(\lambda)$ are called the viscosity relaxation spectrum and the yield relaxation spectrum, and where τ and λ are the relaxation times. Harris did not apply his analysis to experimental data.

Bogue and Goldblatt (50) suggested that viscoelastic constitutive laws may be made to include thixotropy by having the relaxation moduli which is dependent on the extent and intensity of deformation.

Many authors have proposed the constitutive equations and rate equations accompanied with for particular structure models of particle dispersed systems (23, 29, 52, 62, 88, 89, 135, 137). However, the physical structure of particles has not been ascertained well experimentally. Chen (28) discussed the possibility of development of structural model theories to describe the response of a viscoelastic plastic thixotropic system.

B.3 Mechanistic Theory

The viscosity of suspensions can also be described from mechanistic theory. The suspensions can be regarded as homogeneous fluid if the length of motion of the suspension system is much larger than the average size or separation of particles. Since this condition is usually satisfied, suspensions may be treated as a homogeneous system.

There are two ways to explain the viscosity of suspensions. One is Einstein's (34, 35) and the other is Burger (21) and Batchelor's (5). Einstein's approach is related to the energy dissipation of the system. The results from his approach give only the effective viscosity of suspension, but not a complete constitutive equation. Burger and Batchelor's approach started from Cauchy's law of motion.

Einstein (34) in 1906 first developed the theory of viscosity of dilute suspension of spherical rigid particles. He assumed that the particles are separated by each other

so that the interaction forces between particles can be neglected, and that the flow around each particle is described by Navier-Stokes' equation without inertial terms. He considered that the ratio of energy consumption in suspension to that in unfilled Newtonian fluid is related to the relative viscosity.

$$\frac{\eta}{\eta_0} = \frac{\int (g : \nabla V) dV}{\int (g_0 : \nabla V_0) dV} \quad [\text{II.67}]$$

where g is the total stress tensor and superscript 0 implied an unfilled system. From the Navier-Stokes' equation and the boundary condition, he obtained

$$\frac{\eta}{\eta_0} = 1 + 2.5 \phi \quad [\text{II.68}]$$

where ϕ is the volume fraction of the filled particles.

There have been many attempts to generalize the theory for spherical particle filled dilute suspensions to that for non-spherical particle filled dilute suspensions. Jeffery (76) generalized it for a dilute suspension of ellipsoids. Hand (59, 60) and Hinch and Leal (65, 66) proposed a general theory of suspension for anisotropic particle suspensions. They (65, 66) developed a general constitutive equation for a dilute suspension of rigid ellipsoidal particles with Brownian rotation.

Batchelor (5) in 1970 considered in general terms the properties of the bulk stress in a suspension of non-spherical particles, on which a couple may be imposed by external means, immersed in a Newtonian fluid. His result was expressed in terms of three-dimensional stress tensor.

$$\langle \underline{g} \rangle = - p \underline{I} + 2\eta^0 (1 + 2.5 \phi) \langle \underline{d} \rangle \quad [\text{II.69}]$$

where $\langle \underline{g} \rangle$ means the average of the total stress tensor on suspending particles, and $\langle \underline{d} \rangle$ is the average of the rate of deformation tensor.

The theory of dilute suspensions has been extended to the concentrated suspensions. Guth and Simha (55) in 1936 first took into consideration the particle interaction. They considered the additional energy consumption due to the disturbance of fluid caused by the existence of particles and by their interaction. Their formulation is

$$\frac{\eta}{\eta_0} = 1 + 2.5 \phi + 12.6 \phi^2 \quad [\text{II.70}]$$

Batchelor and Green (7) in 1972 treated this problem with a more useful consideration of position of the second sphere. Their result is

$$\frac{\eta}{\eta_0} = 1 + 2.5 \phi + 7.6 \phi^2 \quad [\text{II.71}]$$

The first theory of very concentrated suspensions was proposed by Mooney (110) in 1951. His theory, however, is

not a real hydrodynamic theory. He proposed

$$\frac{\eta}{\eta_0} = \exp \left[\frac{B\phi}{1 - k\phi} \right] \quad [\text{II.72}]$$

In this formulation, when ϕ approaches to zero, the formula reduces to $1 + B\phi$. B can be interpreted as Einstein's coefficient 2.5. The constant k is related to the geometric packing of particles.

A theory for shear flow of concentrated suspensions of spherical particles was developed by Simha (141) in 1952 using a cell model. He assumed that the particles are surrounded by cells of Newtonian fluid. He obtained the viscosity of suspension by solving a slow flow for each cell.

Happel (68) modified this treatment in 1957 assuming a frictionless envelope surrounding each particle.

$$\frac{\eta}{\eta_0} = 1 + 5.5 \psi \phi \quad [\text{II.73}]$$

where

$$\psi = \frac{4\gamma^7 + 10 - 84/11 \gamma^2}{10(1 - \gamma^{10}) - 25 \gamma^3(1 - \gamma^4)} \quad [\text{II.74}]$$

and

$$\gamma = \frac{b}{a} = \phi^{1/3} \quad [\text{II.75}]$$

where a and b are radii of the particle and the cell respectively.

In 1967, Frankel and Acrivos (38) utilized the lubrication theory approximations to compute the viscosity of concentrated suspensions. They computed the energy dissipation between the particles.

$$\frac{\eta}{\eta_0} = \frac{9}{8} \frac{\left(\frac{\phi}{\phi_m}\right)^{1/3}}{1 - \left(\frac{\phi}{\phi_m}\right)^{1/3}} \quad [\text{II.76}]$$

where ϕ_m is the maximum volume concentration. Goddard (48, 49) extruded their theory by applying elastohydrodynamic lubrication theory for a suspension of elastic particles.

Adler (1) in 1978 formulated a theory of flow and gel break-up in the flow of concentrated suspensions using the cell theory. He assumed the gel of suspension of aggregated particles as a porous media and considered the break-up condition of gel using the von Mises yield criterion. He, however, considered only hydrodynamic problems but not non-hydrodynamic particle-particle interactions which must be taken into account in concentrated suspensions.

Elongational flow of concentrated oriented fiber suspensions of Newtonian fluids has been considered by Batchelor (6) using the cell theory. He assumed the constant velocity field entirely along the flow direction, and formulated the effective Trouton viscosity by solving

the two-dimensional hydrodynamic problem. His expression was later extended to the problem of concentrated fiber suspensions of non-Newtonian fluids by Goddard (55).

Although the cell theory has the advantages in mathematical treatment of problems of suspensions, some imperfections have been pointed out by Jeffrey and Acrivos (77). One is the arbitrary choice for the shape of cell and boundary conditions. The other is the most important in the case of concentrated suspensions, that is, the cell model implies that particles are far apart from each other.

Tanaka and White (149, 150) have developed a theory of shear viscosity of concentrated suspensions of small particles in a non-Newtonian fluid using Frankel and Acrivos' cell theory involving particle-particle interaction such as van der Waals-London and electrostatic forces and hydrodynamic interaction. Assuming the matrix fluid to be a power law fluid, they presented

$$\eta(\phi, \dot{\gamma}) = \eta^0(\dot{\gamma}) f(n, \phi) \quad [\text{II.77}]$$

and

$$f(n, \phi) \sim \left[\left(\frac{\phi_m}{\phi} \right)^{1/3} - 1 \right]^{1-2n} \quad [\text{II.78}]$$

where n is an index of the power law fluid model. They computed the dissipation energy between particles caused by van der Waals-London and electrostatic forces. The

theory predicts that the flow behavior of such systems at low shear rates, in which material may be regarded as Newtonian fluid, is dependent upon these non-hydrodynamic interparticle interactions. They suggest that the interaction forces between particles may contribute to yield stress.

$$Y = Y_{vw} + Y_{ES} \quad [II.79]$$

where Y_{vw} is the yield stress due to van der Waals-London forces, and Y_{ES} is the yield stress due to electrostatic forces which may be expressed as

$$Y_{vw} = c_1 \left(\frac{NA}{a^3 y^2} \right) \quad [II.80]$$

and

$$y = \frac{h_0}{2a} \sim \left[\left(\frac{\phi_m}{\phi} \right)^{1/3} - 1 \right] \quad [II.81]$$

where c_1 : constant

N : total number of nearest neighbors of each particle

A : Hamakers constant; $A = \pi^2 v^2 \lambda$

v : number of atoms per unit volume of the particle

λ : van der Waals-London constant

a : diameter of the particle

h_0 : distance between particles.

$$Y_{ES} = c_2 N \epsilon k \psi_0^2 \left(\frac{1}{a} \right) \quad [II.82]$$

where c_2 : positive constant

k : reciprocal Debye thickness of ionic atmosphere

ψ_0 : surface potential of the particle

ϵ : dielectric constant.

Tanaka and White (149) calculated the actual magnitude of the yield stress. They obtained good agreement between theoretical predictions and experimental data for carbon black and titanium dioxide suspensions in polystyrene melt.

CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURES

A. Materials

Polystyrene (Dow Styron 678U) was used as the matrix polymer. This polymer type has been shown by earlier investigators to have $M_w = 240,000$ and $M_n = 80,000$ (73)

The primary filler used was supplied by Pfizer Inc. These calcium carbonates have four different particle diameters. Pfizer also supplied calcium carbonates which were surface treated with stearic acid. The characteristics of the fillers used in this study are summarized in Table III.1.

In addition, carbon black was studied as a filler. The carbon black used was FEF-LS N542 supplied by Continental Carbon Inc. Its characteristics are summarized in Table III.1.

The polystyrene-calcium carbonate compounds were prepared with a 0.30 volume fraction (0.55 weight fraction) loading of calcium carbonate.

The volume fraction of fillers was determined from

$$\phi = \frac{\frac{W_f}{\rho_f}}{\frac{W_f}{\rho_f} + \frac{1 - W_f}{\rho_{PS}}} \quad [III.1]$$

Table III.1
Characteristics of Fillers

Filler	Supplier	Density at 180°C (g/cm ³)	Manufacturing Process	Grade	Average Particle Size (μm)	BET Surface Area (m ² /g)	Volume Fraction in Compound		
Uncoated Calcium- Carbonate	Pfizer	2.7	Natural Ground	Marble White 325	17	1.2	0.3		
				Vicron 15-15	3	3.6			
			Precipitated	Albaglos	0.5	6.0			
				Multifex MM	0.07	20			
Coated Calcium- Carbonate			Natural Ground	Marble White 325	17	1.2			
				Hi-Phlex 100	3	3.6			
			Precipitated	Super-Phlex 200	0.5	6.0			
				Ultra-Phlex	0.07	20			
Carbon Black			Continental Carbon	1.8	-	FEF-LS N542	0.045	-	0.2 0.3

Matrix polymer = Polystyrene (Dow Styrene 678U); $\rho_{PS} = 0.96 \text{ g/cm}^3$ at 180°C.

where W_f is the weight fraction of filler, ρ_f is the density of the filler at 180°C and ρ_{PS} is the density of PS at 180°C. The density of PS, the fillers and the volume fractions of the prepared samples are summarized in Table III.1.

B. Preparation of Samples

The fillers were dispersed in to the PS melt using a two-roll laboratory mill ($D = 3$ in and $L = 7$ in) at 150°C and 0.03 wt% of BHT (Butylatedhydroxytoluene) was added as an antioxidant. At first PS was melted on the surface of the roll mill, then filler was added. The mixing time was about 30 minutes at 15 rpm for one batch (300 gm of compound). The total time required for this process was 45 minutes per batch. The same mastication procedure was given to the pure PS sample, to give it the same shear and thermal history. This was to correct for the effects of the mixing treatment on the rheological properties of the matrix.

The compounds were compression molded at 180°C to form a sheet which has a thickness of about 1.5 mm for shear flow measurements in a cone-plate geometry. Other compounds were crushed into small pieces and extruded at 180°C using a Brabender extruder ($D = 3/4$ in and $L/D = 10$) at a screw rotation speed of about 30 rpm to form strands for uniaxial elongation flow measurements. The processing histories are summarized in Figure III.1.

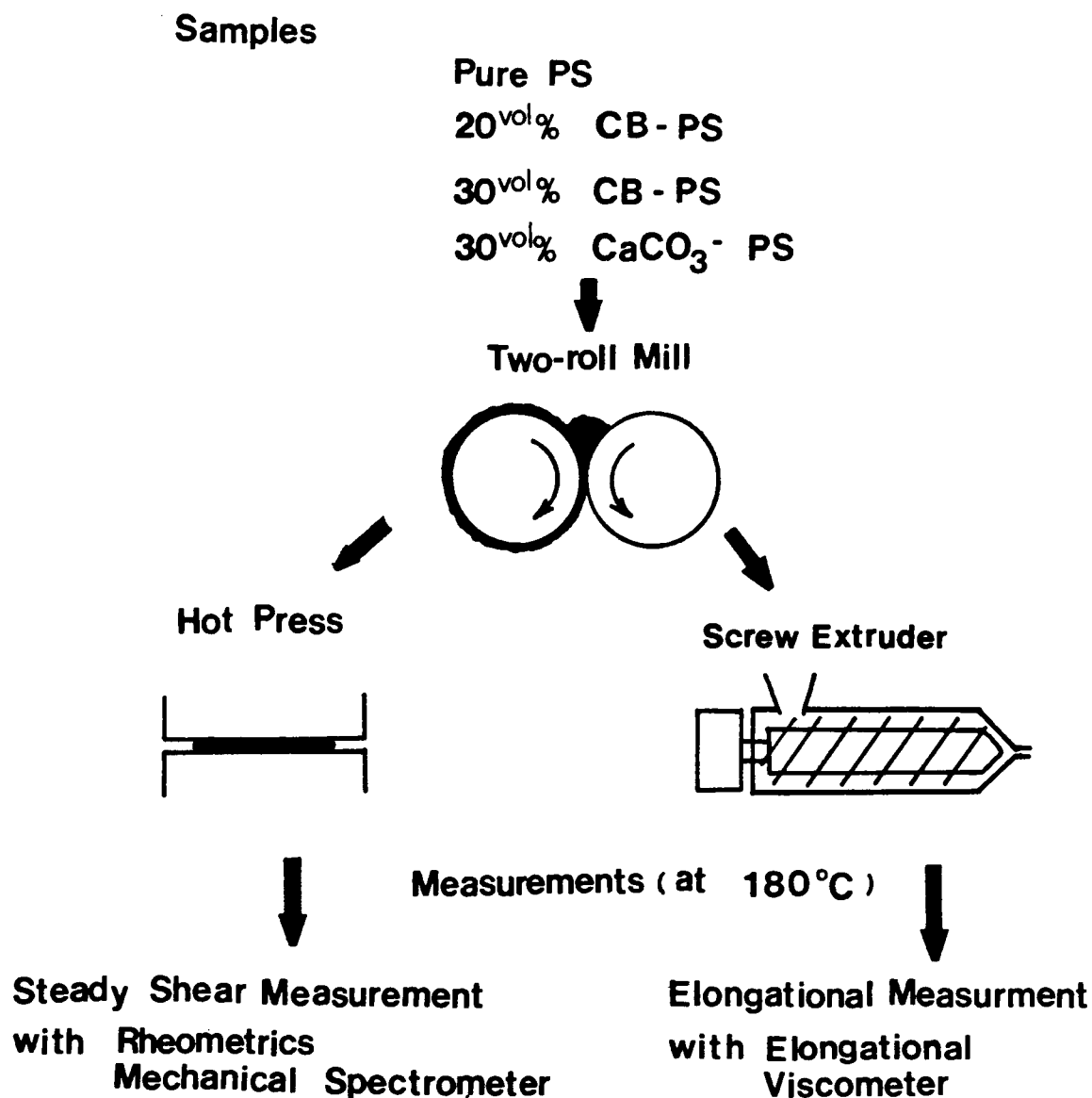


Figure III.1. Processing histories of samples.

The compounds were dried in a vacuum oven at 70°C for about 12 hours between each processing step and before measurements. Samples were kept in desiccators or jars with silica gel.

C. Rheological Measurements

C.1 Steady Shear Flow Measurements

Steady shear flow measurements were carried out in a Rheometrics Mechanical Spectrometer (Model RMS 7200) at 180°C. A cone-and-plate geometry was used. The cone has a diameter of 2.5 cm and an angle of 0.1 radian. A schematic drawing is given in Figure III.2. While this apparatus may in principle reach shear rates of 0.010 sec^{-1} , the experimental data presented here begins with a shear rate of 0.016 sec^{-1} . This is because of experimental difficulties such as noise. The upper limit of measurable shear rate was due to the occurrence of secondary flows or a shear fracture instability which preceded the steady states of the torque and the normal force.

C.1.a Sample insertion procedure. As discussed in Section B of this chapter, the fillers were dispersed into the PS melt using a two-roll laboratory mill, and then the compounds were compression molded to form a sheet which has a thickness of about 1.5 mm for shear flow measurements.

There were two types of sample trimming procedures applied to the samples. One was the normal method. The

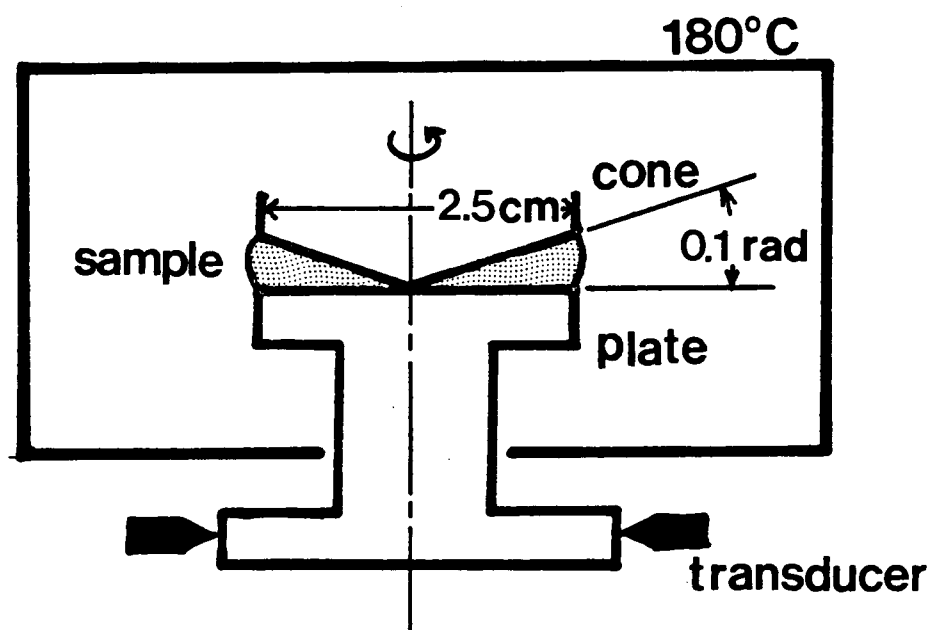


Figure III.2. Schematic diagram of Cone-Plate Mode test section.

sample was pressed between cone and plate into a 60 μm gap between the top of the cone and plate, and then trimmed by a wedge-shaped soldering iron. It was then pressed again to 50 μm .

The other was a special method. Since some filled compounds were not easily pressed into a 60 μm gap between cone and plate, a more complex method was applied to them.

1. The sample was pressed between cone and plate with a 10,000 g load along the normal direction.
2. When the normal force on the sample did not relax readily, the sample was trimmed by a soldering iron.
3. Repeating procedures 1 and 2, the sample was pressed into the 60 μm gap between the cone and plate.
4. The sample was trimmed.
5. A steady shear ($\dot{\gamma} = 0.063 \text{ sec}^{-1}$) was applied to the sample for a few minutes to allow the extra sample to come out.
6. The extra sample was trimmed again.
7. The sample was pressed to 50 μm .

The normal method was applied to pure PS, uncoated CaCO_3/PS (average particle diameter = 17 μm , 3 μm) and coated CaCO_3/PS (average particle diameter = 17 μm , 3 μm , 0.5 μm) and CB/PS (volume content = 0.2, 0.3).

The special method was applied to uncoated CaCO_3/PS (average particle diameter = $0.5\ \mu\text{m}$, $0.07\ \mu\text{m}$) and coated CaCO_3/PS (average particle diameter = $0.07\ \mu\text{m}$). The special X procedure is summarized in Figure III.3.

C.1.b Transient viscosity measurements. The samples were thermally equilibrated and stresses allowed to relax for a period of 60 minutes before the beginning of shear flow. The thermal degradation during a period of 60 minutes at 180°C in the Rheometrics Mechanical Spectrometer was investigated for pure PS. The pure PS samples were kept at 180°C between cone and plate for 30 minutes in dried nitrogen, and for 30 and 60 minutes in air. Steady shear viscosity measurements were then carried out. No effect on the shear viscosity behavior was observed.

The viscosity η was determined from the following equations:

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad [\text{III.2}]$$

$$\eta = \frac{\sigma_{12}}{\dot{\gamma}} = \frac{3T}{2\pi R^3 \dot{\gamma}} \quad [\text{III.3}]$$

where $\dot{\gamma}$ is the shear rate, Ω the angular velocity of the cone, α the cone angle (0.1 radian), σ_{12} the shear stress, T the torque and R the radius of the cone ($2.5\ \text{cm}$).

Two types of shear history experiments were investigated in this study. One was a simple single step steady

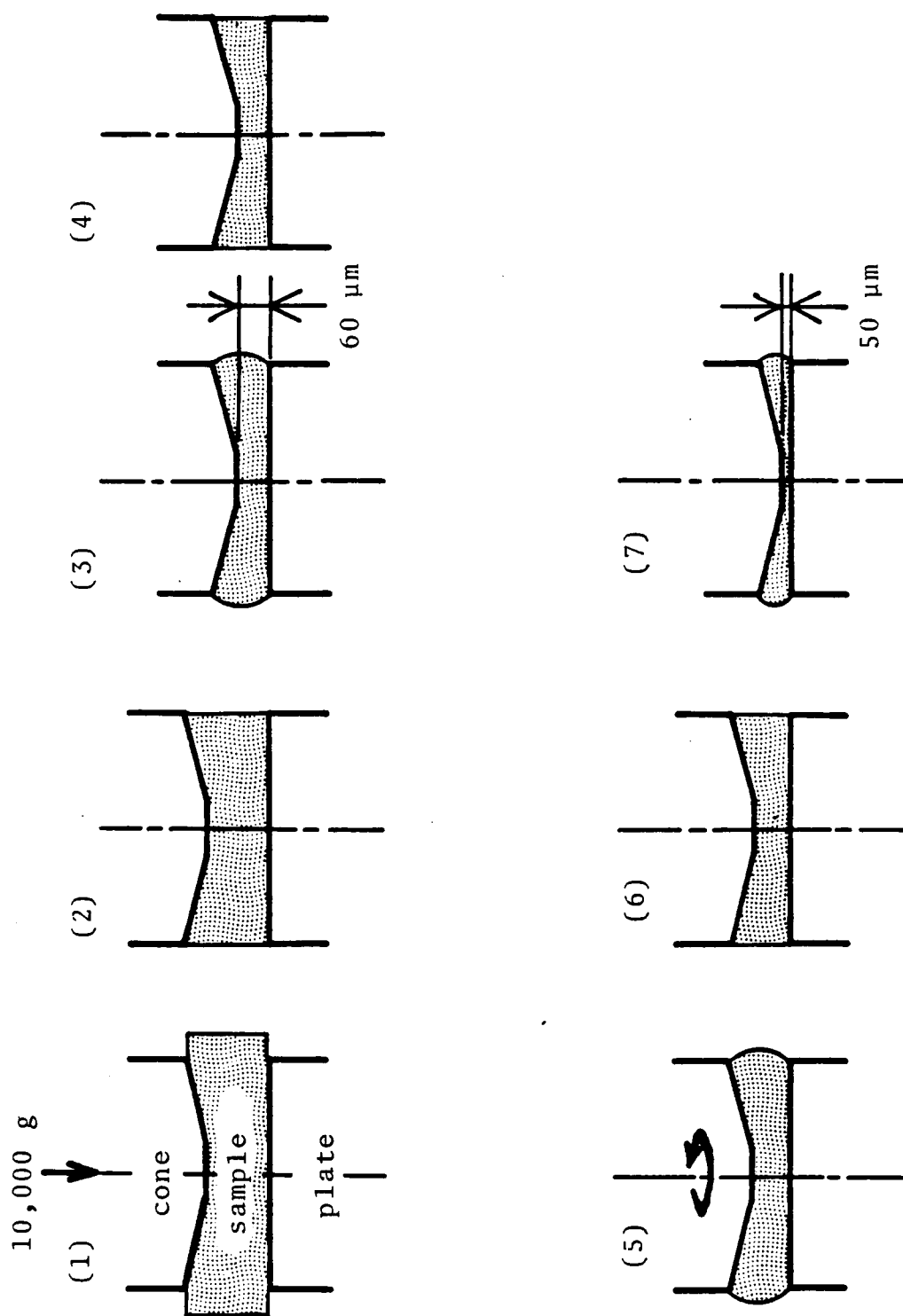


Figure III.3. Special sample insertion procedure.

shear history. In this measurement, the sample was sheared at a constant shear rate for about 15 minutes. Transient and steady state viscosity data and steady state first normal stress difference data were obtained. The second more complex shear measurement was carried out to investigate the time dependence of the behavior of the filled polymer melt. In this measurement, the sample was sheared at a steady shear rate for a certain period (90 seconds) during which the viscosity reaches a steady state. The cone rotation was then stopped at a constant position (or strain) for various periods. The cone rotation was then started again and the sample was sheared at the same shear rate as before. Transient viscosity data was obtained. These simple and complex shear histories are summarized in Figure III.4.

The determination of the possibility of slip between the melt sample and the cone and plate during flow was carried out by marking fine straight lines on the side of the sample and cone and plate and observing their variation during flow. No slip was observed.

Transient measurements for uncoated CaCO_3 filled PS compounds having average particle diameters of 0.5 μm and 0.07 μm were not carried out accurately. The influences of the earlier shear history in the sample insertion procedure were found to too strongly influence the shear transients in non-reproducible manners.

Simple Shear History



Complex Shear History

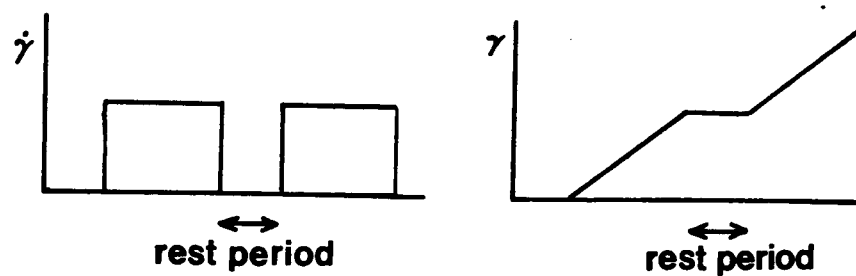


Figure III.4. Simple and complex shear histories applied in steady shear viscosity measurement.

Transient viscosity measurements for coated CaCO_3 filled PS compounds having average particle diameters of $0.5\ \mu\text{m}$ and $0.07\ \mu\text{m}$ were found to change depending upon rest period before the initiation of flow of 60 minutes. For example, a compound which has an average particle diameter of $0.5\ \mu\text{m}$ showed a shear viscosity of $5 \times 10^5\ \text{Pa}\cdot\text{sec}$ after an aging period of less than 5 minutes and $3 \times 10^5\ \text{Pa}\cdot\text{sec}$ for 60 minutes for a shear rate of $0.16\ \text{sec}^{-1}$ respectively. This behavior was only incompletely characterized.

Complex shear history experiments were limited to the samples which allow the second shear to take place without secondary flows. This experiment was carried out for pure PS, uncoated CaCO_3 (average particle diameter = $17\ \mu\text{m}$) filled PS, and carbon black filled PS (volume content = 0.2).

C.1.c Steady state viscosity measurements. Steady state viscosities were determined from transient measurements for the samples for which transient viscosities were measured. Steady state viscosities of the samples that transient viscosities were not measured (see Section C.1.b of this chapter) and were determined at about 15 minutes after the sample insertion procedure, that is, after an aging period of about 15 minutes.

C.1.d Normal stress measurements. The first normal stress difference N_1 was determined from the following

equation:

$$N_1 = \frac{2F_z}{\pi R^2} \quad [\text{III.4}]$$

where F_z is the normal force and R is the cone radius.

It was not possible to determine accurately the first normal stress difference of some filled PS compounds, that is, uncoated CaCO_3 (average particle diameters of 0.5 μm and 0.07 μm) and coated CaCO_3 (average particle diameters of 0.5 μm , 0.07 μm) filled PS. Following the sample insertion procedure, the normal force did not recover to zero but always asymptote to a positive value. The transient behavior of these samples will be carefully discussed in Section IV.C. The measurements for each sample are summarized in Table III.2.

C.2 Elongational Flow Measurements

Elongational flow measurements were carried out at 180°C in the elongational viscometer shown in Figures III.5 and III.6. The rheometer developed by Ide (72, 73) in our laboratory was modified (Figures III.5 and III.6). The changes were as follows:

1. The sample stretching mechanism was changed from a single horizontal roller to double-gear shaped vertical rollers. This provides a better control of elongation of the samples and gives less possibility of temperature fluctuation during measurements.

Table III.2
Applied Steady Shear Flow Measurements

Volume Content of Filler (-)		Average Particle Size (μm)	Transient Viscosity Measurement	Complex Shear History Measurement	Steady State Viscosity Measurement	Transient Normal Stress Measurement	Steady State Normal Stress Measurement
PS	0	-	Yes	Yes	Yes	Yes	Yes
Uncoated CaCO ₃ /PS	0.3	17	Yes	Yes	Yes	Yes	Yes
		3	Yes	No	Yes	Yes	Yes
		0.5	Yes	No	Yes	Yes	No
		0.07	Yes	No	Yes	Yes	No
Coated CaCO ₃ /PS	0.3	17	Yes	No	Yes	Yes	Yes
		3	Yes	No	Yes	Yes	Yes
		0.5	No	No	Yes	Yes	No
		0.07	No	No	Yes	Yes	No
CB/PS	0.2	0.045	Yes	Yes	Yes	Yes	Yes
	0.3		Yes	No	Yes	Yes	Yes
Reference Chapter and Section			III.C.1.b IV.A	III.C.1.b IV.A	III.C.1.c IV.B	III.C.1.d IV.C	III.C.1.d V.D

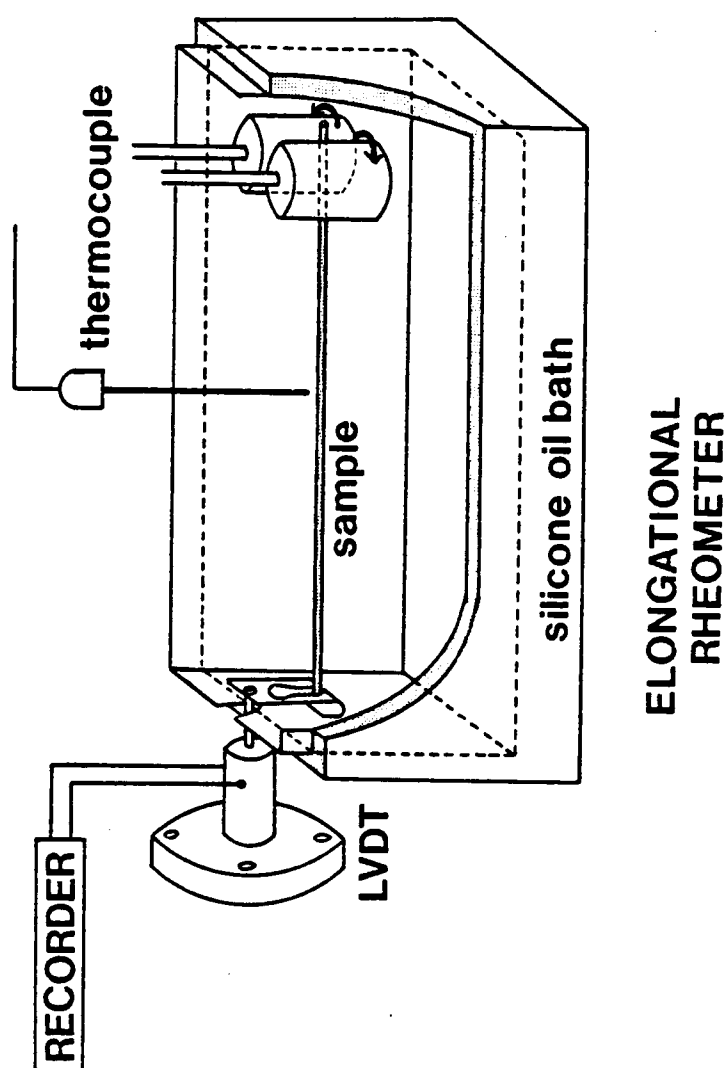
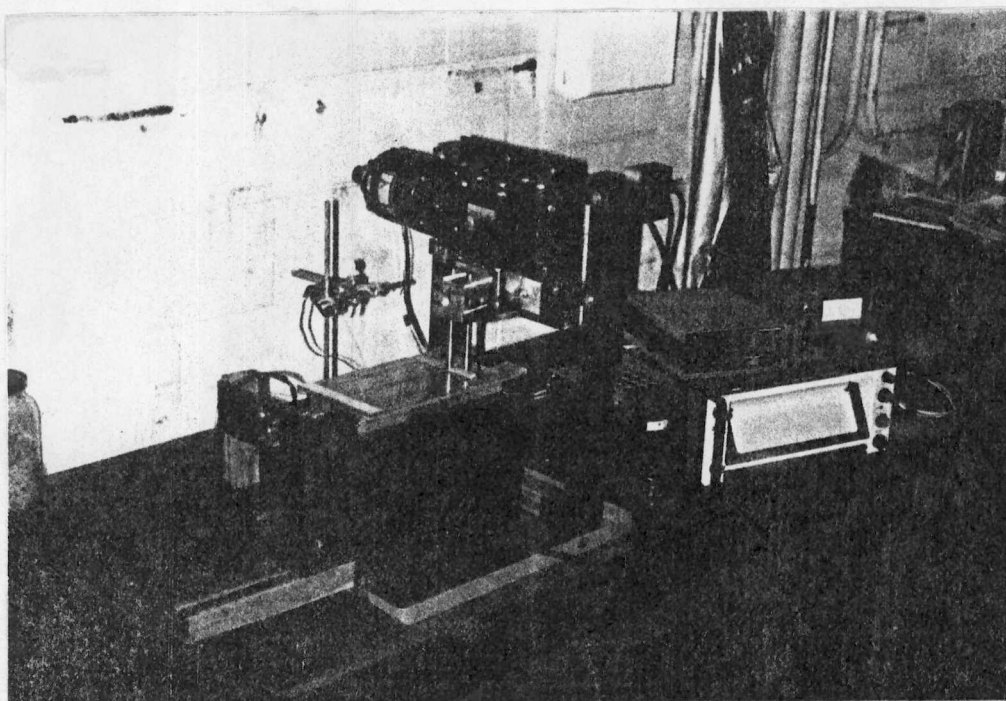
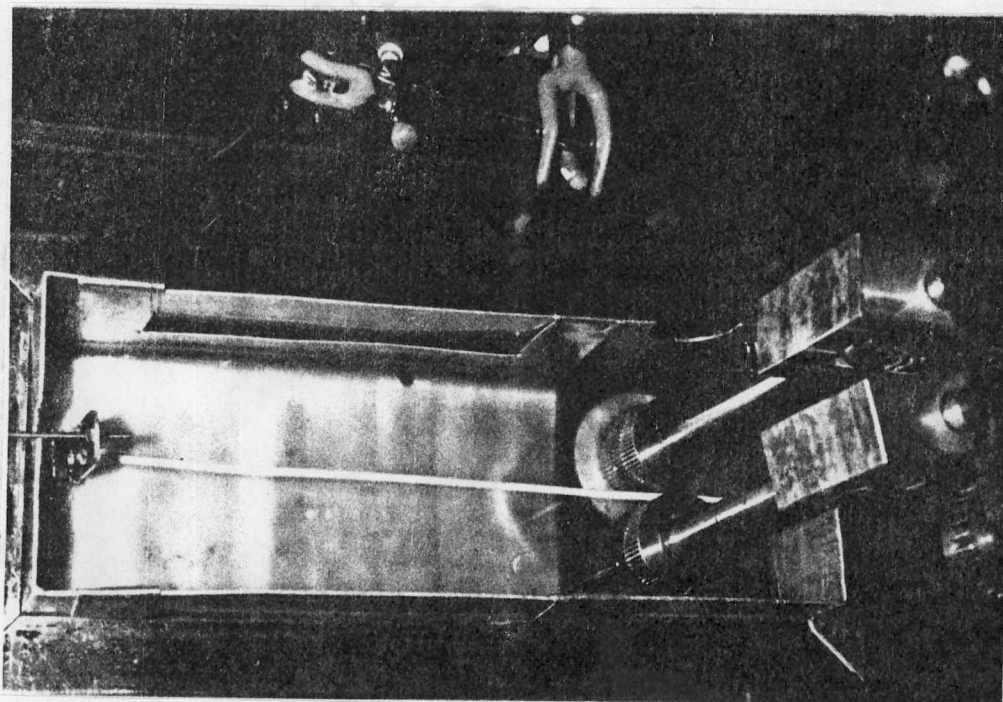


Figure III.5. Schematic diagram of elongational rheometer.



(a) Overall view of apparatus.



(b) Close-up view of the gear-shaped rolls.

Figure III.6. Elongational rheometer.

2. The force detecting system was changed to an AC-operated 50-g force transducer which is more accurate.
3. The sample clamping method and insertion procedure was improved and simplified.
4. The temperature was controlled by a proportional temperature controller.

A Hallikainen tube block heater which was set at the bottom of the silicone oil bath was controlled by a proportional type temperature controller. The temperature was measured with an iron-constantan thermocouple at a distance of 1 cm horizontally away from the sample. The temperature fluctuation was within $\pm 0.5^{\circ}\text{C}$ at the maximum.

The force was determined by an AC-operated force transducer (Schaevitz FtA-G-50). The maximum linear operation region of force transducer is ± 50 g. The displacement of the core due to the stretching force of 50 g is very small in comparison with the 22-cm length of the sample. The force transducer was connected to a digital transducer readout (Schaevitz Model DTR-450) and then a recorder.

The double-gear shaped rollers were designed to press the sample in between them. The radius of the rollers was 1.75 cm. The rollers were rotated by two 1/15 HP B and B motors controlled by a B and B controller. The elongational

rates achieved were in the range of $4.66 \times 10^{-3} \text{ sec}^{-1}$ to $1.47 \times 10^{-1} \text{ sec}^{-1}$.

One end of a rod-shaped sample was glued with a nut by quick-set epoxy. This side was inserted into the sample holder joined to the force transducer through a narrow gap of cover glass. The other end of the sample was held between rollers.

A silicone oil (Dow Corning, Fluid 200[®], kinetic viscosity: 100 centistokes at 25°C, density: 0.968 g/cm³ at 25°C) was used as the oil bath medium. The degradation temperature of this silicone oil is about 200°C.

The samples were first annealed for 10 minutes at 180°C in the silicone oil bath to eliminate residual stresses and orientation. The cross sectional area at 180°C, A was calculated from Equation III.5.

$$A = \frac{L_0}{L} \frac{\rho_0}{\rho} A_0 = \frac{1}{1 + \int_{105}^{180} \alpha dT} \frac{1}{\rho} \frac{W}{L_0} \quad [\text{III.5}]$$

where L is the length of a sample, ρ is the density, α is the linear thermal expansion coefficient of the filament. The symbols with and without subscript o are the values at room temperature, 25°C, and at 180°C, respectively. An average value of " A " was calculated from the measurement of 10 samples using Equation III.5. It was assumed in the calculation that the densities of filaments are constant

during deformation, and that the thermal expansion of filaments is due to only that of the matrix polystyrene, that is,

$$\alpha = (1 - \phi) \alpha_{PS} \quad [III.6]$$

where ϕ is the volume fraction of filler and α_{PS} is the thermal expansion of PS, equal to $5.55 \times 10^{-4}/^{\circ}\text{C}$ above T_g and $1.85 \times 10^{-4}/^{\circ}\text{C}$ below T_g .

The filament was connected between the sample holder and the take-up rollers. After 10 minutes, the filament was stretched at a constant elongational rate. The elongational rate E is defined by

$$E = \frac{\partial V_1}{\partial \chi_1} = \frac{1}{L} \frac{dL}{dt} = \frac{V_L}{V} = \frac{R\Omega}{L} \quad [III.7]$$

where in this experiment $R = 1.75$ cm, $L = 22$ cm and Ω is the angular velocity of rollers. Under an assumption of uniform deformation, the tensile stress $\sigma_{11}(t)$ is

$$\sigma_{11}(t) = \frac{F(t)}{A(t)} = \frac{F(t)}{A(o)} e^{Et} \quad [III.8]$$

where $F(t)$ is the total tensile force at $t = t$, and $A(t)$ and $A(o)$ are the cross sectional area given by Equation III.5 at $t = t$ and $t = 0$, respectively. The elongational viscosity $\chi(t)$ is defined by

$$\chi(t) = \frac{\sigma_{11}(t)}{E} \quad [III.9]$$

The elongation to break was calculated from the time to failure, estimated by the strips of chart. Since a cylinder deforms with time according to

$$L(t) = L(o) e^{Et} \quad [III.10]$$

we obtain

$$\ln \frac{L_B}{L_o} = Et_B$$

where L_B and L_o denote sample lengths at the time of failure and in the initial state, respectively.

CHAPTER IV

EXPERIMENTAL STUDIES ON STEADY SHEAR FLOW

Experimental studies on rheological behavior on steady shear flow using Rheometrics Mechanical Spectrometer are presented in this chapter. All experiments were carried out at 180°C. The shear viscosities and the first normal stress difference were calculated from Equations III.3 and III.4, respectively.

A. Transient Shear Viscosity

A.1 Results

Figures IV.1 to IV.9 show transient shear viscosities as a function of time. The shear viscosities start from zero, exhibit an overshoot, and reach a steady state. At high shear rates, the overshoot phenomena are more striking. An undershoot phenomenon follows before the steady state. The shear viscosities oscillate or decrease with time after the steady states. This phenomenon occurs after a shorter shearing period at high shear rates.

Uncoated CaCO_3 filled PS melts show larger overshoot and more conspicuous decreases of shear viscosity before and after the steady state respectively than coated CaCO_3 compounds. The transient viscosity of the 20 vol% CB filled PS melts exhibit the largest overshoot among the

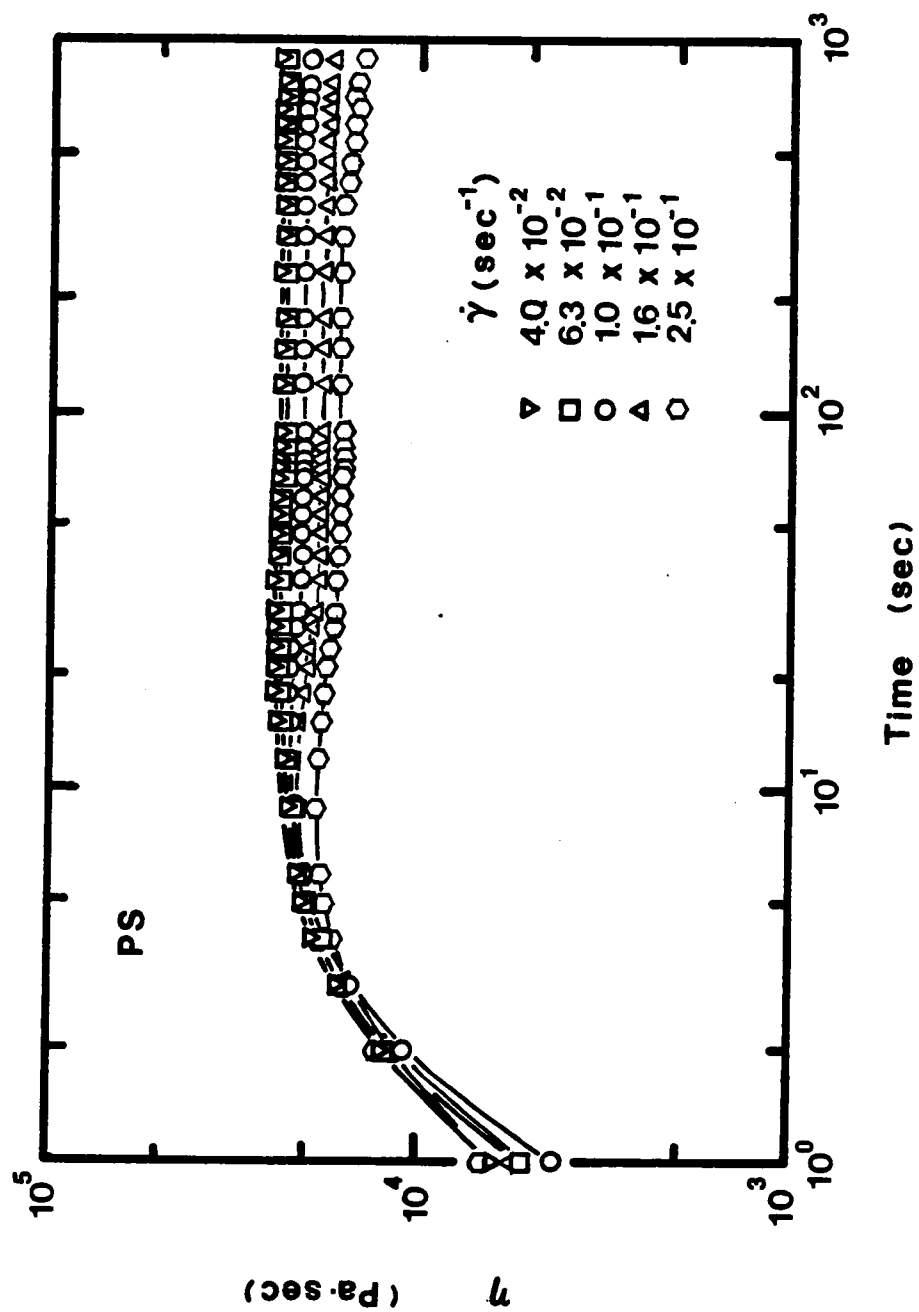


Figure IV.1. Transient shear viscosity of PS as a function of shear rate and time at 180°C.

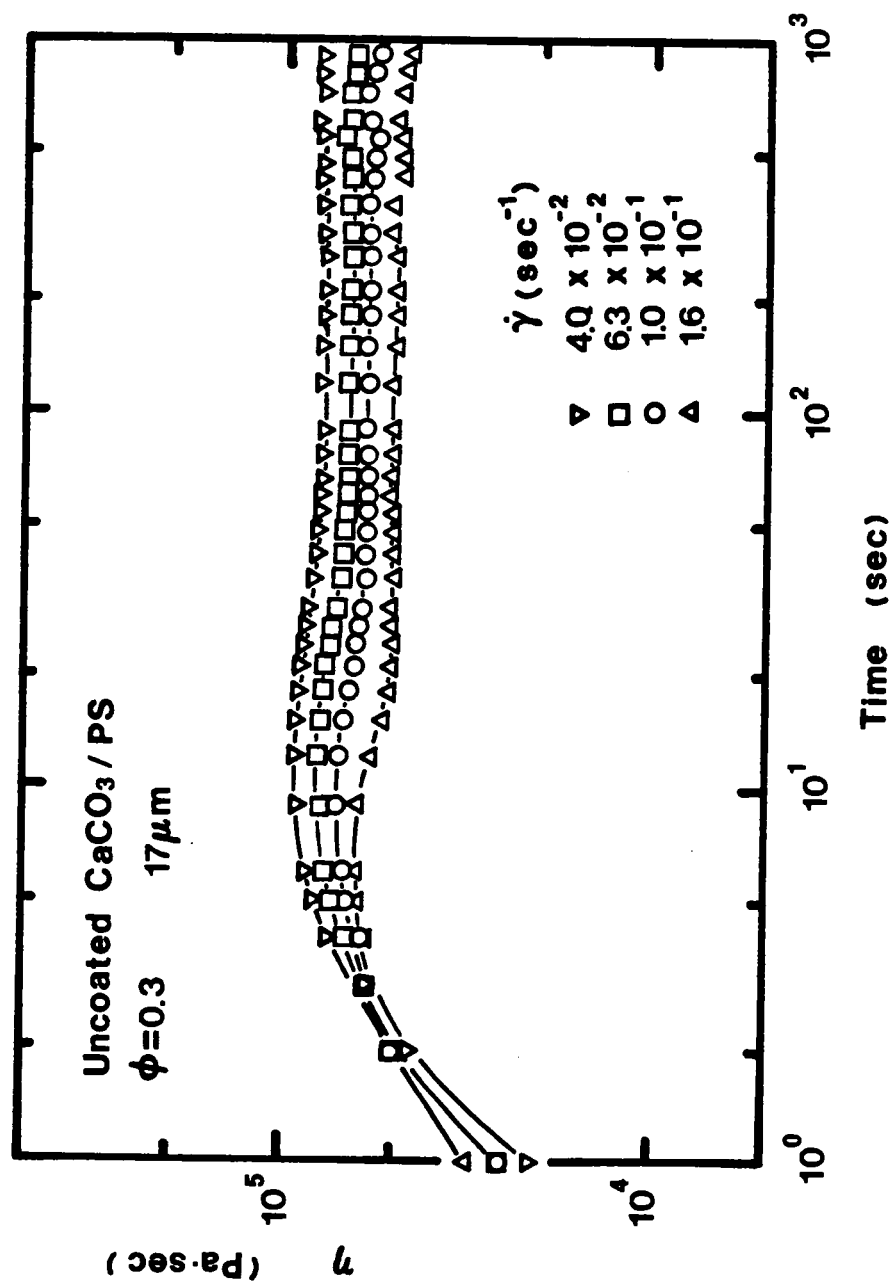


Figure IV.2. Transient shear viscosity of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 17\mu\text{m}$) as a function of shear rate and time at 180°C .

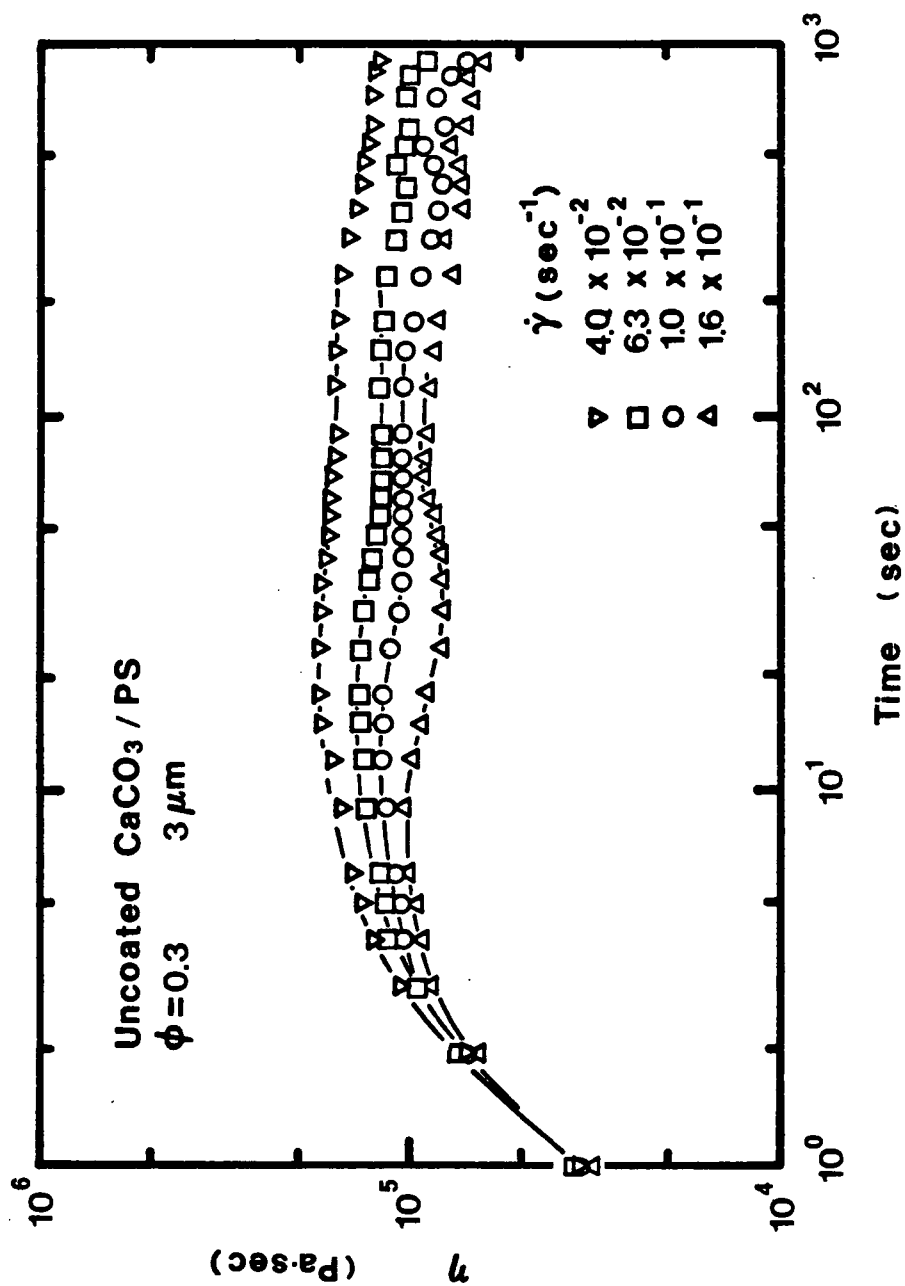


Figure IV.3. Transient shear viscosity of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 3 \mu\text{m}$) as a function of shear rate and time at 180°C .

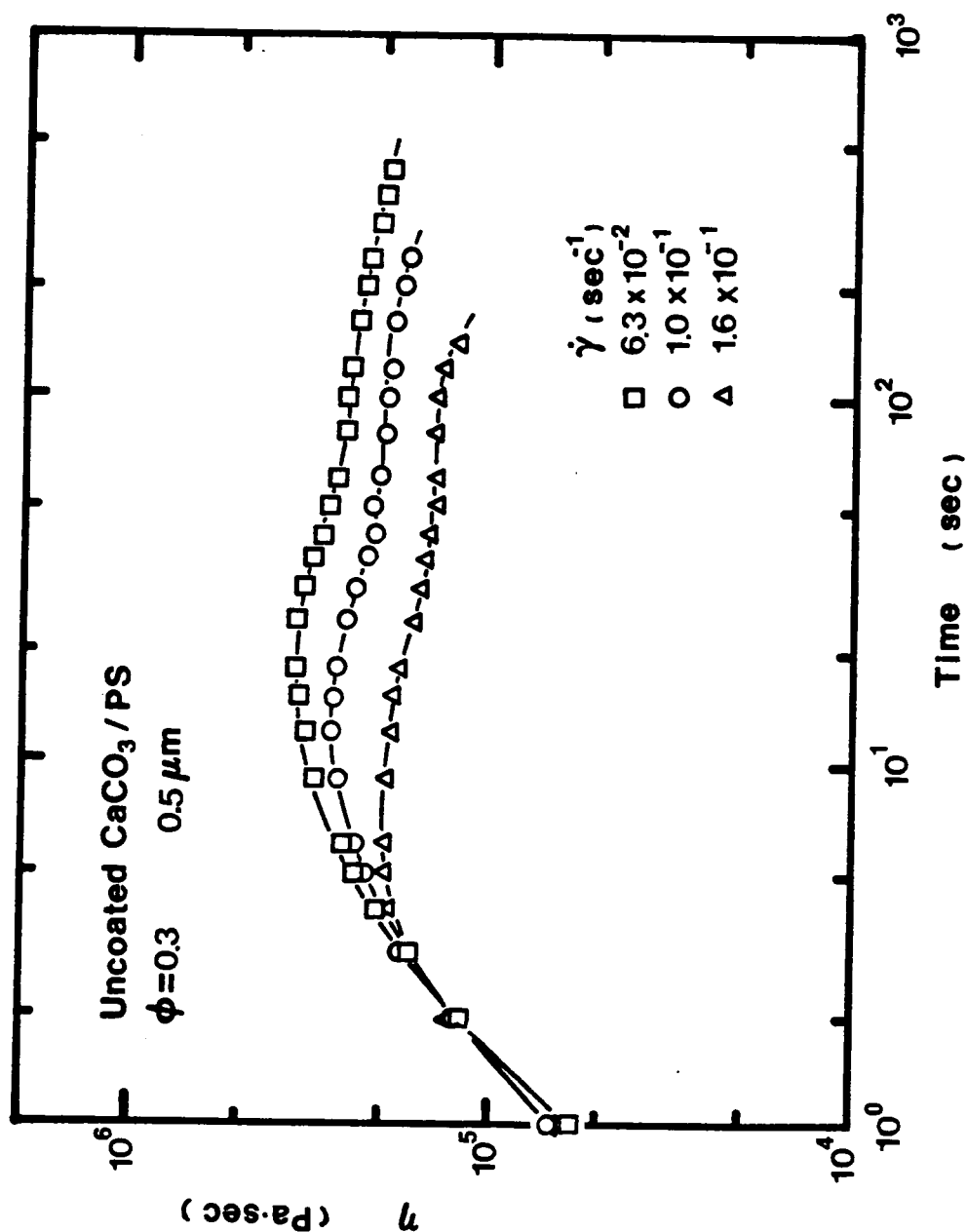


Figure IV.4. Transient shear viscosity of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.5 \mu\text{m}$) as a function of shear rate and time at 180°C .

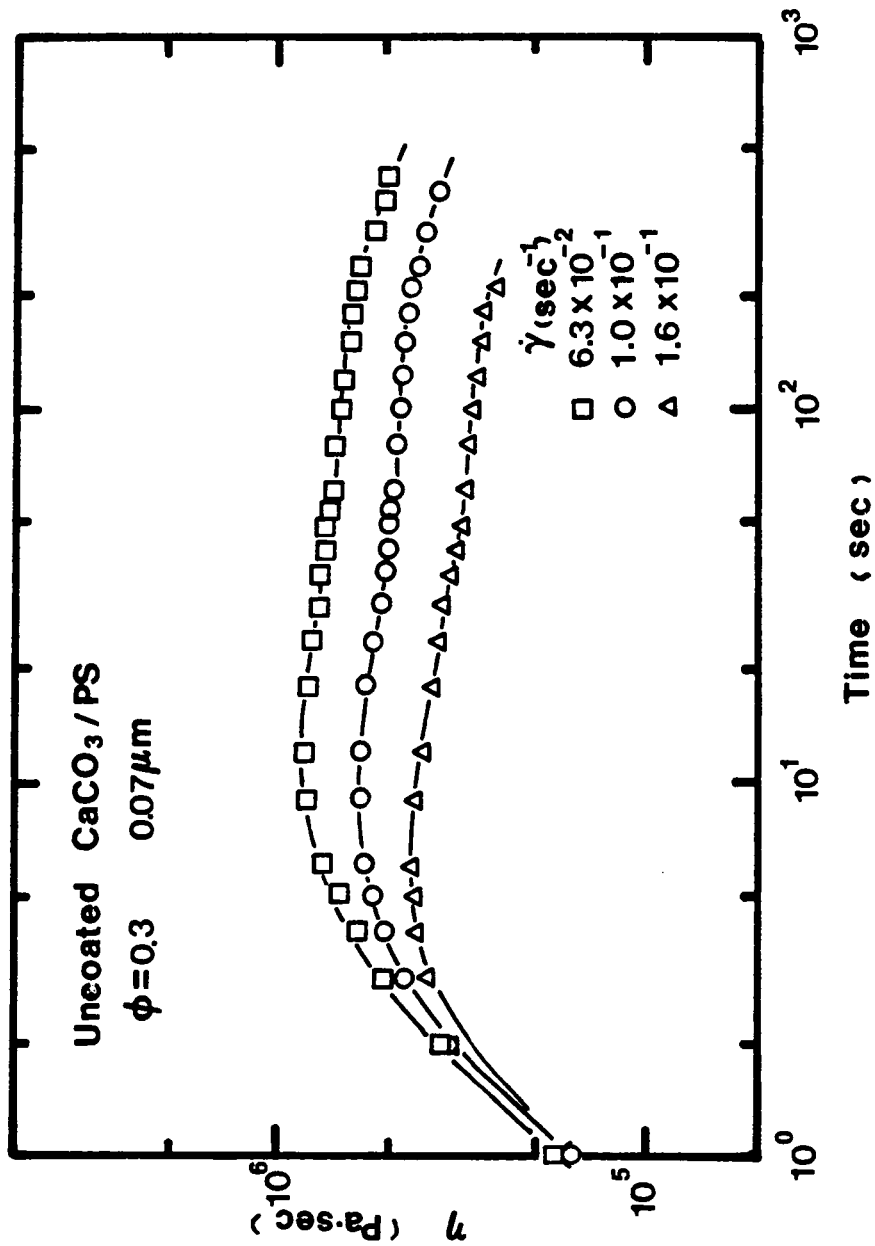


Figure IV.5. Transient shear viscosity of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.07 \mu\text{m}$) as a function of shear rate and time at 180°C .

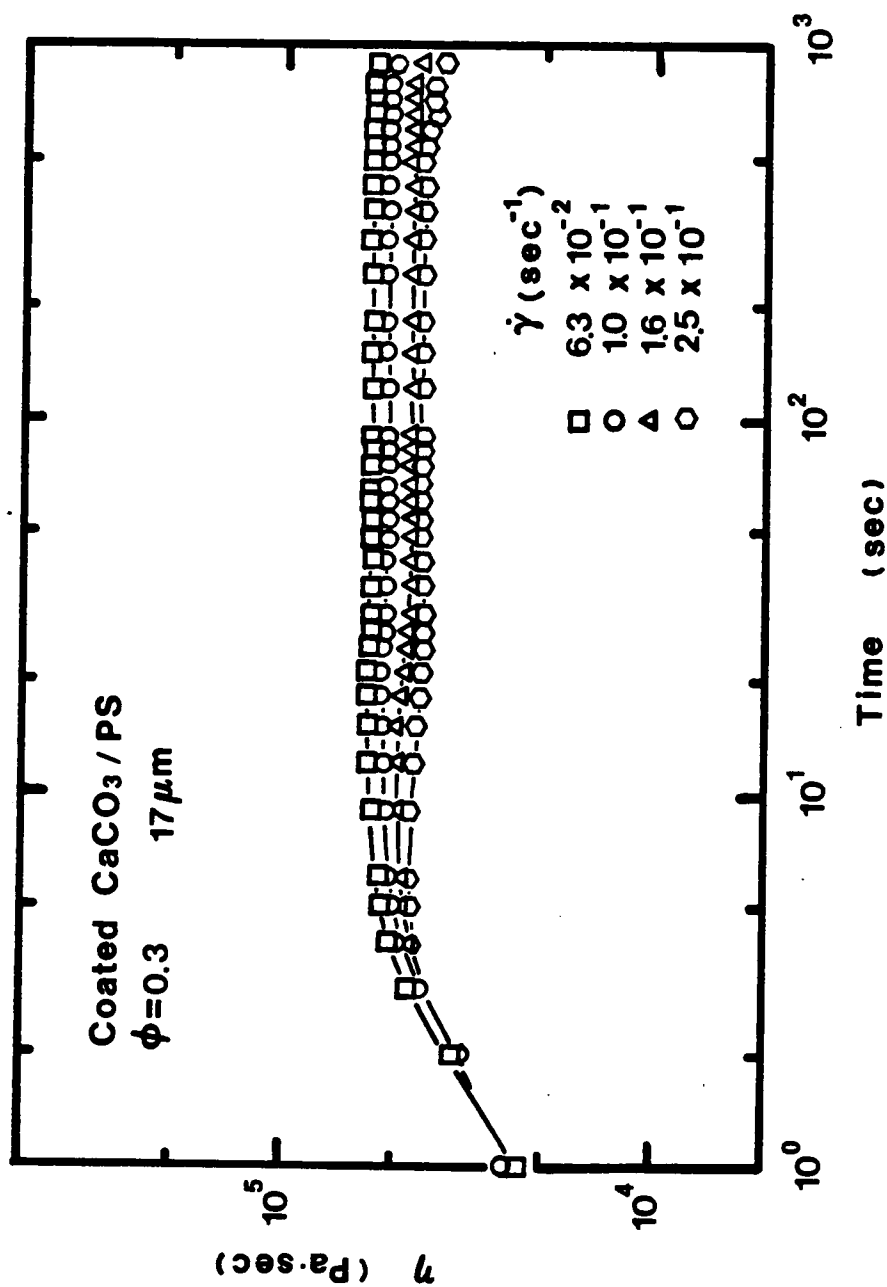


Figure IV.6. Transient shear viscosity of coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 17 \mu\text{m}$) as a function of shear rate and time at 180°C .

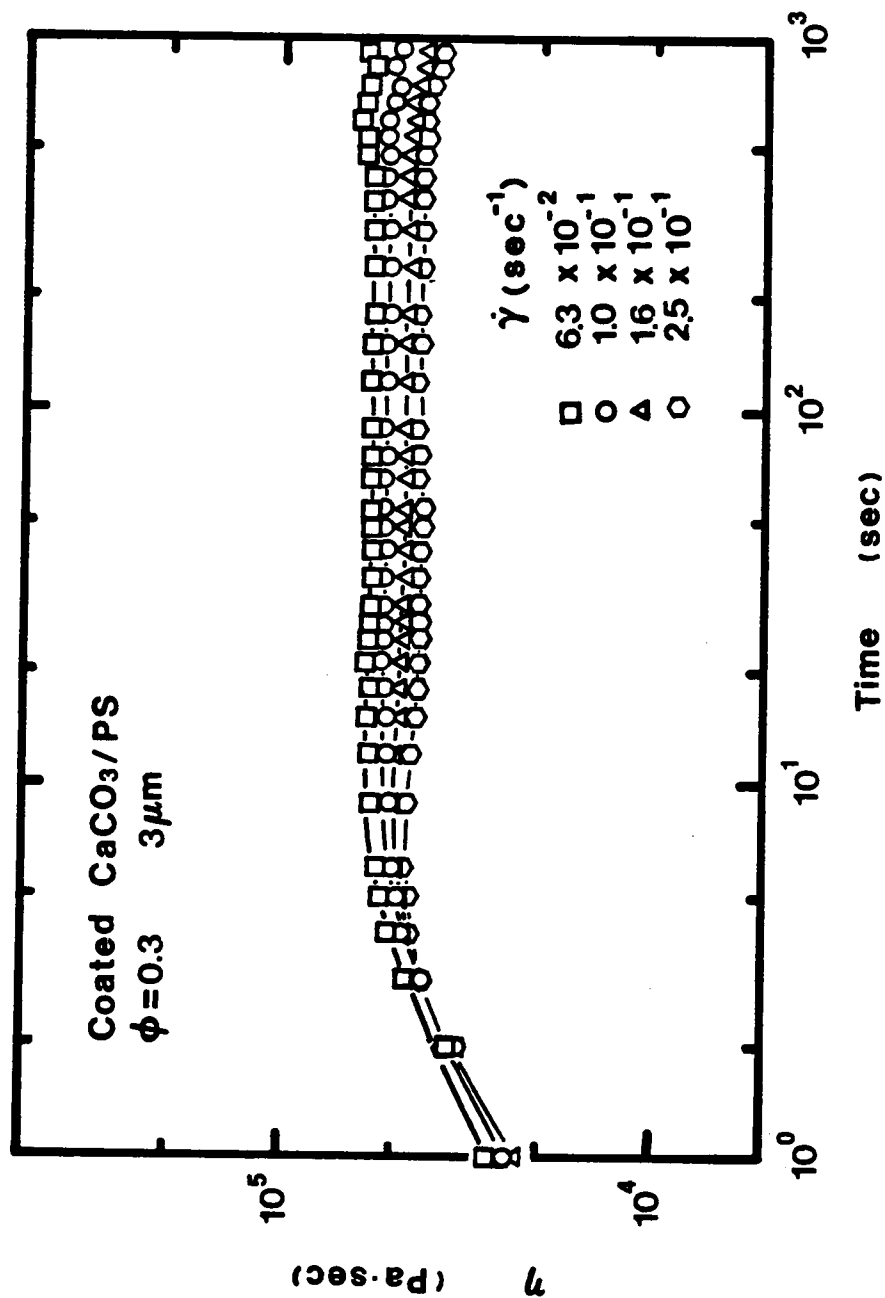


Figure IV.7. Transient shear viscosity of coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 3\mu\text{m}$) as a function of shear rate and time at 180°C .

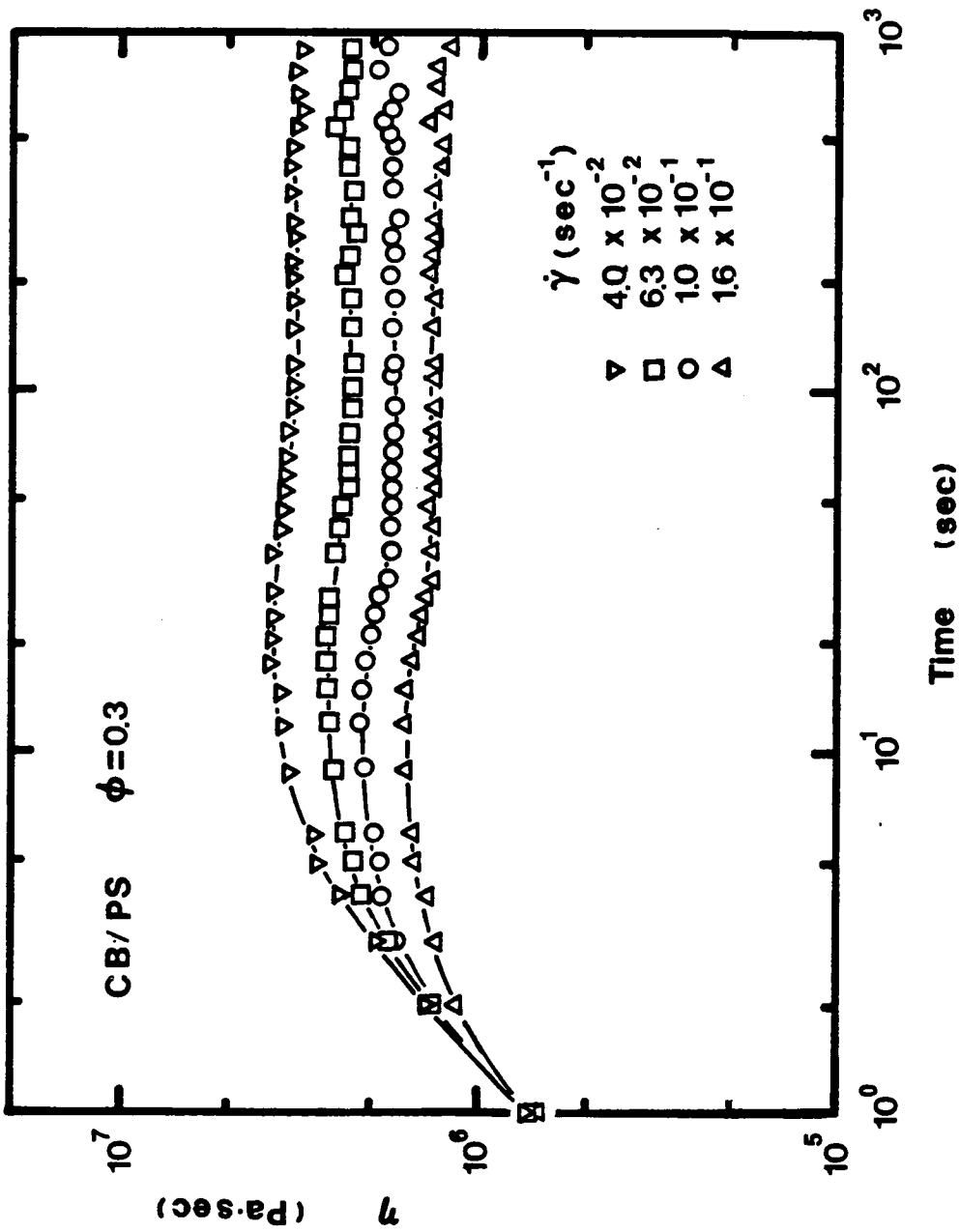


Figure IV.8. Transient shear viscosity of CB filled PS ($\phi = 0.3$, $d_p = 0.045 \mu\text{m}$) as a function of shear rate and time at 180°C .

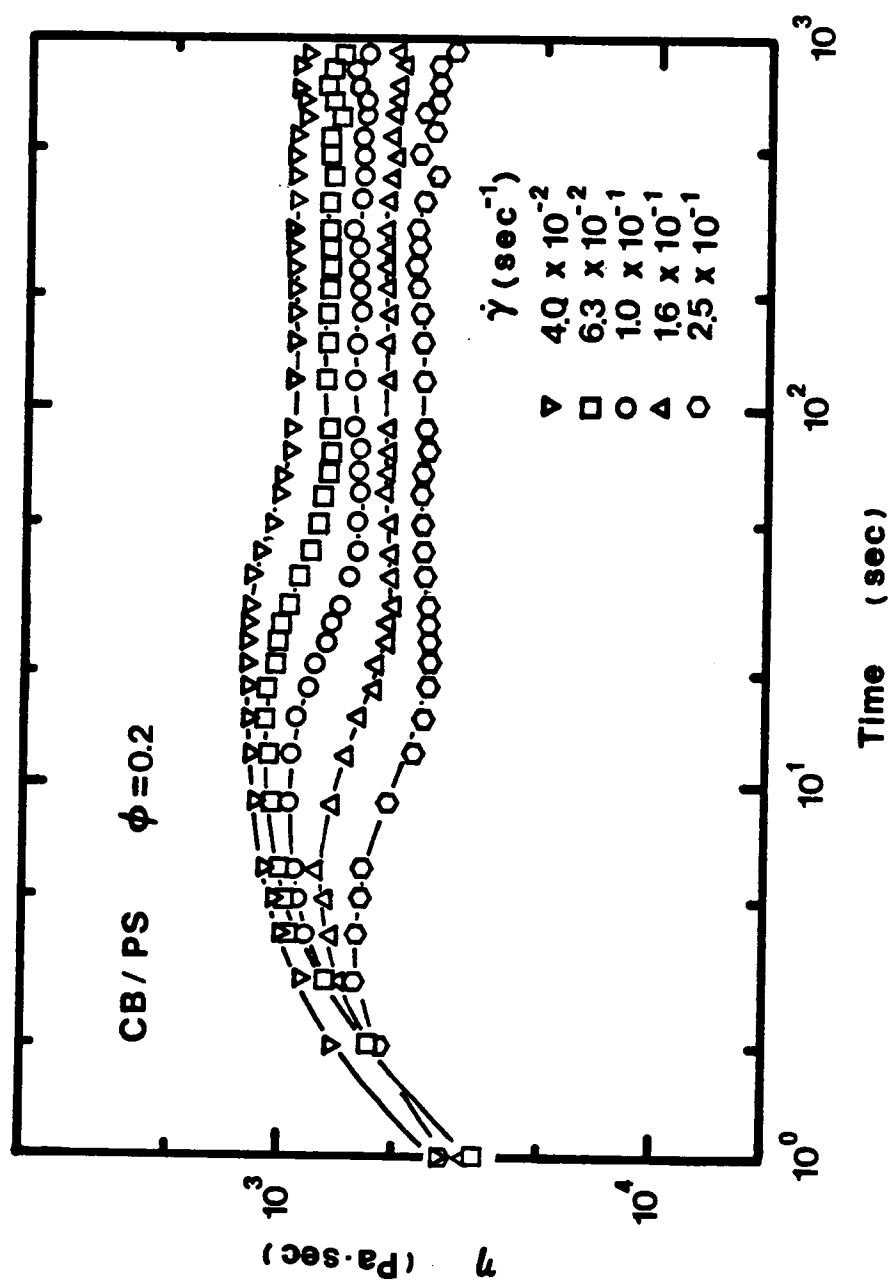


Figure IV.9. Transient shear viscosity of CB filled PS ($\phi = 0.2$, $d_p = 0.045 \mu\text{m}$) as a function of shear rate and time at 180°C .

studied filled systems. The overshoot phenomenon of the 30 vol% CB filled PS melts is smaller than those of the 20 vol% CB filled PS melts.

A.2 Discussion

A transient shear viscosity overshoot function, $F(t, \dot{\gamma})$, can be represented as

$$F(t, \dot{\gamma}) = \frac{\eta(t, \dot{\gamma}) - \eta(\infty, \dot{\gamma})}{\eta(\infty, \dot{\gamma})} \quad [\text{IV.1}]$$

where $\eta(t, \dot{\gamma})$ is the viscosity of time t and $\eta(\infty, \dot{\gamma})$ is the steady state viscosity at a certain shear rate. Figures IV.10 and IV.11 show the transient shear viscosity overshoot function of various compounds at shear rates of 0.063 sec^{-1} and 0.16 sec^{-1} , respectively. Steady states are achieved in about 70 seconds at $\dot{\gamma} = 0.063 \text{ sec}^{-1}$. At a higher shear rate, $\dot{\gamma} = 0.16 \text{ sec}^{-1}$, the period to achieve the maximum value of overshoot function, $F(t, \dot{\gamma})$, and steady state decrease. The remarkable difference on the periods to reach steady states was not observed among the various compounds.

The steady state of uncoated CaCO_3 (average particle diameter = $0.5 \mu\text{m}$, $0.07 \mu\text{m}$) filled PS compounds is not clear as shown in Figures IV.4 and IV.5 (pp. 67, 68). We can find the steady states at about 80 seconds and at about 60 seconds for $\dot{\gamma} = 0.063 \text{ sec}^{-1}$ and $\dot{\gamma} = 0.16 \text{ sec}^{-1}$ respectively.

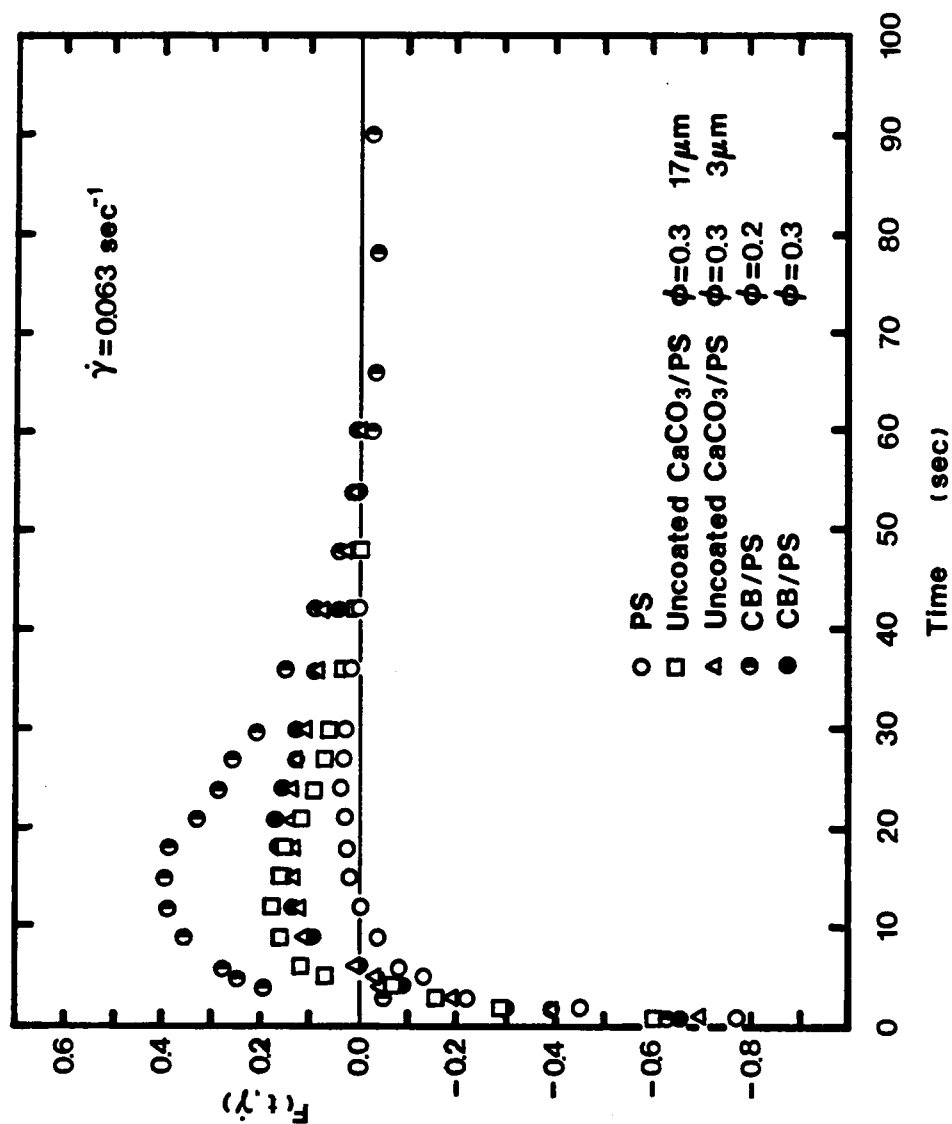


Figure IV.10. Transient viscosity overshoot function of various compounds at $\dot{\gamma} = 0.063 \text{ sec}^{-1}$.

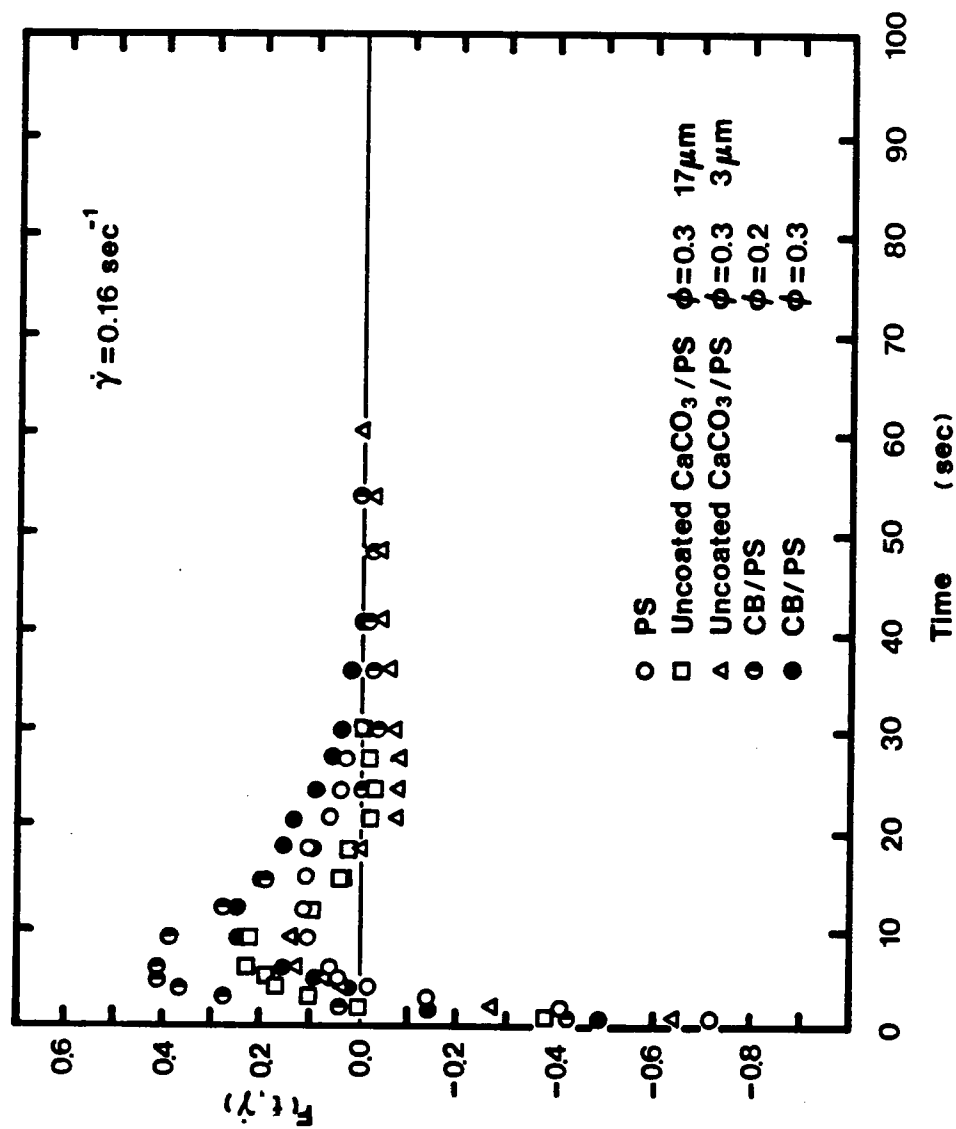


Figure IV.11. Transient viscosity overshoot function of various compounds at $\dot{\gamma} = 0.16 \text{ sec}^{-1}$.

Table IV.1 shows the maximum values of shear viscosity overshoot function $F(\dot{\gamma})_{\max}$, that is,

$$F(\dot{\gamma})_{\max} = \frac{\eta(\dot{\gamma})_{\max} - \eta(\infty, \dot{\gamma})}{\eta(\infty, \dot{\gamma})} \quad [\text{IV.2}]$$

The maximum value of shear viscosity overshoot function increases with increasing shear rate. Addition of uncoated CaCO_3 and CB makes $F(\dot{\gamma})_{\max}$ larger. $F(\dot{\gamma})_{\max}$ of coated CaCO_3 filled PS melts are smaller than those of PS melt.

B. Complex Shear History Experiment

B.1 Results

Figures IV.12 to IV.14 show the transient shear viscosity of the complex shear history measurements. Figure IV.12 shows the behavior of the pure PS melt. The maximum values of the viscosity overshoot occurring after 210 seconds and 510 seconds do not show very remarkable differences from the maximum overshoot value of the virgin sample (open circle symbol in Figure IV.12). The viscosity overshoot grows during the intervening period. The longer interval period shows the more recovery of overshoot. The transient viscosity after 1800 interval agrees with the virgin sample's.

The transient viscosity of complex shear history for uncoated CaCO_3 ($d_p = 17 \mu\text{m}$)/PS is shown in Figure IV.13. We can observe the viscosity overshoot recovery after the

Table IV.1

Maximum Values of Shear Viscosity Overshoot
Function, $F(\dot{\gamma})_{\max}$, for PS and
Filled Systems

System	Volume Content (-)	Average Particle Size (μm)	Shear Rate (sec^{-1})	$F(\dot{\gamma})_{\text{max}}$ (-)
PS	0.0	-	0.063	0.04
			0.16	0.13
Uncoated CaCO_3/PS	0.3	17	0.063	0.18
			0.16	0.20
		3	0.063	0.13
			0.16	0.14
		0.5	0.063	0.34
			0.16	0.42
		0.07	0.063	0.21
			0.16	0.34
Coated CaCO_3/PS	0.3	17	0.063	0.01
			0.16	0.09
		3	0.063	0.01
			0.16	0.09
CB/PS	0.2	0.045	0.063	0.40
			0.16	0.41
	0.3		0.063	0.18
			0.16	0.24

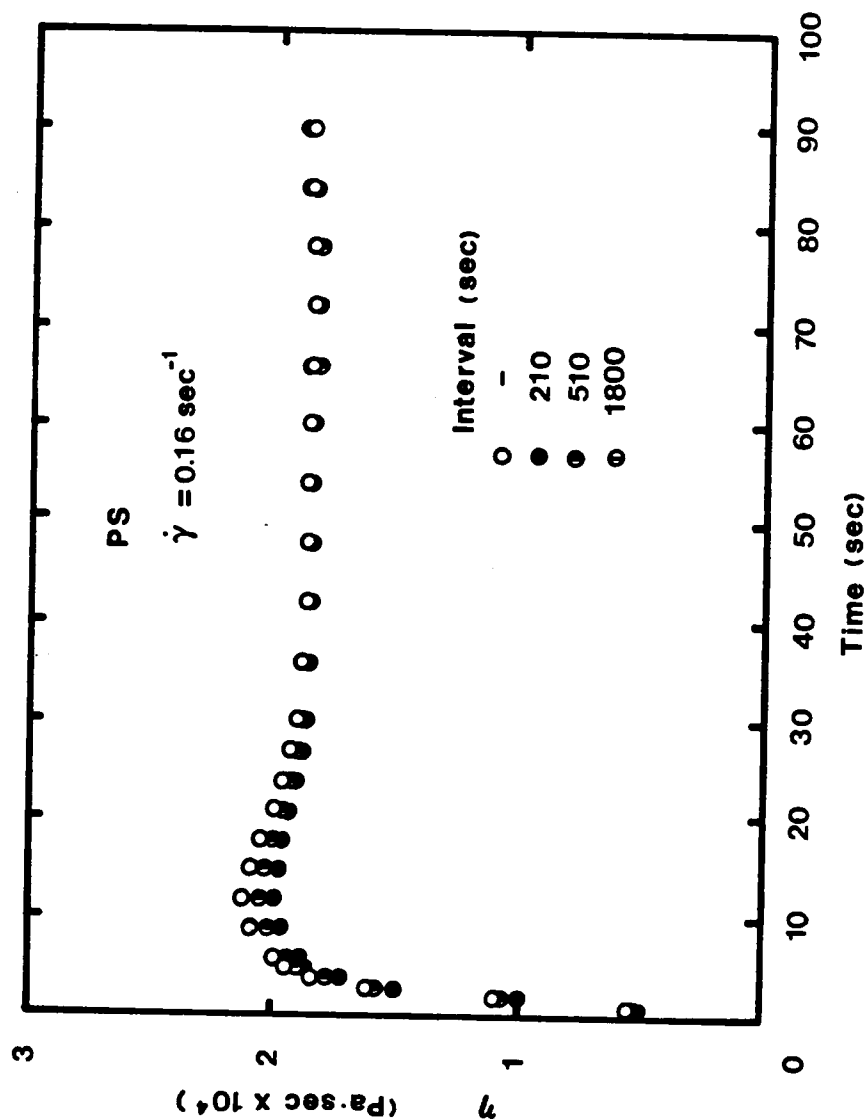


Figure IV.12. Transient shear viscosity of PS in complex shear history experiment at 180°C.

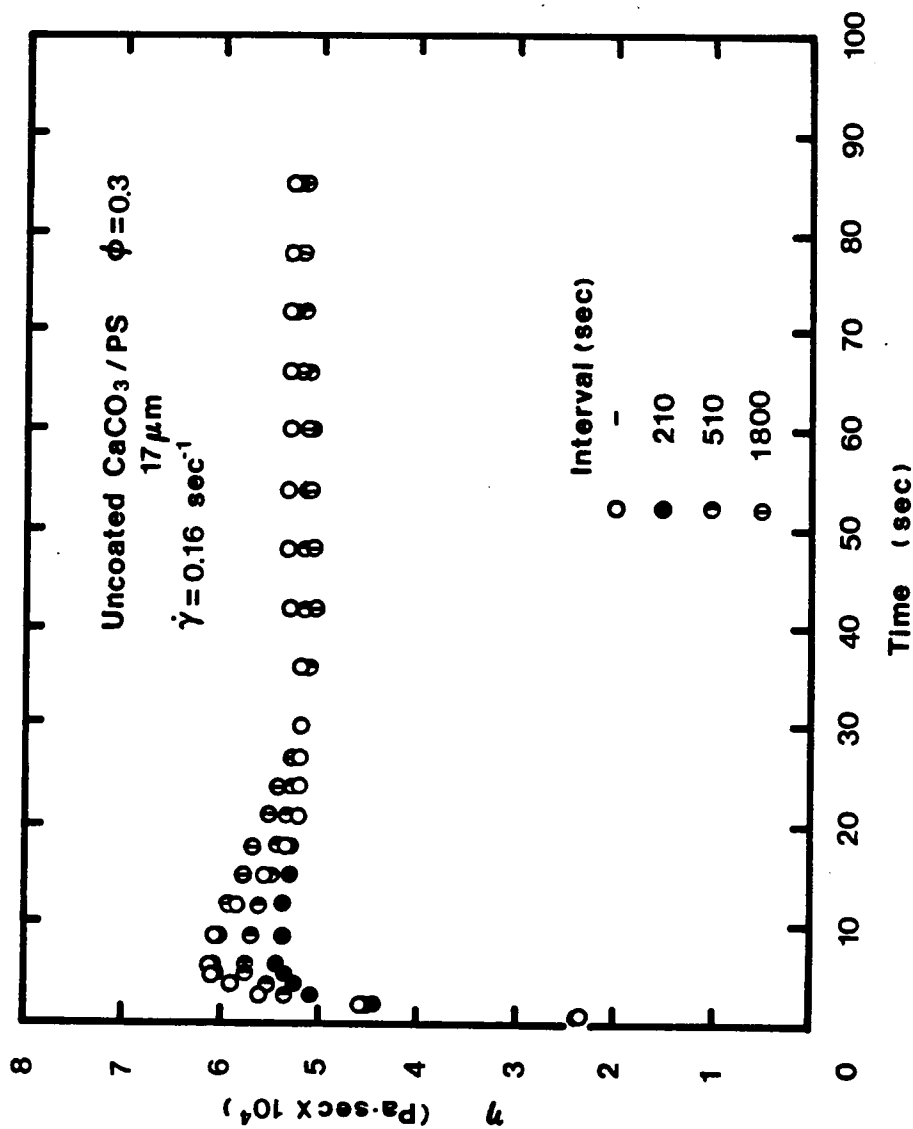


Figure IV.13. Transient shear viscosity of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 17 \mu\text{m}$) in complex shear history experiment at 180°C .

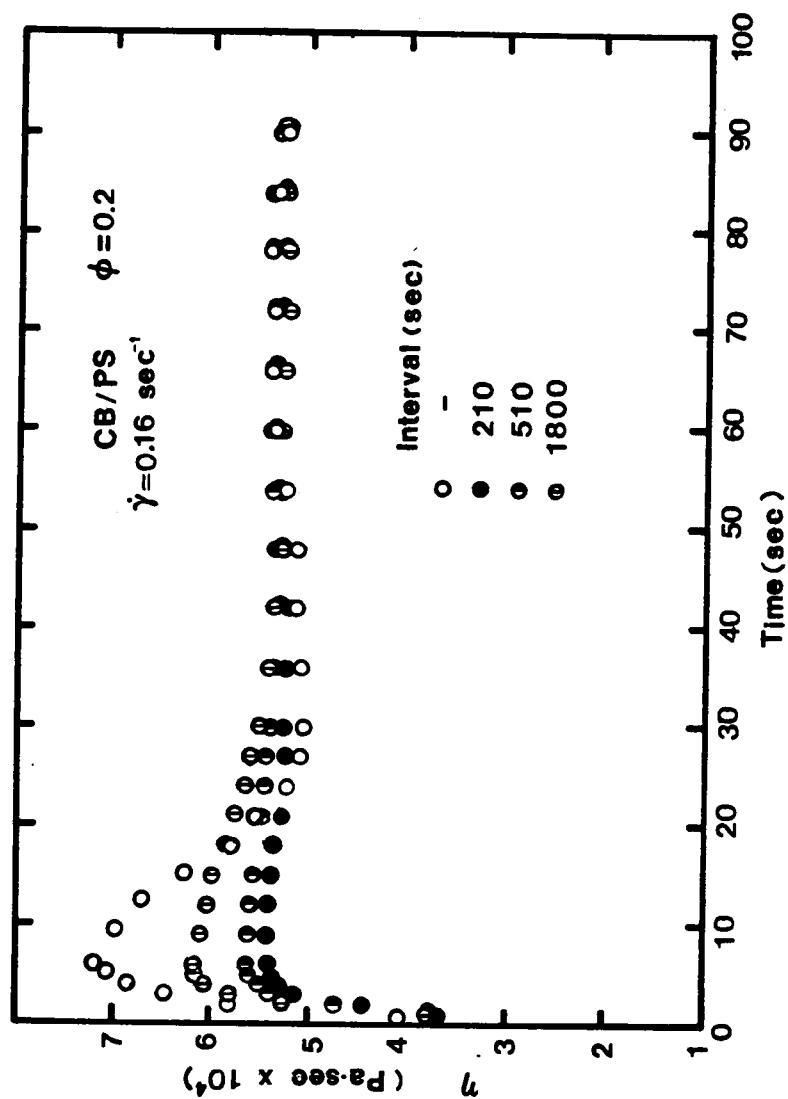


Figure IV.14. Transient shear viscosity of CB filled PS ($\phi = 0.2$, $d_p = 0.045 \mu\text{m}$) in complex shear history experiment at 180°C .

intervals again. The maximum value of the viscosity overshoot after the interval of 1800 seconds almost agrees with that of the virgin sample. The viscosity decay after the maximum value is, however, different from that of the virgin sample. The viscosity decay of the sample which has a previous deformation (interval = 1800 seconds) is slower than that of the original sample. The undershoot phenomenon after the overshoot is unclear in the case of previously sheared sample.

Figure IV.14 shows the case of CB filled PS melt ($\phi = 0.2$). This compound has the largest overshoot among the samples used for this work. This shows that the overshoot recovers more with longer interval periods between the first shear deformation and the second shear deformation. However, the maximum value of the overshoot does not reach that of the virgin sample even after the interval of 1800 seconds. Again, the undershoot phenomenon is unclear in the previously sheared sample.

B.2 Discussion

The viscosity overshoot function, $F(\dot{\gamma})_{\max}$, has been summarized in Table IV.2. The percentage recovery of $F(\dot{\gamma})_{\max}$, that is,

$$\frac{F(\dot{\gamma})_{\max} \text{ of sheared sample}}{F(\dot{\gamma})_{\max} \text{ of virgin sample}} \times 100 \quad [\text{IV.3}]$$

is also indicated. PS melt shows the fastest recovery,

Table IV.2

Maximum Values of Overshoot Function, $F(\dot{\gamma})_{\max}$,
of Complex Shear History Experiment
at $\dot{\gamma} = 0.16 \text{ sec}^{-1}$

Interval (sec)	PS		Uncoated CaCO_3/PS $dp = 17 \text{ } \mu\text{m}$ $\phi = 0.3$		CB/PS $dp = 0.045$ $\phi = 0.2$	
	$F(\dot{\gamma})_{\max}$ (-)	Recovery of $F(\dot{\gamma})_{\max}$ (%)	$F(\dot{\gamma})_{\max}$ (-)	Recovery of $F(\dot{\gamma})_{\max}$ (%)	$F(\dot{\gamma})_{\max}$ (-)	Recovery of $F(\dot{\gamma})_{\max}$ (%)
Virgin	0.13	-	0.20	-	0.41	-
210	0.06	46	0.04	20	0.04	10
510	0.10	77	0.12	60	0.08	20
1800	0.13	100	0.17	85	0.19	46

followed by uncoated CaCO_3 ($d_p = 17 \mu\text{m}$, $\phi = 0.3$) filled PS melt. The slowest recovery is shown by 20 vol% CB filled PS. This order agrees with the order of the yield stress and viscosity. The PS melt has no yield stress and the lowest viscosity. The 20 vol% CB filled PS has the largest yield stress ($1.3 \times 10^3 \text{ Pa}$) and the highest viscosity among these three. (Uncoated CaCO_3 filled PS has the yield stress of $1 \times 10^2 \text{ Pa}$.)

C. Steady State Shear Viscosity

C.1 Results

Figures IV.15 to IV.17 show the steady state shear viscosities as a function of shear rate for PS, as well as uncoated CaCO_3 , coated CaCO_3 and CB filled PS melts.

The steady state shear viscosities of uncoated CaCO_3 filled PS melts are dependent on the average particle sizes of fillers (Figure IV.15). The systems which are filled with smaller particles show higher steady state shear viscosities. Uncoated CaCO_3 filled PS systems do not possess a Newtonian region at low shear rates, but are always non-Newtonian. The differences in viscosities of the PS melt and the compounds are greater in the low shear rate region.

The steady state shear viscosities of the coated CaCO_3 filled PS melts exhibit less dependence on average particle sizes of fillers (Figure IV.16). In case of large particle

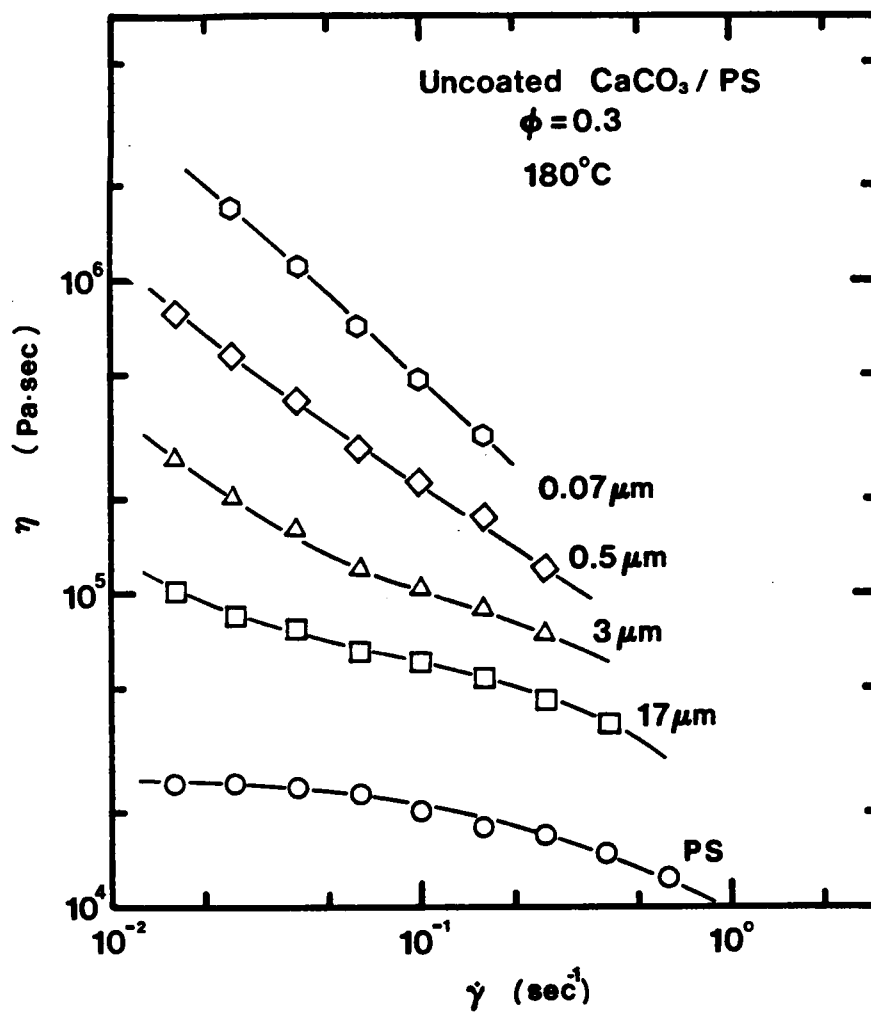


Figure IV.15. Steady state shear viscosity of uncoated CaCO_3 filled PS as a function of shear rate at 180°C .

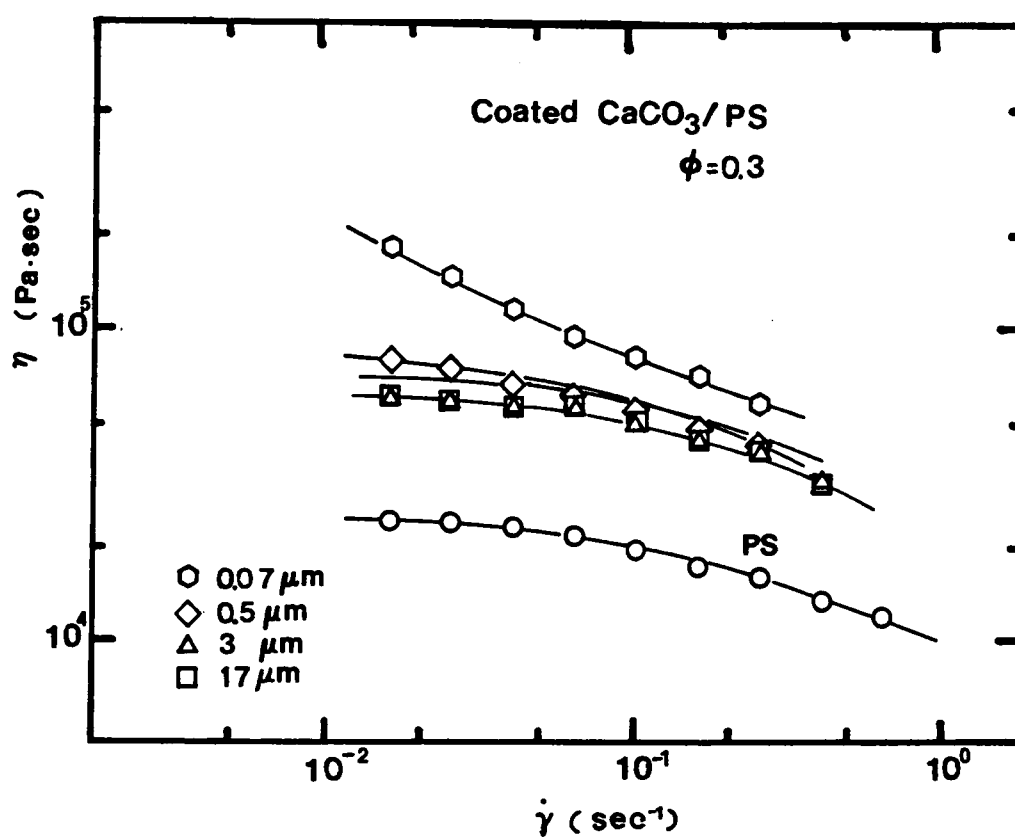


Figure IV.16. Steady state shear viscosity of coated CaCO_3 filled PS as a function of shear rate at 180°C .

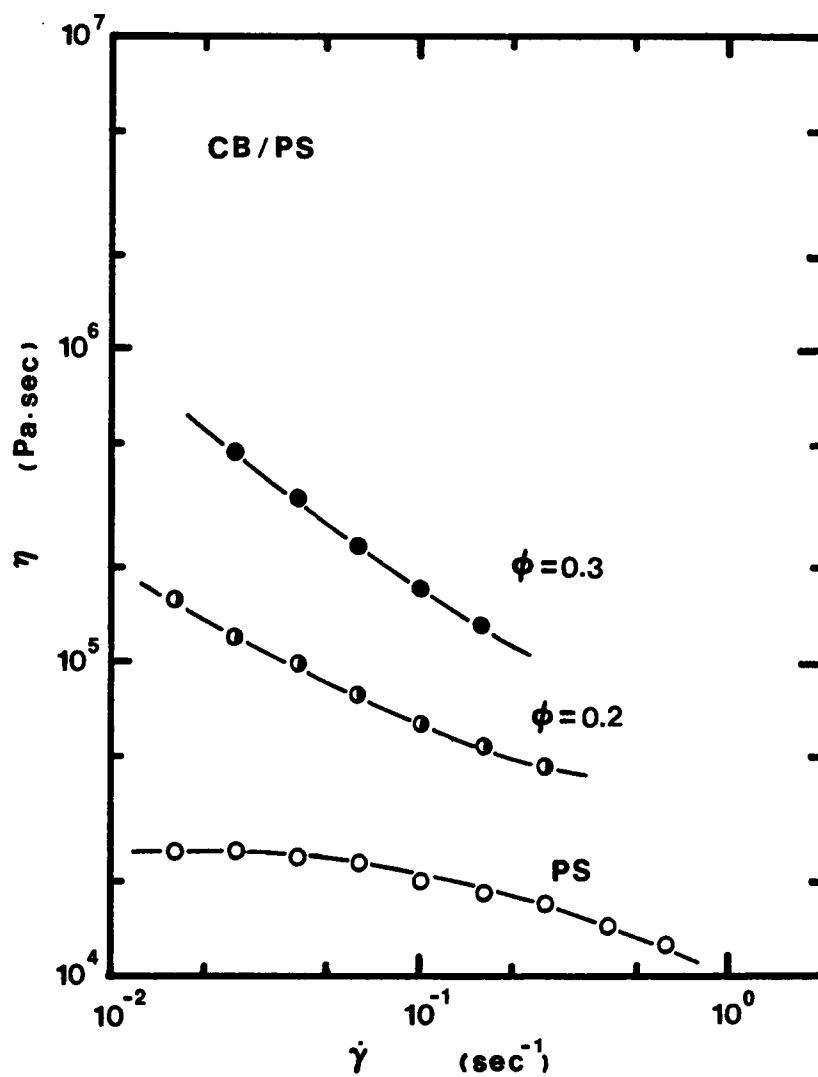


Figure IV.17. Steady state shear viscosity of CB filled PS as a function of shear rate at 180°C.

filled systems, there exist Newtonian regions at low shear rates.

The steady state shear viscosity increased with loading level of CB (Figure IV.17). The CB filled PS melts do not possess a Newtonian region and show greater differences in viscosities from PS melt in the low shear rate region.

C.2 Discussion

Figures IV.18 to IV.20 show steady state shear viscosities as a function of shear stress. The viscosities of uncoated CaCO_3 and CB filled PS tend to infinity at certain shear stresses. These shear stresses are considered yield stresses. The yield stress of uncoated CaCO_3 filled PS systems varies with the average particle sizes (Figure IV.18). Increasing yield stresses are observed with decreasing particle sizes. The effect of loading level on yield stresses is shown in CB filled PS systems (Figure IV.20). The yield stress increases with increasing loading level of filler.

Stearic Acid surface coating on CaCO_3 reduces the yield stress of systems (Figure IV.19). Indeed, the existence of yield stresses is uncertain within the shear rate region of this study except for the smallest coated particle compound.

Figures IV.21 to IV.23 show the Casson's plots (C-4) of compounds. Casson's equation is

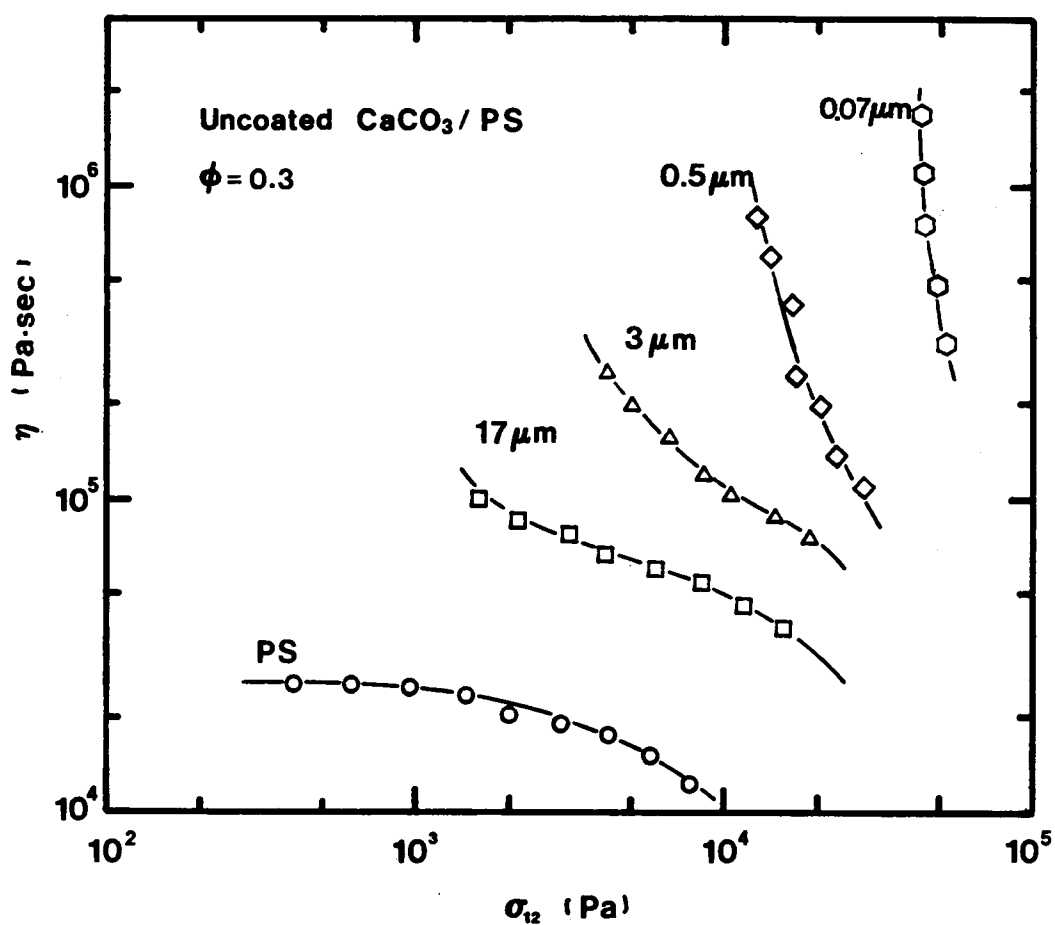


Figure IV.18. Steady state shear viscosity of uncoated CaCO_3 filled PS as a function of shear stress at 180°C .

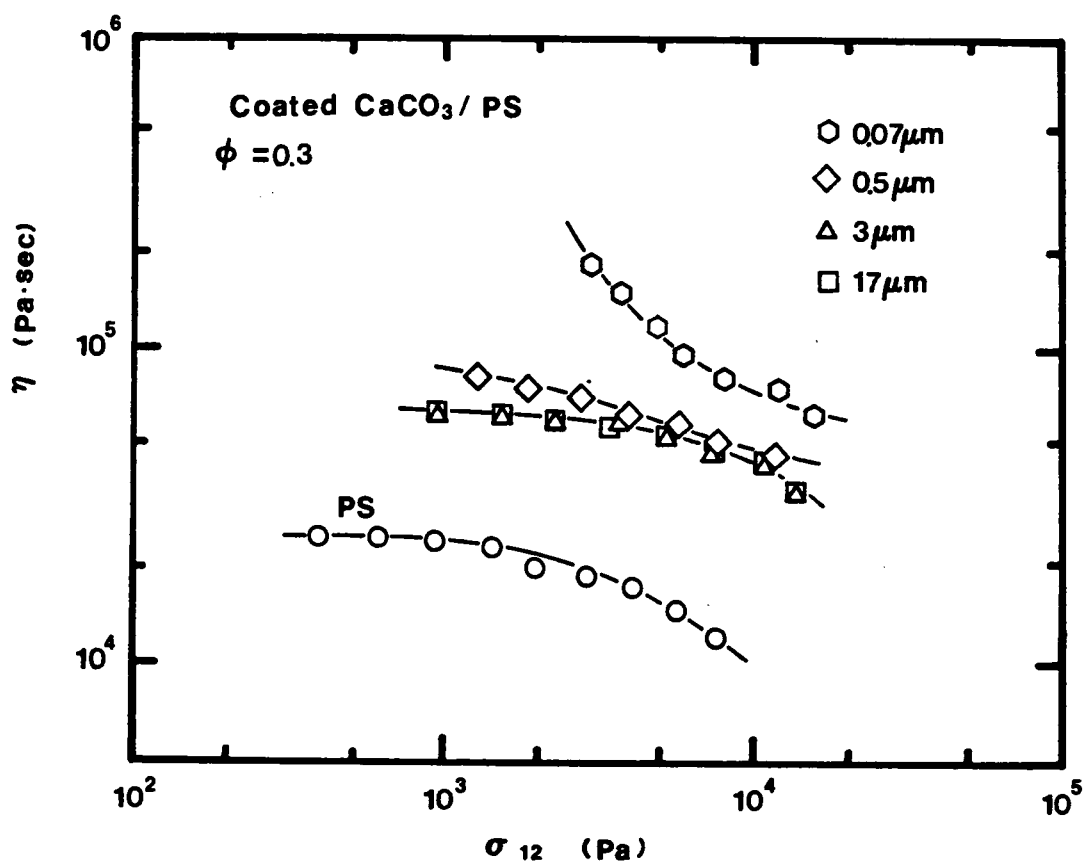


Figure IV.19. Steady state shear viscosity of coated CaCO_3 filled PS as a function of shear stress at 180°C .

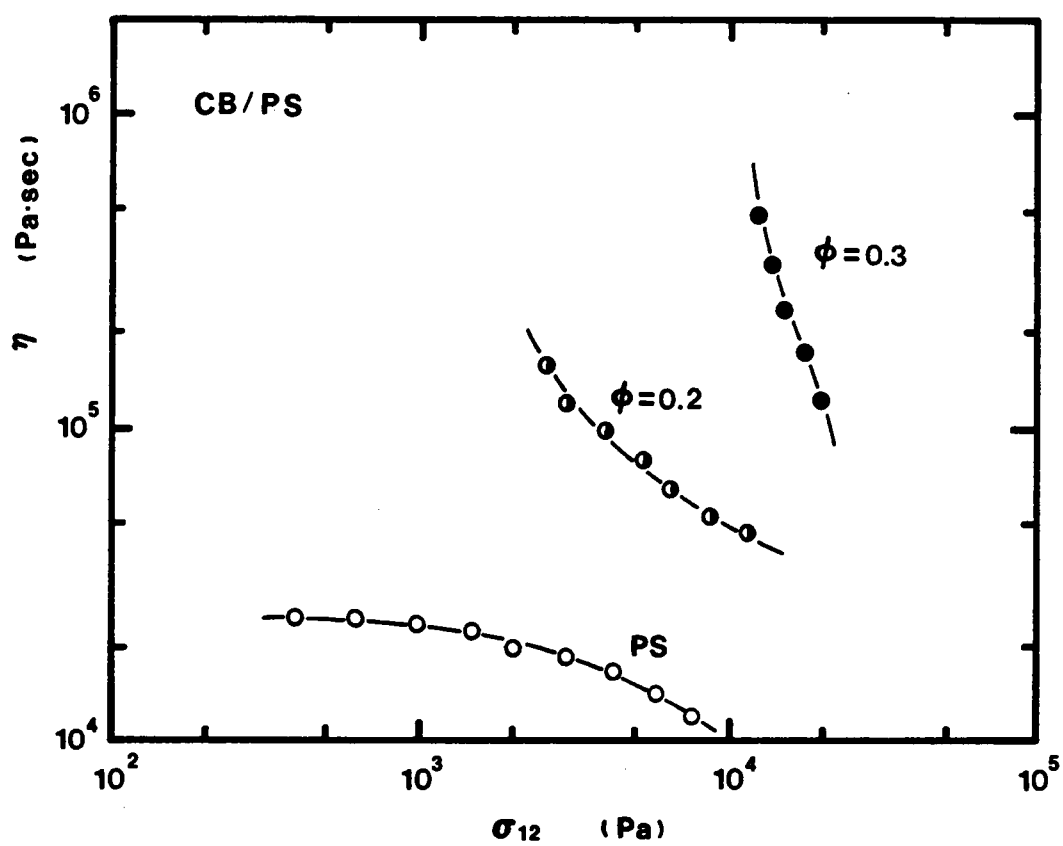


Figure IV.20. Steady state shear viscosity of CB filled PS as a function of shear stress at 180°C.

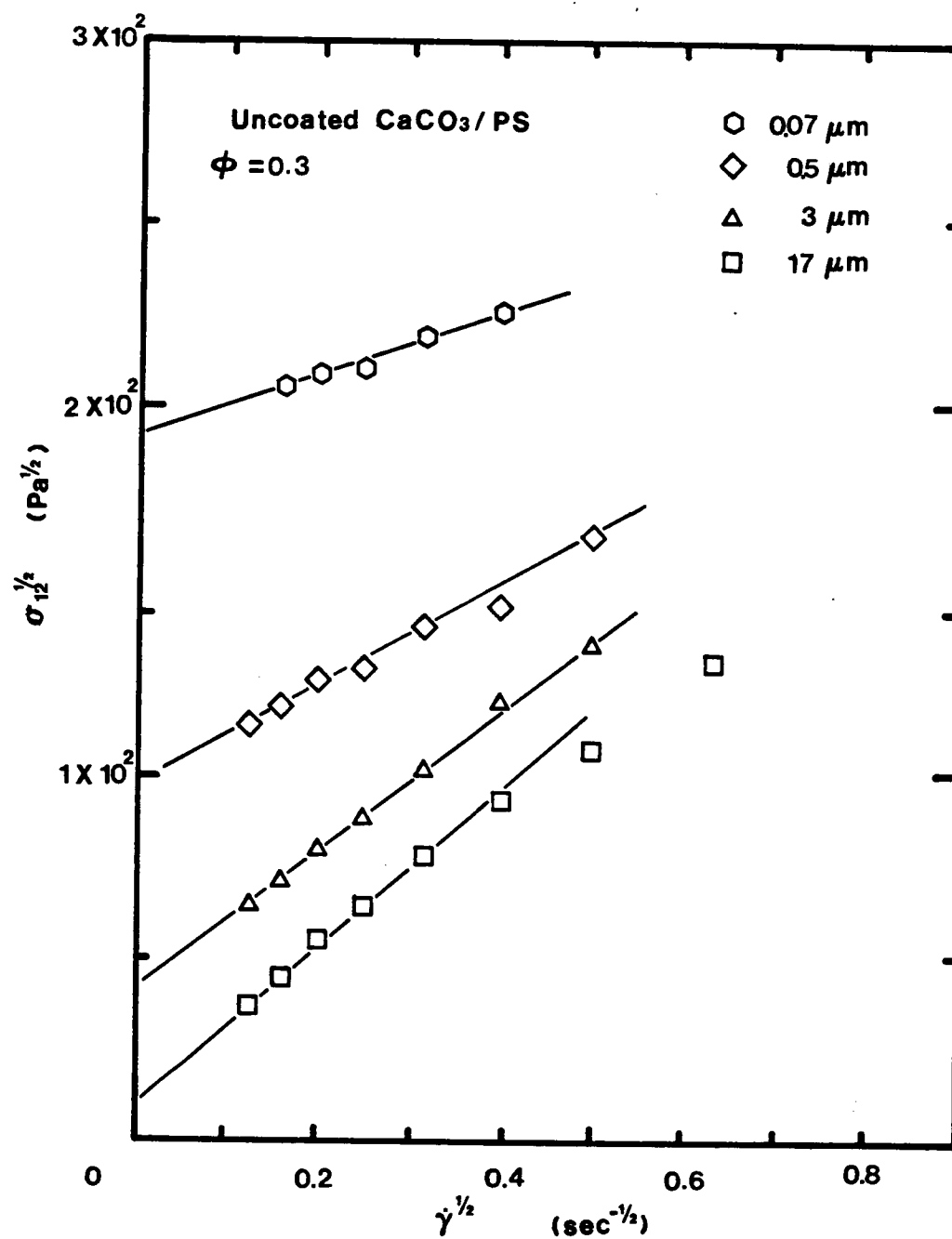


Figure IV.21. Casson's plot for uncoated CaCO_3 filled PS.

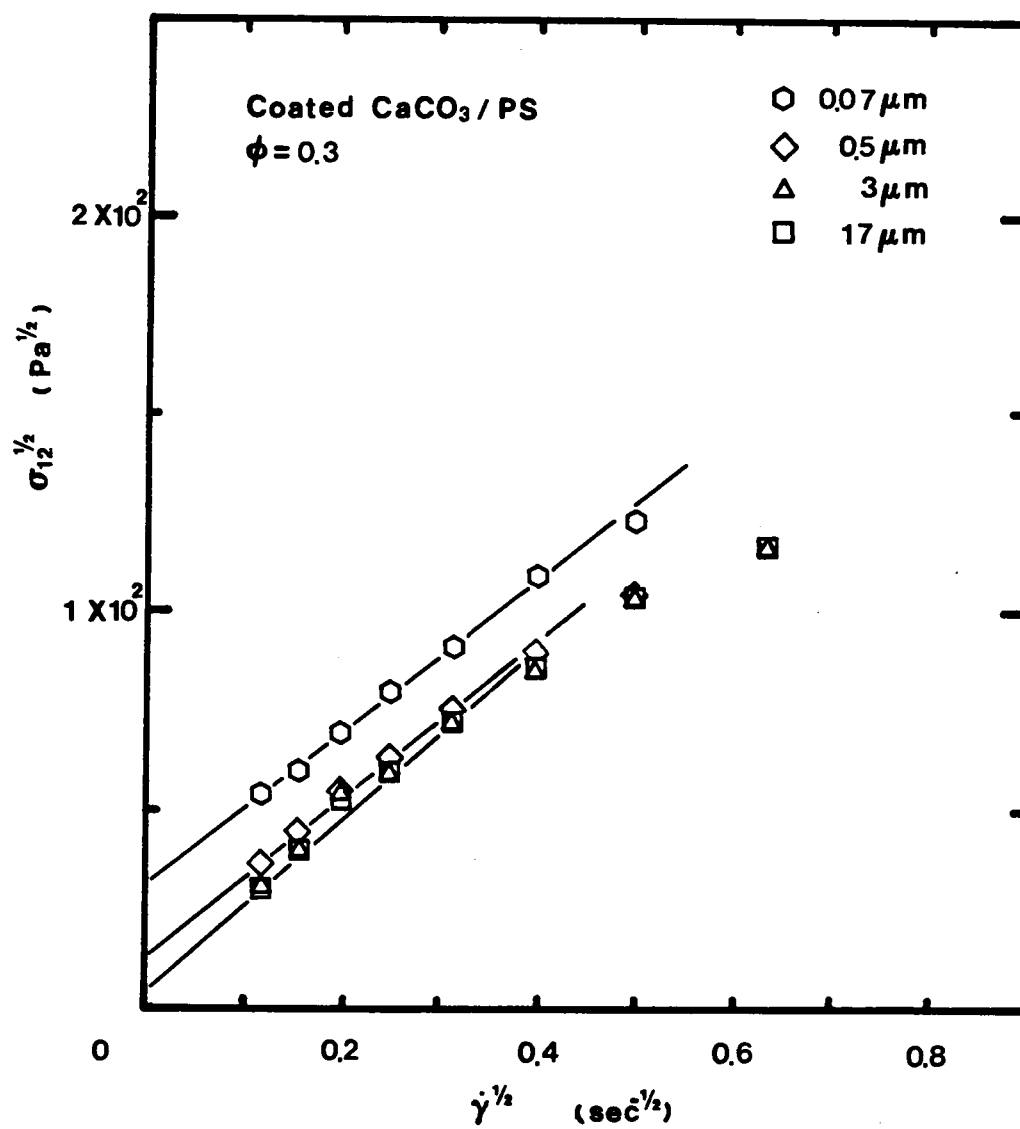


Figure IV.22. Casson's plot for coated CaCO_3 filled PS.

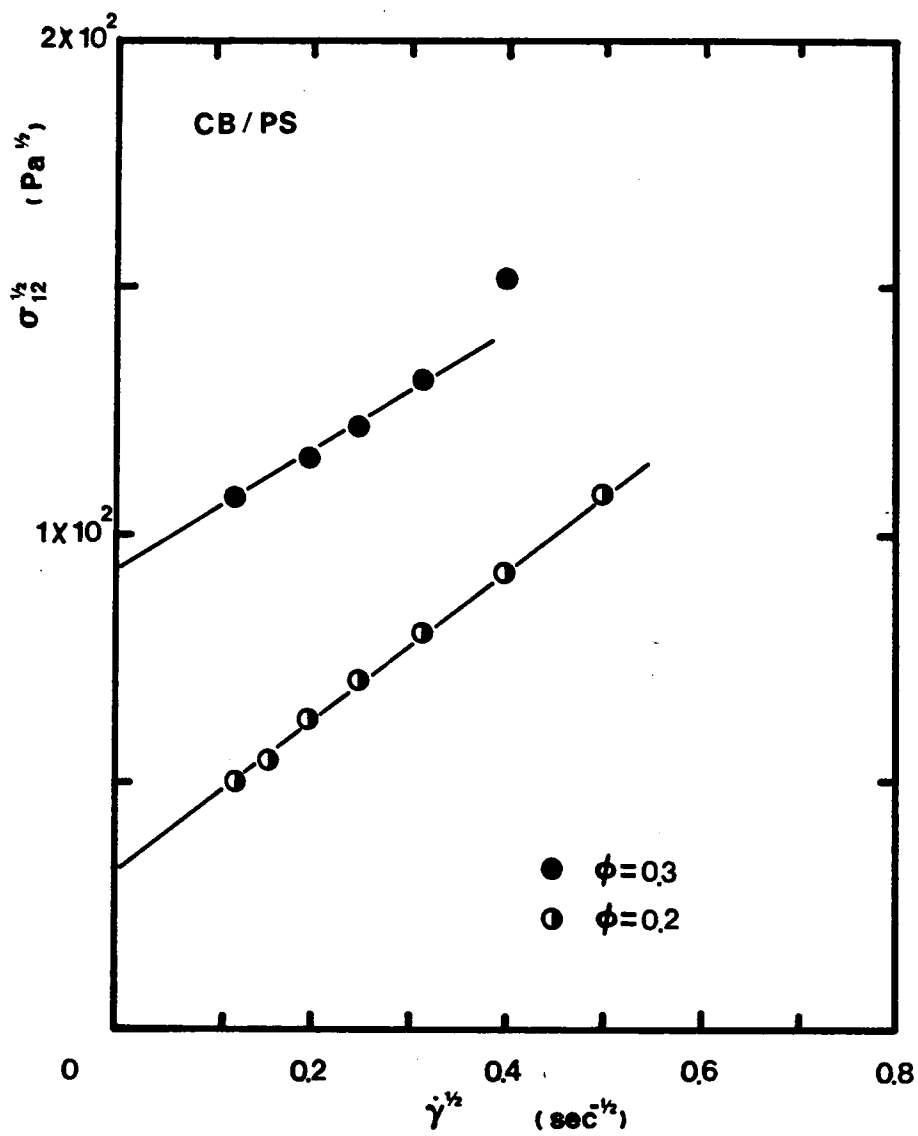


Figure IV.23. Casson's plot for CB filled PS.

$$\sigma_{12}^{1/2} = Y^{1/2} + k\dot{\gamma}^{1/2} \quad [\text{IV.4}]$$

where σ_{12} is the shear stress, Y is the yield stress and k is a constant. The yield stress is evaluated as an extrapolated value of $\sigma_{12}^{1/2}$ to $\dot{\gamma} = 0$. Casson's plot gives a clearer yield stress than the η versus σ_{12} plot. The yield stresses obtained from Casson's plot and η versus σ_{12} plot are shown in Table IV.3. Yield stresses reported by Tanaka and White (150) for CaCO_3 filled PS and CB filled PS agree with those of this present work.

Figure IV.24 shows the yield stresses for various systems as a function of volume content of filler. The yield stress increase drastically with increasing the volume content of filler in all systems.

Figures IV.25 to IV.27 show the yield stresses of various systems as a function of average particle diameter of filler. The yield stresses of CB, uncoated and coated CaCO_3 filled compounds increase roughly inversely with decreasing average particle size of fillers at a constant volume content (Figures IV.25 and IV.26). Large particle filled systems, however, do not show a clear relation between the yield stress and average particle size as shown in Figure IV.27. This may be because the yield stresses are too small to be estimated accurately in these systems.

Table IV.3

Yield Stresses in Steady Shear Flow

Filler	Particle Size (μm)	Matrix	Temperature ($^{\circ}\text{C}$)	Loading (vol%)	$Y_s \times 10^{-3}$ (Pa)*	References
Carbon black	0.1	PIB		29a	3	Zakarenko et al. (183)
Carbon black	0.019	PS	170	20	12	Lobe and White (91)
Carbon black	0.019	PS	170	25	60	Lobe and White (91)
Carbon black	0.02	PIB	22,66	9a	1	Vinogradov et al. (168)
Carbon black	0.02	PIB	22,60	13a	2	Vinogradov et al. (168)
Carbon black	0.025	GR	100	20	35	Montes and White (109)
Carbon black	0.025	IR305	100	20	40	Montes and White (109)
Carbon black	0.025	HR	100	20	60	Montes and White (109)
Carbon black	0.025	IR2200	100	20	60	Montes and White (109)
Carbon black	0.025	SBRI500	100	30	12	Toki and White (154)
Carbon black	0.045	PS	180	20	25	Tanaka and White (150)
Carbon black	0.045	PS	180	20	~2	The Present Work
Carbon black	0.045	PS	180	30	10	Tanaka and White (150)
Carbon black	0.045	PS	180	30	9	The Present Work
Uncoated CaCO_3	17	PS	180	30	unclear	The Present Work
Uncoated CaCO_3	3	PS	180	30	~1.5	The Present Work
Uncoated CaCO_3	0.5	PS	180	30	12	Tanaka and White (150)
Uncoated CaCO_3	0.5	PS	180	30	10	The Present Work
Uncoated CaCO_3	0.07	PS	180	30	40	The Present Work
Coated CaCO_3	17	PS	180	30	unclear	The Present Work
Coated CaCO_3	3	PS	180	30	unclear	The Present Work
Coated CaCO_3	0.5	PS	180	30	0.4	Tanaka and White (150)

Table IV.3 (Continued)

Filler	Particle Size (μm)	Matrix	Temperature ($^{\circ}\text{C}$)	Loading (vol%)	$Y_s \times 10^{-3}$ (Pa)*	References
Coated CaCO_3	0.5	PS	180	30	unclear	The Present Work
Coated CaCO_3	0.07	PS	180	30	unclear	The Present Work
TiO_2	0.18	LDPE	180	22	2.5	Minagawa and White (107)
TiO_2	0.18	HDPE	180	24	0.5	Minagawa and White (107)
TiO_2	0.18	PS	180	20	~ 1	Tanaka and White (150)
TiO_2	0.18	PS	180	30	2.2	Tanaka and White (150)
Talc	?	PP	200	17 ^b	0.14	Chapman and Lee (25)
Silas balloon		PS		~ 8	(~ 0.0003)	Kataoka et al. (80)
Silas balloon		PS		~ 12	(~ 0.001)	Kataoka et al. (80)
Silas balloon		PS		~ 20	(~ 0.0013)	Kataoka et al. (80)
Silas balloon		PS		~ 24	(~ 0.0018)	Kataoka et al. (80)
Silas balloon		PS		~ 34	(~ 0.003)	Kataoka et al. (80)
Silas balloon		PS		~ 40	(~ 0.019)	Kataoka et al. (80)
Silas balloon		PS		~ 55	(~ 0.16)	Kataoka et al. (80)
Glass balloon	52.9	PE	200	25.0	(~ 0.008)	Kataoka et al. (80)
Glass balloon	52.9	PE	200	30.2	(~ 0.01)	Kataoka et al. (80)
Glass balloon	52.9	PE	200	45.2	(~ 0.09)	Kataoka et al. (80)
Glass balloon	73.8	PE	200	23.0	(0.011)	Kataoka et al. (80)
Glass balloon	73.8	PE	200	35.0	(0.0084)	Kataoka et al. (80)
Glass balloon	73.8	PE	200	42.0	(0.056)	Kataoka et al. (80)

Table IV.3 (Continued)

Filler	Particle Size (μm)	Matrix	Temperature ($^{\circ}\text{C}$)	Loading (vol%)	$Y_S \times 10^{-3}$ (Pa)*	References
Glass bead	36	PE	200	11.8	(~0.00022)	Kataoka et al. (80)
Glass bead	36	PE	200	19.2	(~0.00035)	Kataoka et al. (80)
Glass bead	36	PE	200	23.5	(~0.0021)	Kataoka et al. (80)
Glass bead	68.2	PE	200	19.2	(~0.00088)	Kataoka et al. (80)
Glass bead	68.2	PE	200	25.2	(~0.0018)	Kataoka et al. (80)
Glass bead	68.2	PE	200	33.5	(~0.02)	Kataoka et al. (80)

*Values without parentheses are estimated from η versus σ_{12} plot; values with parentheses are estimated from Casson's plot.

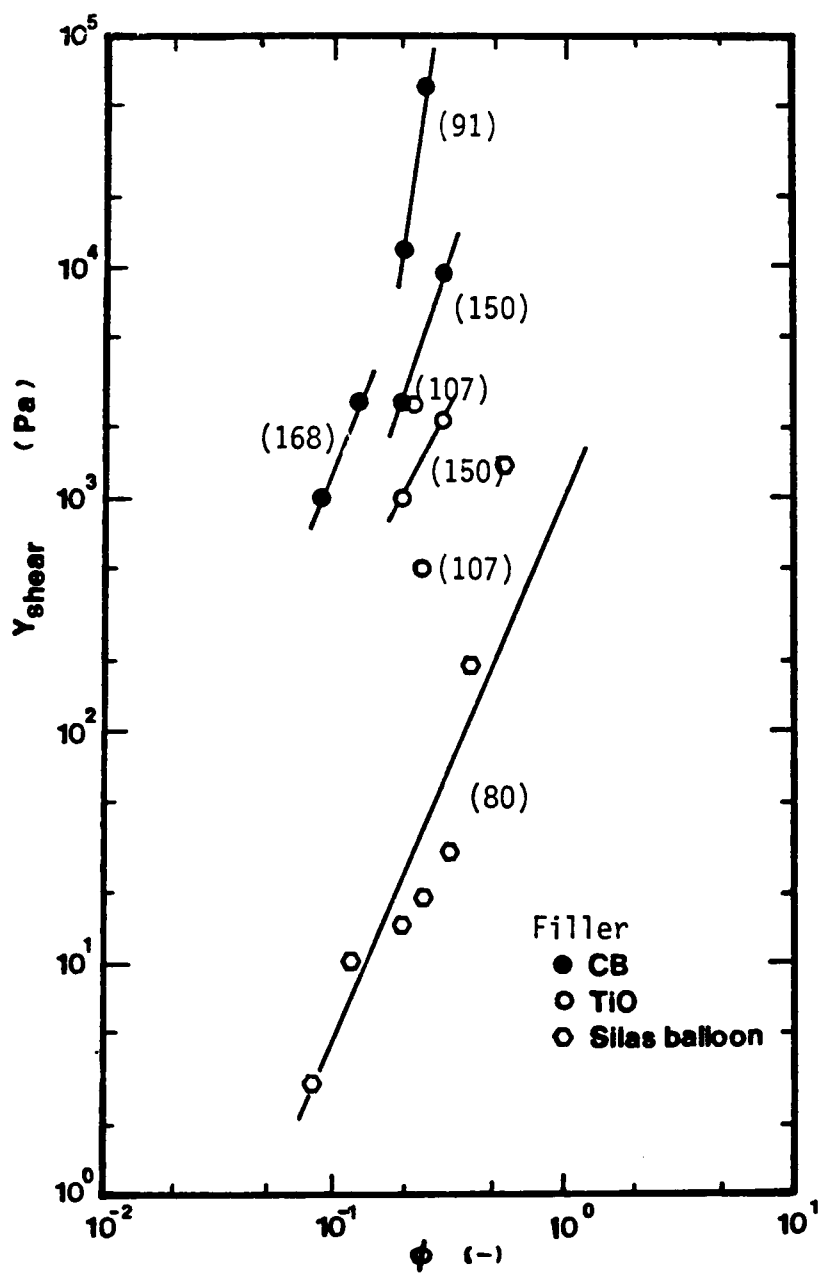


Figure IV.24. Yield stress as a function of volume content of filler for various systems from reference.

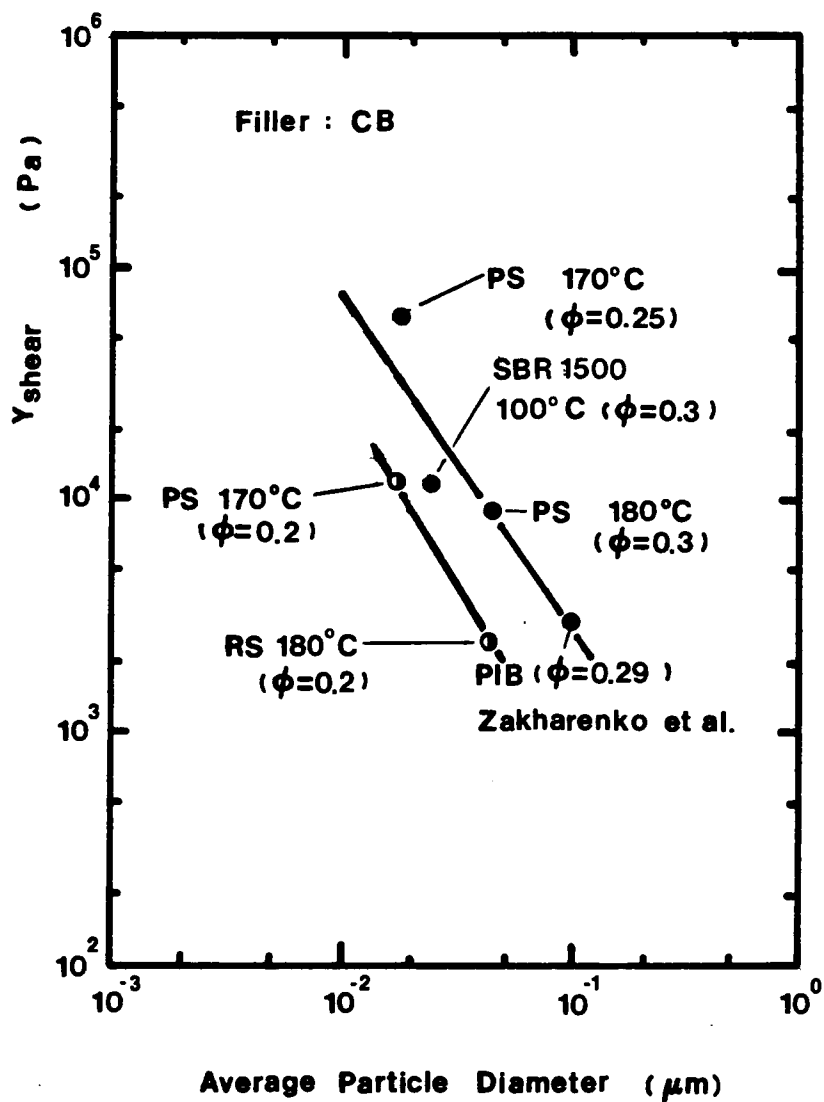


Figure IV.25. Yield stress as a function of particle size for CB filled systems.

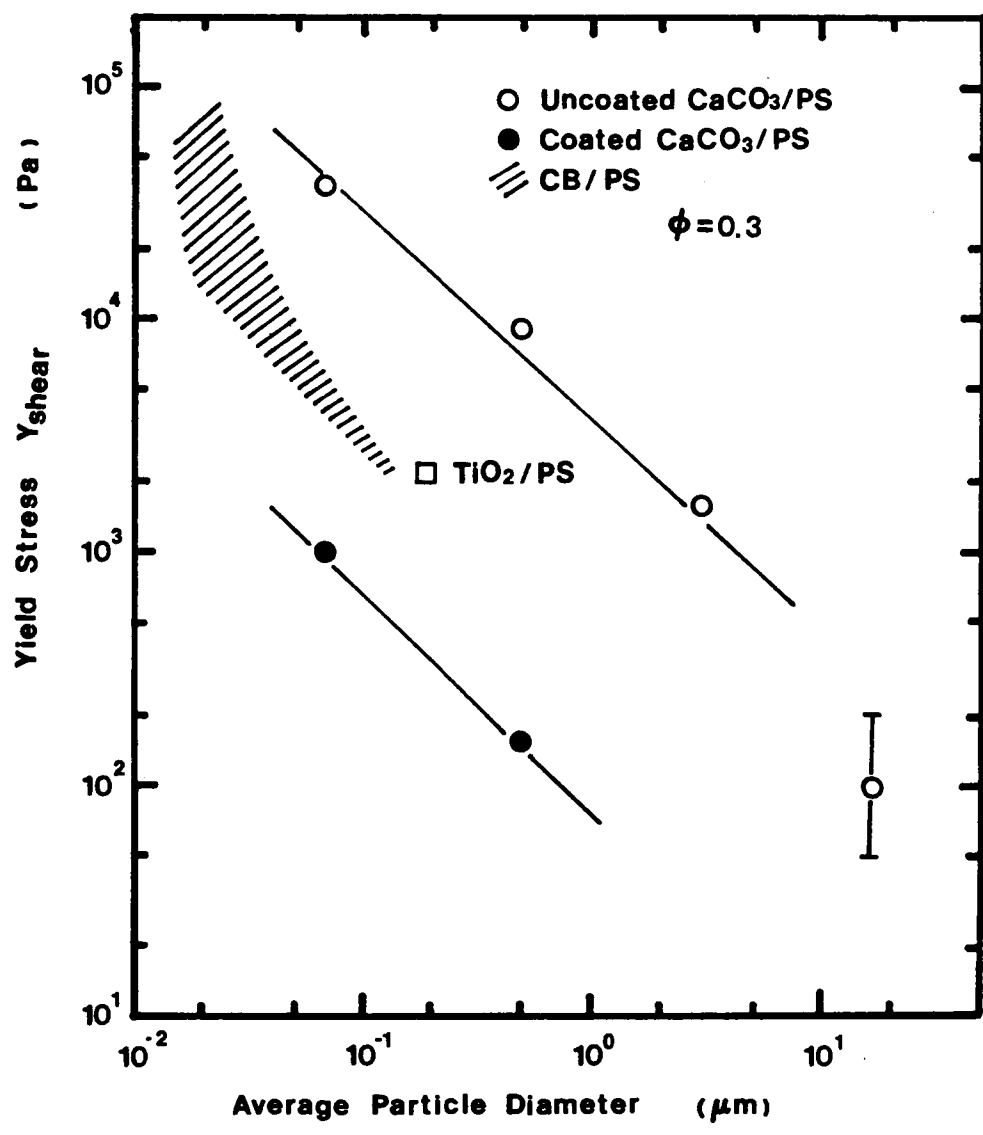


Figure IV.26. Yield stress as a function of particle size for small particle filled systems.

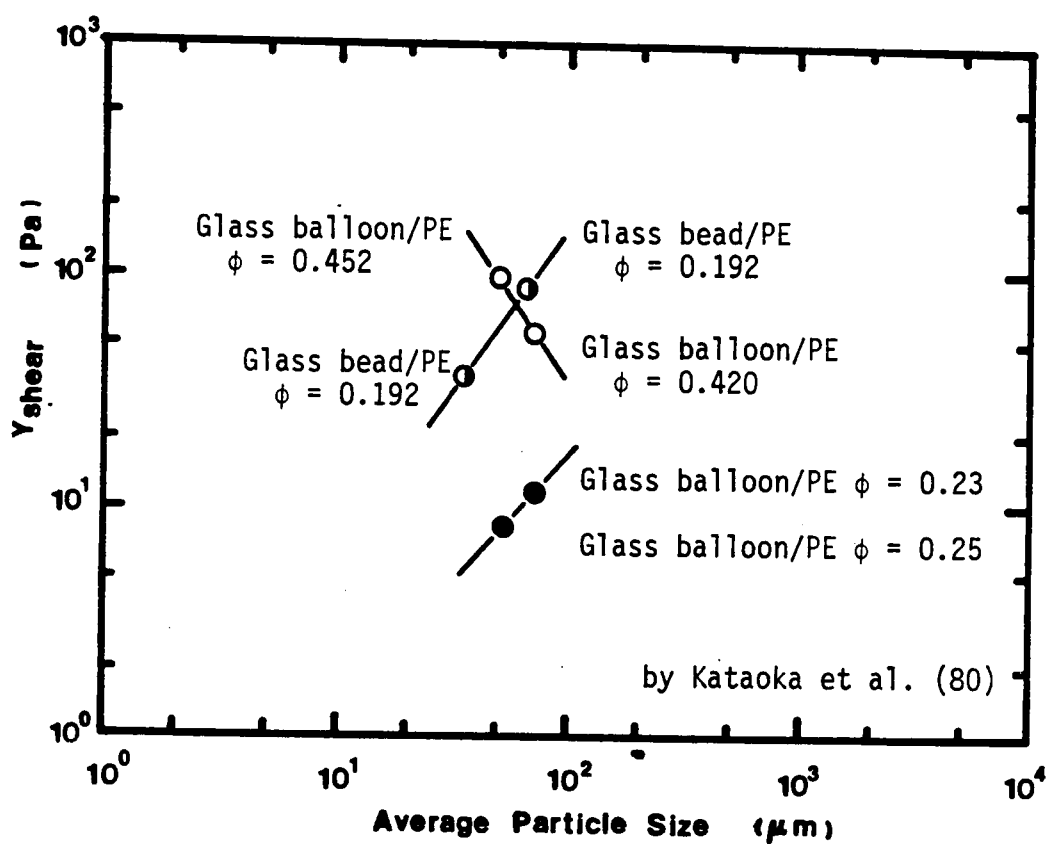


Figure IV.27. Yield stress as a function of particle size for large particle filled systems.

An empirical expression for the yield stress may be developed in terms of both volume fraction, ϕ , and average particle diameter, d_p , of form

$$Y = C \frac{\phi^a}{d_p^b} \quad [\text{IV.5}]$$

where C is a constant. The values of a and b have been estimated for various compounds and summarized in Table IV.4. The value of b is roughly unity and the values of a in most cases range from 2.5 to 4.

Viscosity reduction by stearic acid surface coating of CaCO_3 particles may be expressed as

$$H(\dot{\gamma}) = \frac{\eta_{\text{uncoated}}(\dot{\gamma}) - \eta_{\text{coated}}(\dot{\gamma})}{\eta_{\text{uncoated}}(\dot{\gamma})} \quad [\text{IV.6}]$$

where $\eta_{\text{uncoated}}(\dot{\gamma})$ and $\eta_{\text{coated}}(\dot{\gamma})$ denote the viscosities of uncoated and coated CaCO_3 filled compounds at a shear rate $\dot{\gamma}$. Figure IV.28 shows the viscosity reduction function, $H(\dot{\gamma})$, as a function of shear rate. Viscosity reduction function decreases with increasing shear rate and increasing average particle diameter.

The viscosity or modulus increase due to the volume content of filler was written as (149)

$$f(\phi) = \frac{\eta^*}{\eta^0} = \frac{\eta - \frac{Y_{\text{shear}}}{\dot{\gamma}}}{\eta^0} \quad [\text{IV.7}]$$

Table IV.4

"a," "b" and "c" Values in Equation IV.5 for Various Compounds

Sample	Average Particle Size (μm)	Volume Loading (vol%)	a	b	c	References
CB/PIB	0.02	9, 13	2.5	1.6*		Vinogradov et al. (168)
CB/PS	0.019	20, 25	7.2			Lobe and White (91)
CB/PS	0.045	20, 30	3.1			Tanaka and White (150)
CB/PS	0.045	20, 30	3.1			The Present Work
Uncoated CaCO_3/PS	17, 3 0.5, 0.07	30	-	1.1	-	The Present Work
Coated CaCO_3/PS	0.5, 0.07	30	-	0.9	-	The Present Work
Glass bead/PE	36	11.8, 19.2, 23.5	2.8	?	-	Kataoka et al. (80)
Glass bead/PE	68.2	19.2, 25.2, 33.5	5.6			
Glass balloon/PE	52.9	25.0, 30.2, 45.2	4.0	1.4**		
Glass balloon/PE	73.8	23.0, 35.0, 42.0	2.1			
Silas balloon/PS	?	8 ~ 55	2.6	-		Kataoka et al. (80)

*Evaluated for $0.25 \leq \phi \leq 0.3$.

**Evaluated for $0.42 \leq \phi \leq 0.452$.

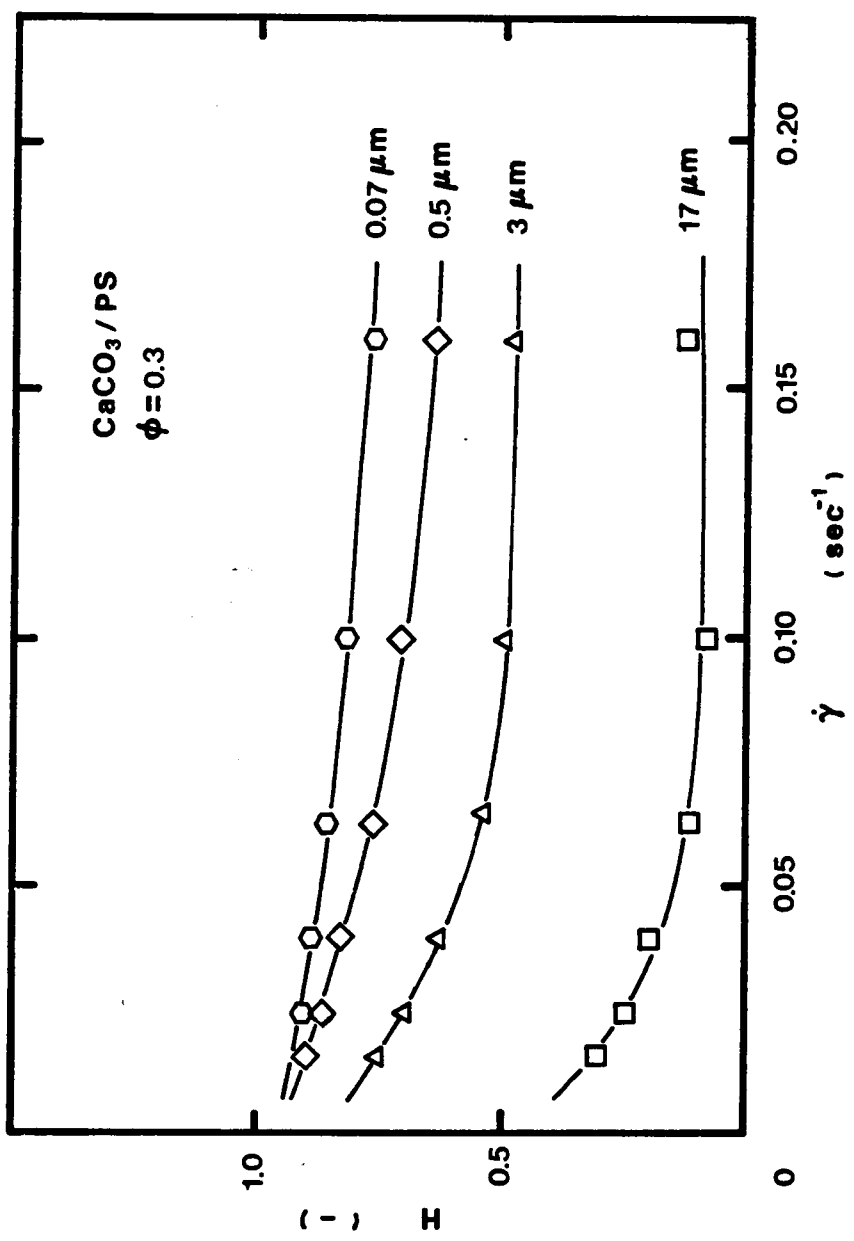


Figure IV.28. Viscosity reduction function as a function of shear rate for CaCO₃ filled PS.

where η and η^0 denote viscosity of a filled and an unfilled system at shear rate $\dot{\gamma}$ respectively.

Figure IV.29 shows the η^*/η^0 plot as a function of shear rate for all compounds. The η^*/η^0 value should be the same for all compounds and should depend on volume fraction only. However, the η^*/η^0 values of compounds with a volume content of 0.3 are not exactly the same. They are divided into two groups. The first group which has η^*/η^0 values of 4.0 to 4.6 consists of uncoated CaCO_3 ($d_p = 0.07, 0.5, 3 \mu\text{m}$), coated CaCO_3 ($d_p = 0.07 \mu\text{m}$), and CB filled PS ($\phi = 0.3$). The second group which has η^*/η^0 values of 2.4 to about 3 consists of uncoated CaCO_3 ($d_p = 17 \mu\text{m}$), and coated CaCO_3 ($d_p = 0.5, 3, 17 \mu\text{m}$) filled PS melts. The compounds which have low or unclear yield stress belong to the second group. The inaccuracy of yield values may be one reason for this disagreement.

Average values of η^*/η^0 are summarized in Table IV.5. The η^*/η^0 values of coated CaCO_3 filled PS in this present work are larger than Tanaka's data. This may be related to the viscosity reduction effects of coated CaCO_3 filled PS (Chapter III). Other data agrees fairly well with Tanaka's.

D. Transient First Normal Stress Difference

D.1 Results

Figures IV.30 to IV.40 show transient Z-force data. The aging periods which are usually one hour as indicated

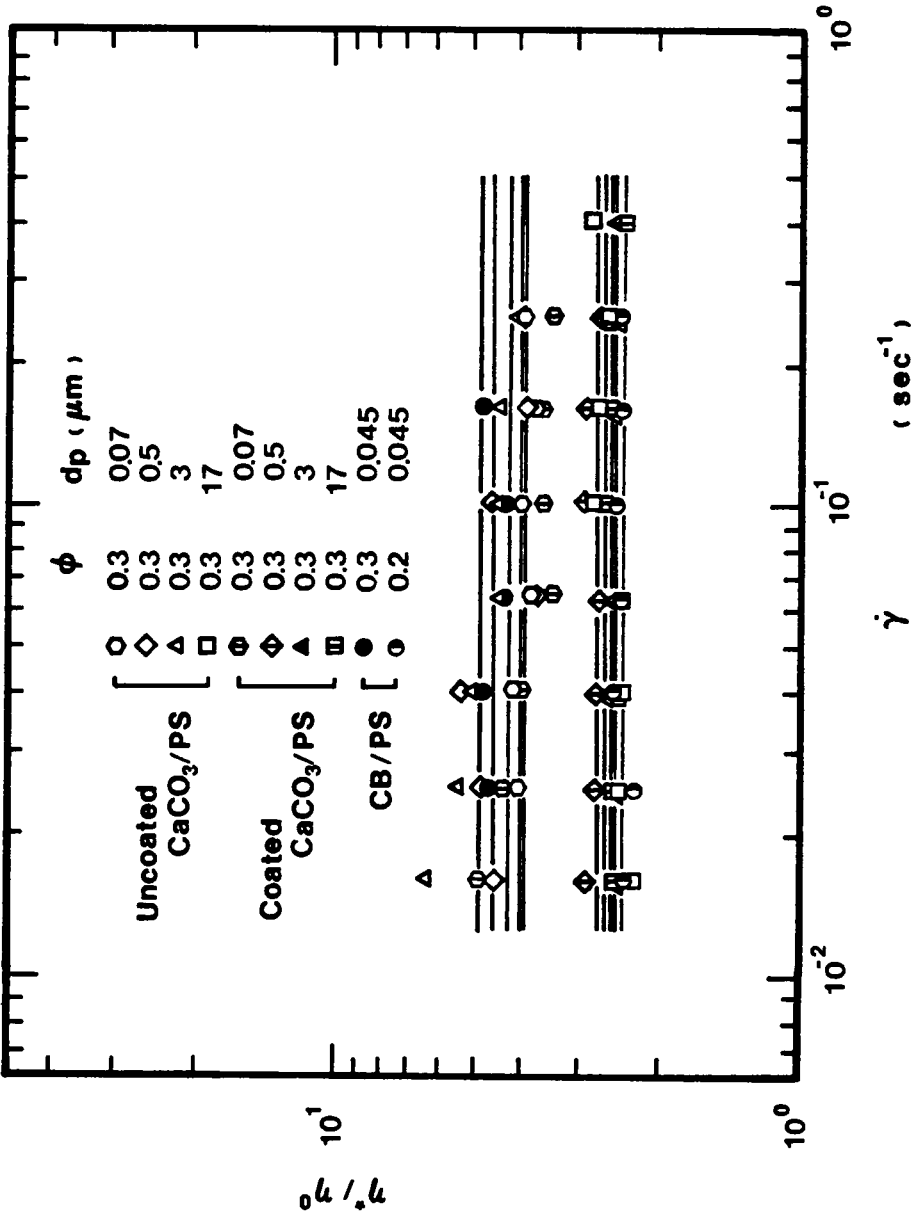


Figure IV.29. η^*/η^0 as a function of shear rate for all compounds.

Table IV.5
Average Values of η^*/η^0 for Various Compounds

Filler	Volume Content ϕ (-)	Average Particle Size dp (μm)	η^*/η^0 (Present Work) (-)	η^*/η^0 (Tanaka) (-)
Uncoated CaCO_3	0.3	0.07	4.0	-
		0.5	4.6	~4
		3	4.5	-
		17	2.5~3.0	-
Coated CaCO_3	0.3	0.07	3.9	
		0.5	2.5~2.9	~1.5
		3	2.5	-
		17	2.5	-
CB	0.3	0.045	4.4	~5
	0.2		2.4	~2.5

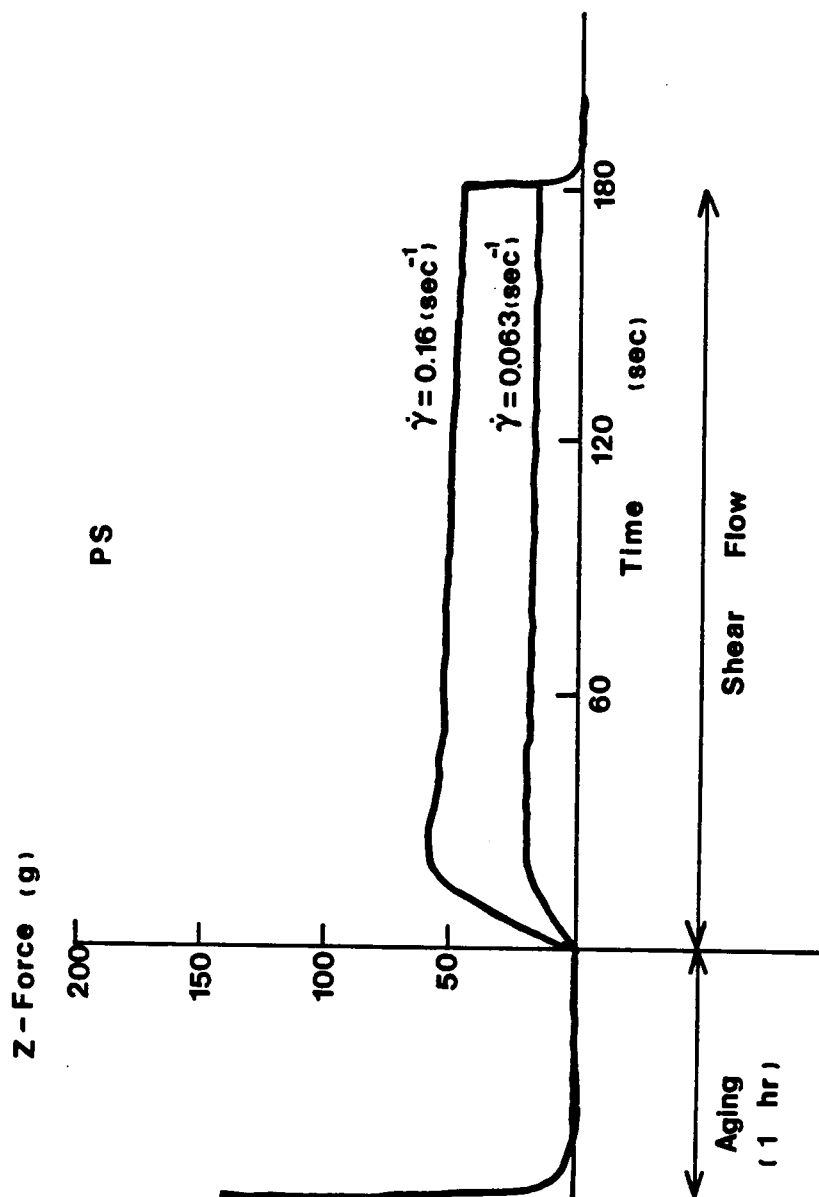


Figure IV.30. Transient Z-force of PS at 180°C.

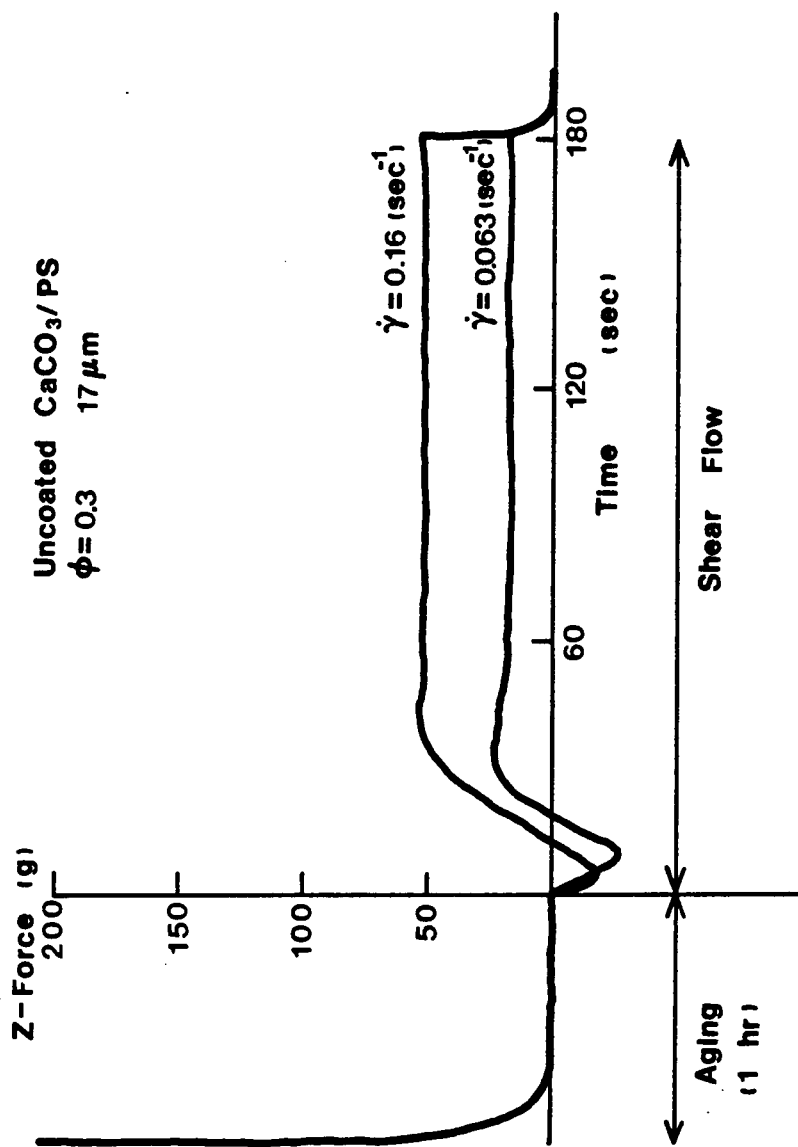


Figure IV.31. Transient Z-force behavior of uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 17\text{ }\mu\text{m}$) at 180°C .

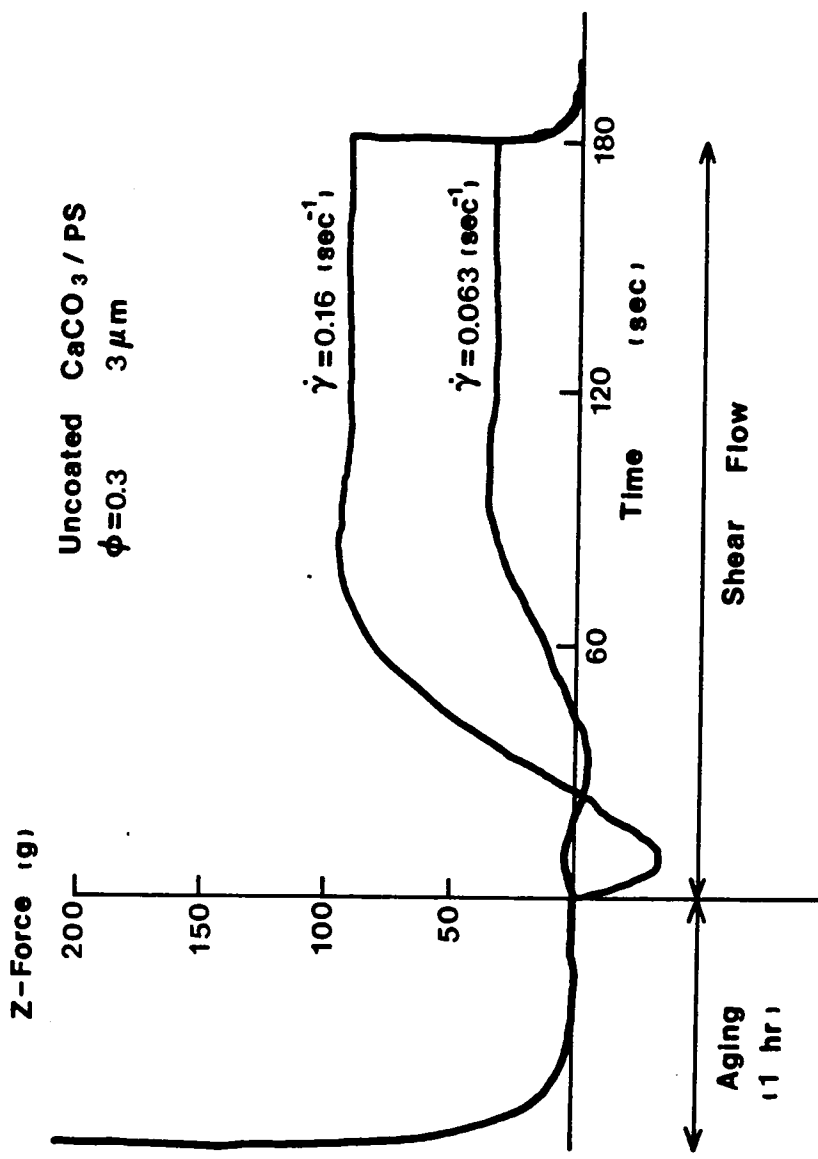


Figure IV.32. Transient Z-force behavior of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 3 \mu\text{m}$) at 180°C .

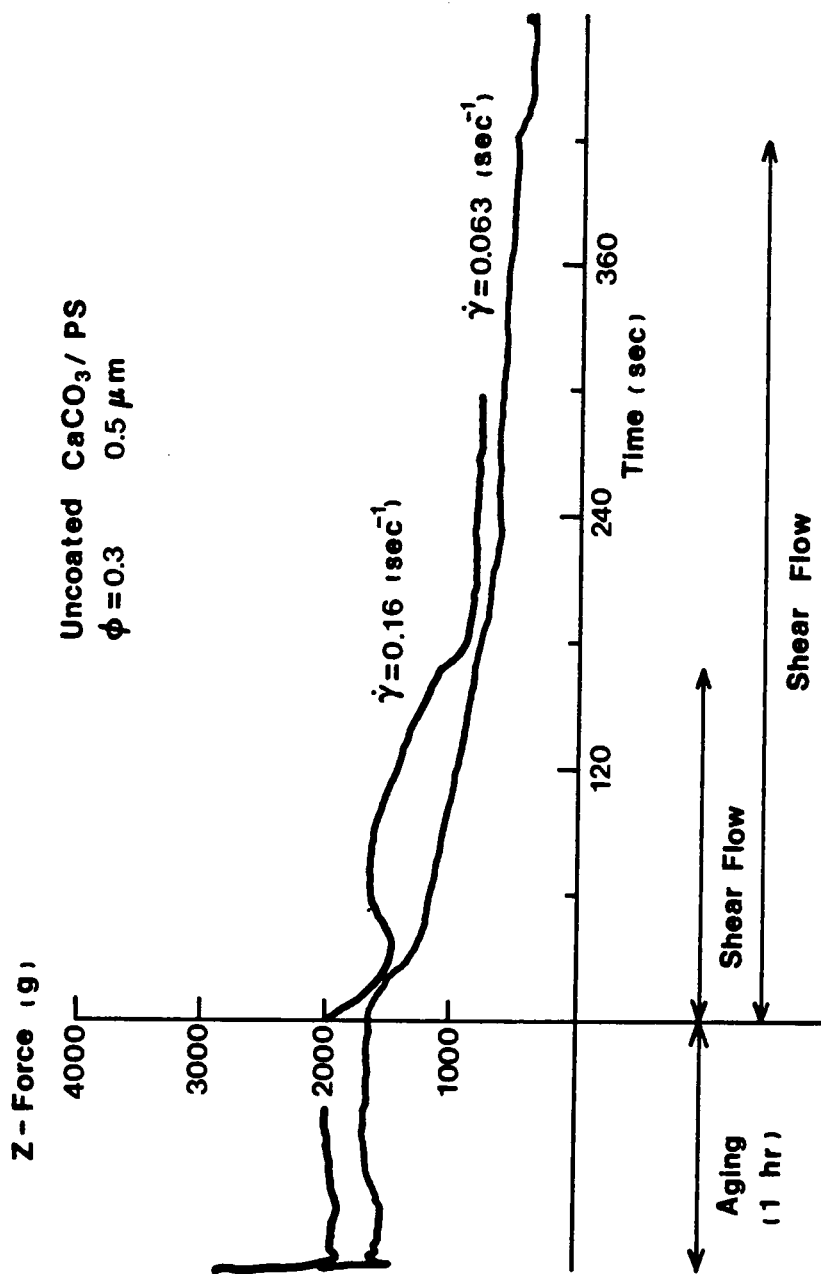


Figure IV.33. Transient Z-force behavior of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.5 \mu\text{m}$) at 180°C .

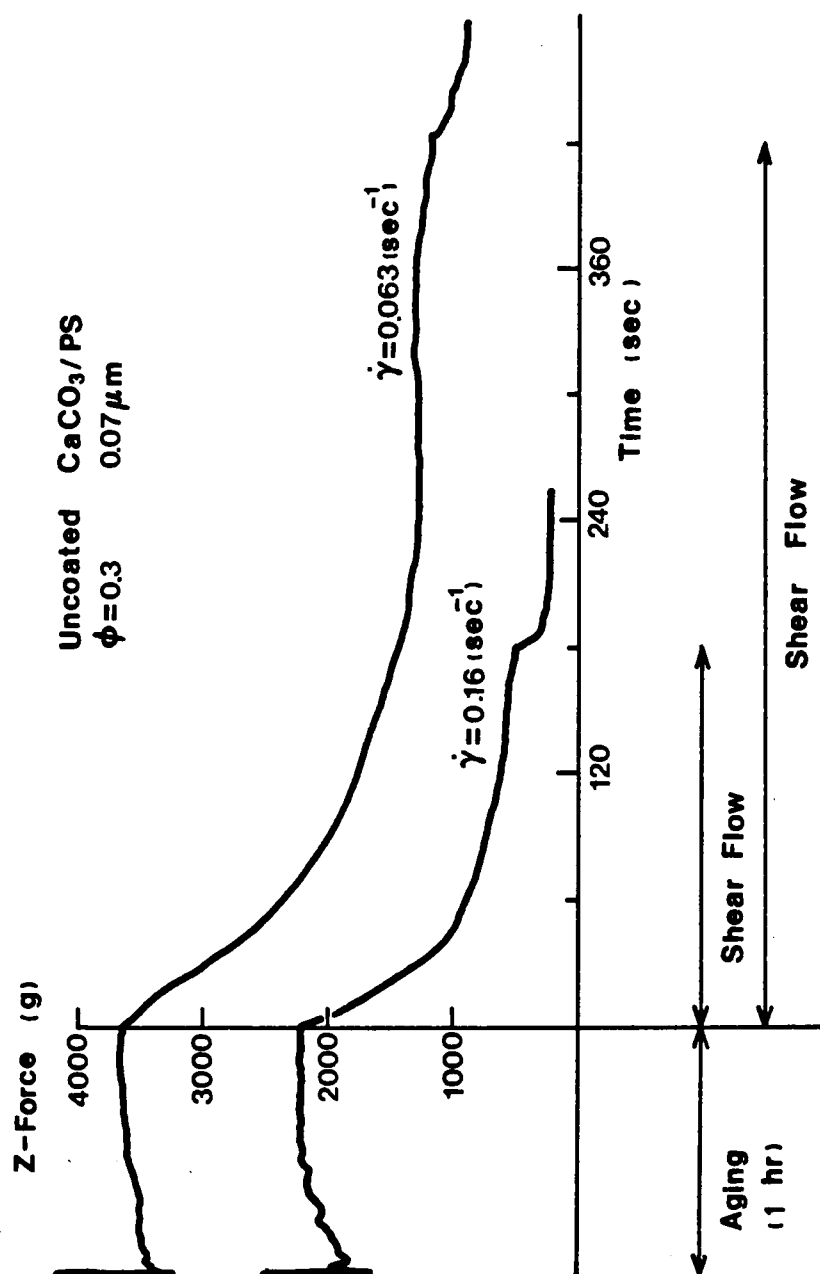


Figure IV.34. Transient Z-force behavior of uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.07 \mu\text{m}$) at 180°C .

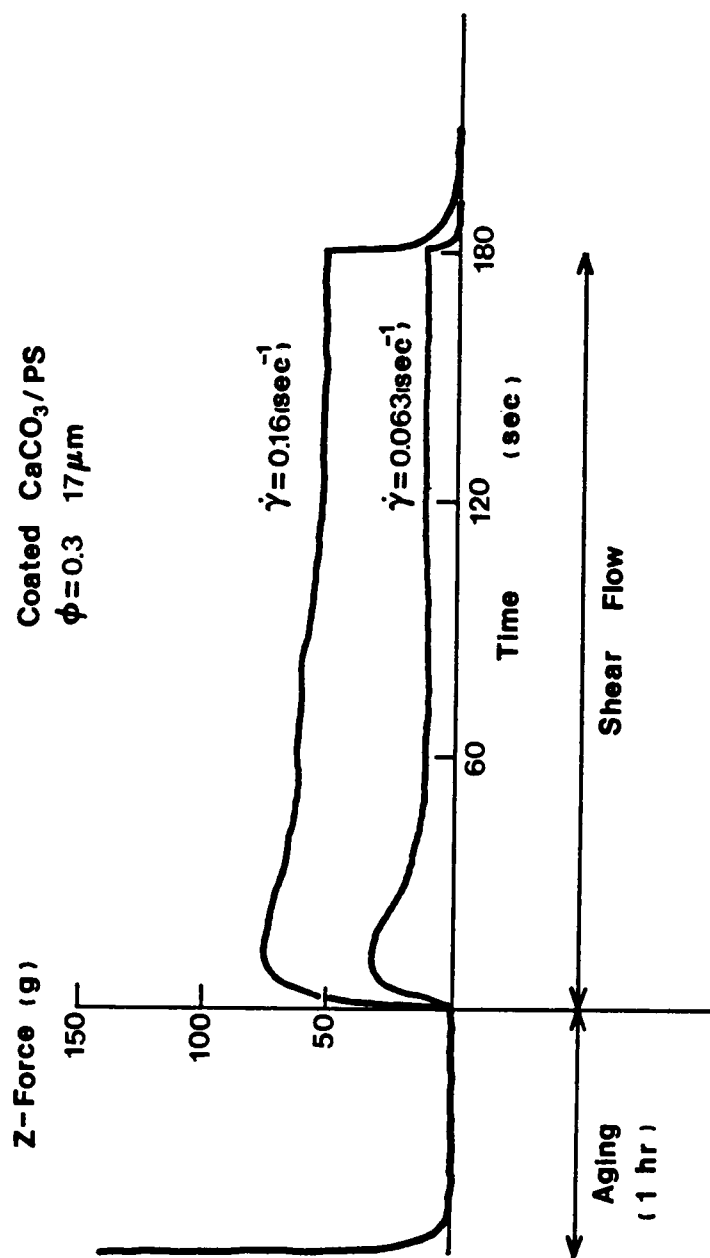


Figure IV.35. Transient Z-force behavior of coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 17\mu\text{m}$) at 180°C .

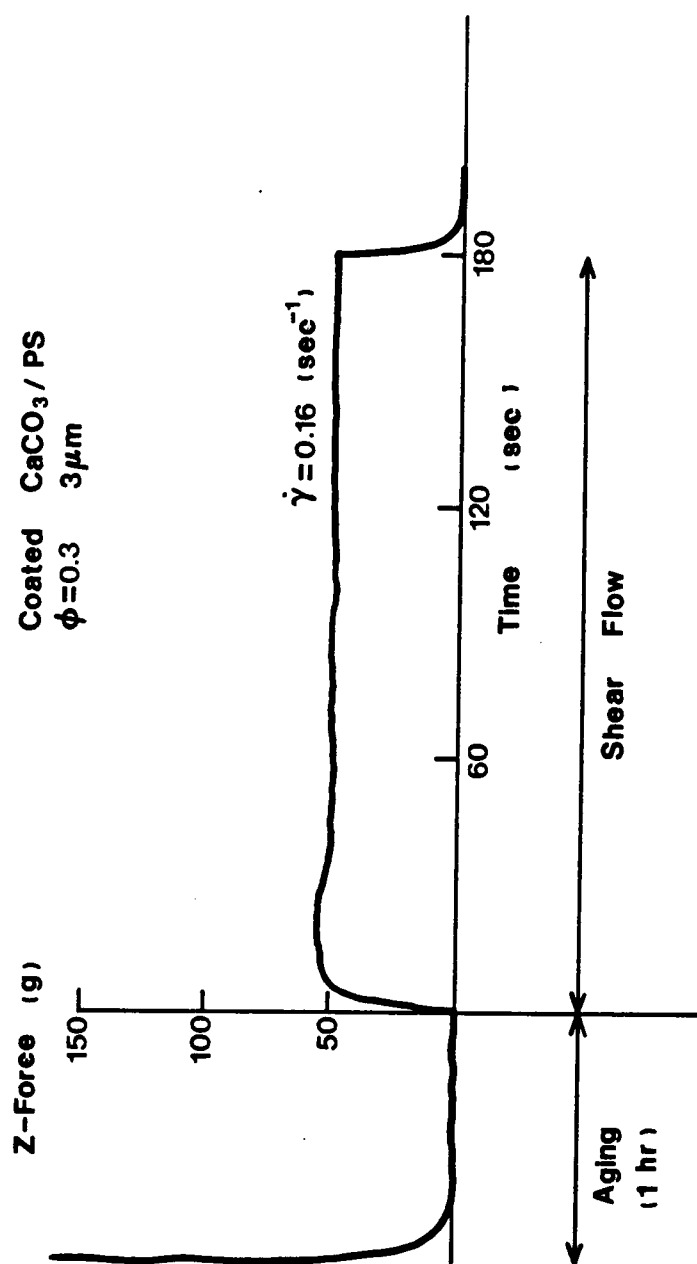


Figure IV.36. Transient Z-force behavior of coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 3 \mu\text{m}$) at 180°C .

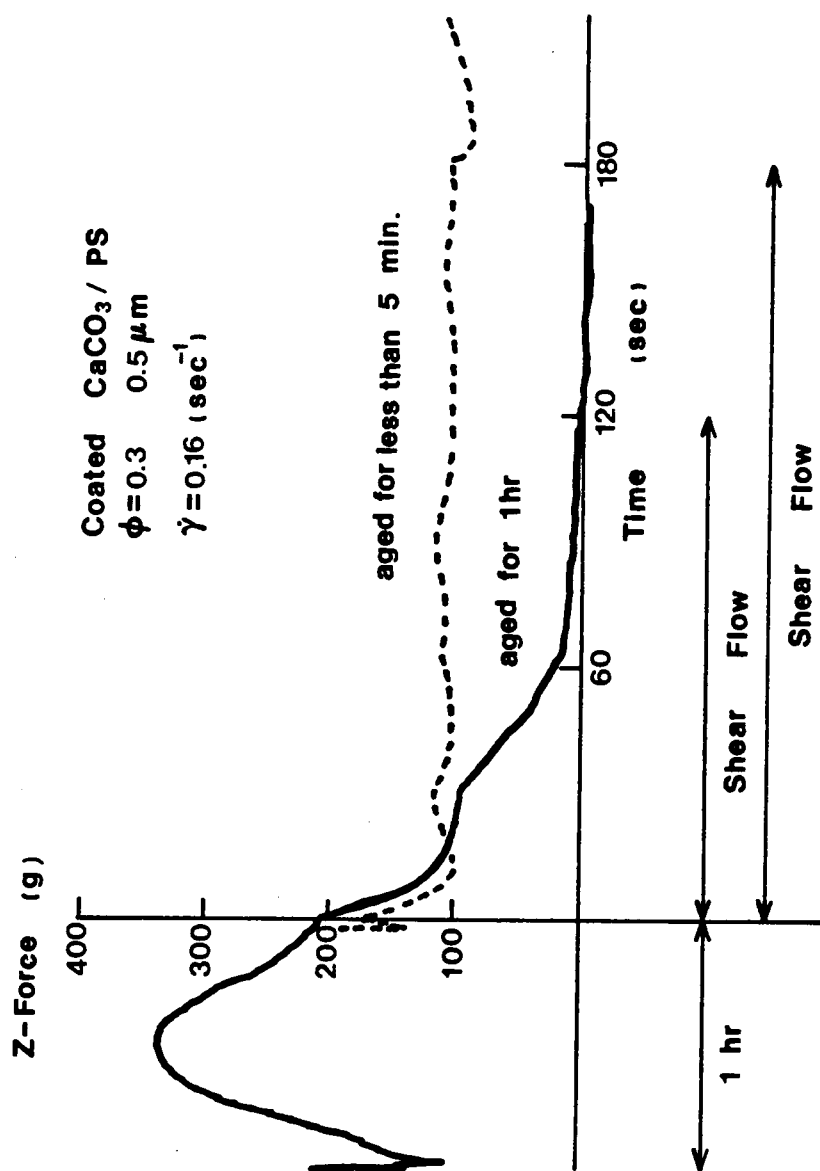


Figure IV.37. Transient Z-force behavior of coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.5 \mu\text{m}$) at 180°C .

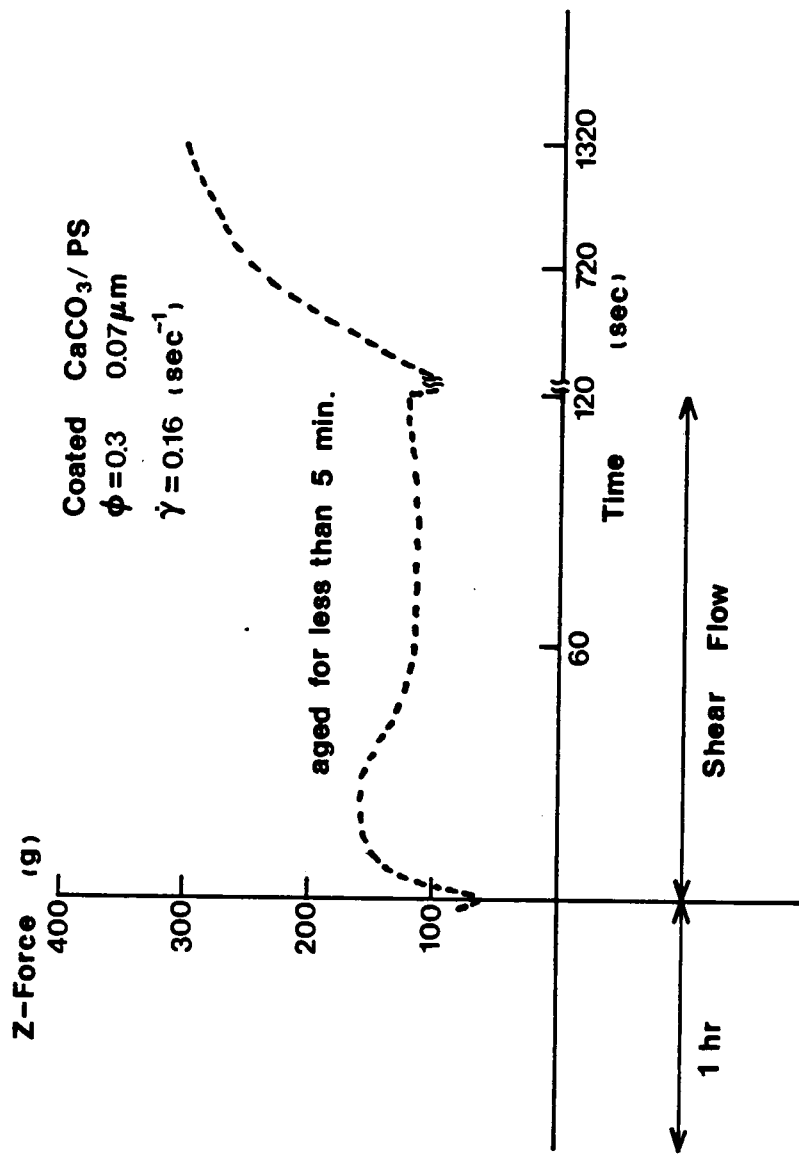


Figure IV.38. Transient Z-force behavior of coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.07 \mu\text{m}$) at 180°C .

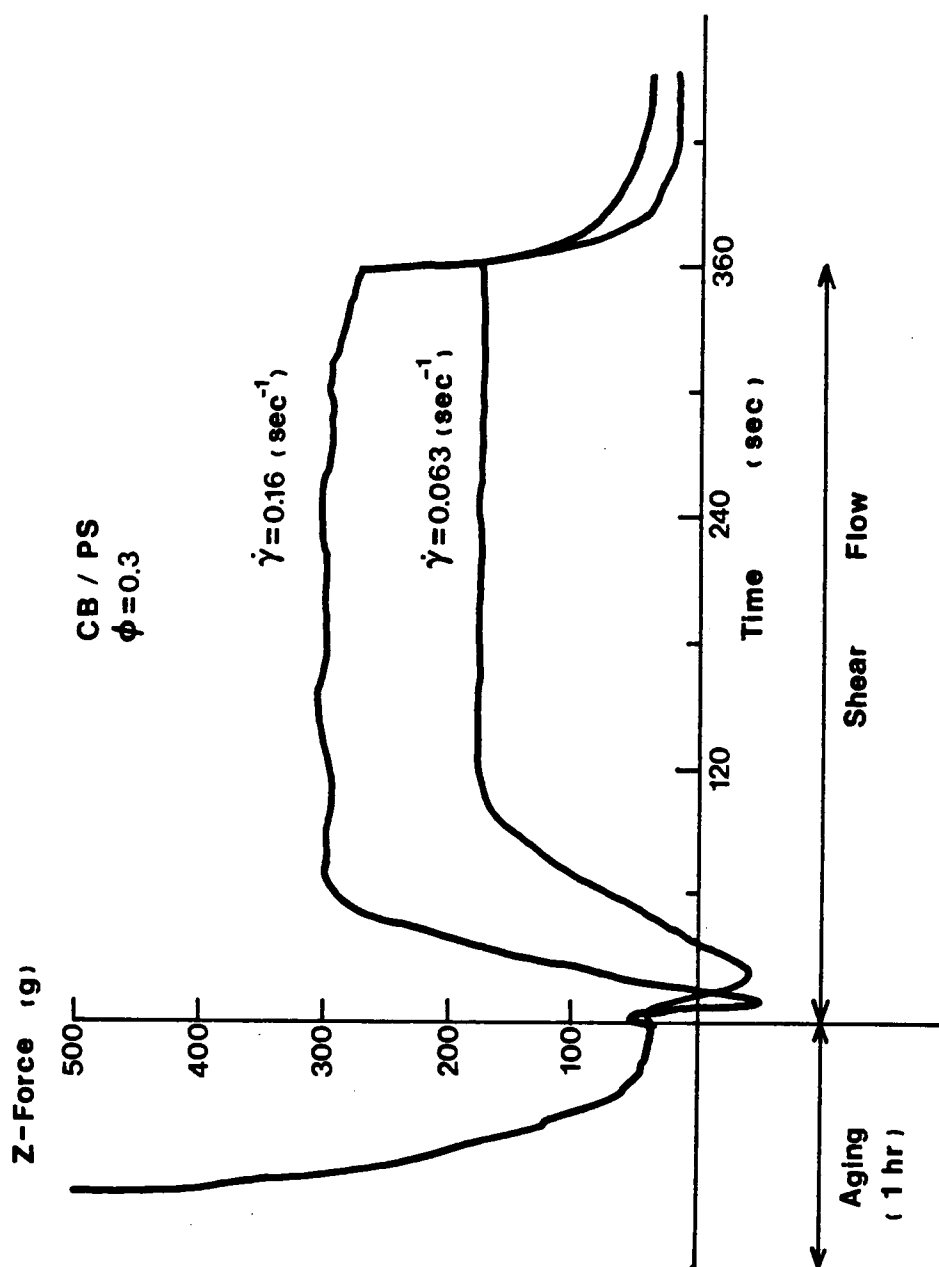


Figure IV.39. Transient Z-force behavior of CB filled PS ($\phi = 0.3$, $d_p = 0.045 \text{ }\mu\text{m}$) at 180°C .

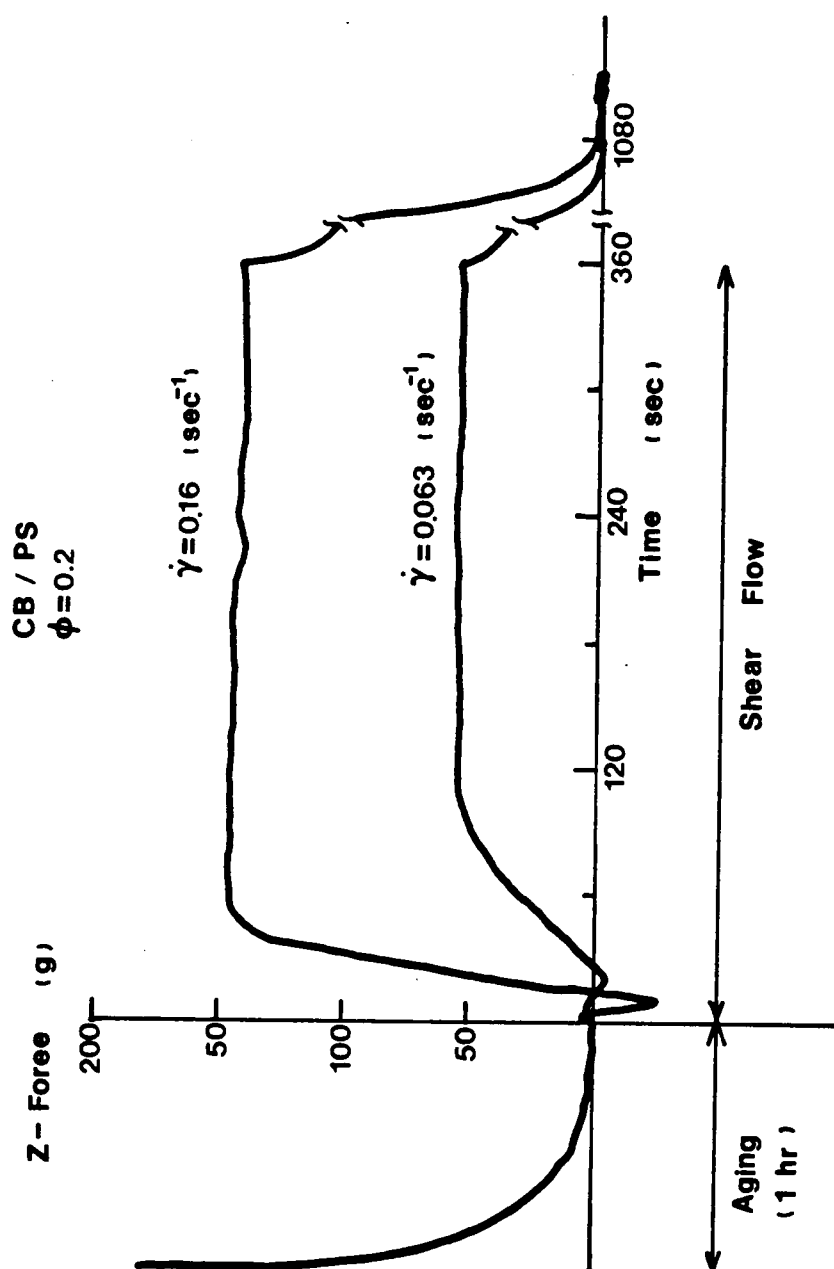


Figure IV.40. Transient Z-force behavior of CB filled PS ($\phi = 0.2$, $d_p = 0.045 \text{ }\mu\text{m}$) at 180°C .

in Figures IV.30 to IV.40 mean the period after completing the sample insertion and before applying the shear flow.

Transient Z-force was measured for pure PS uncoated and coated CaCO_3 filled PS ($d_p = 17, 3, 0.5, 0.07 \mu\text{m}$), and CB filled PS ($\phi = 0.2, 0.3$). Transient behaviors of Z-force of these samples may be classified into three categories.

The first category contains pure PS, uncoated CaCO_3 filled PS ($d_p = 17, 3 \mu\text{m}$), coated CaCO_3 filled PS ($d_p = 17, 3 \mu\text{m}$) and CB filled PS ($\phi = 0.2$). In these systems, Z-force relaxes to the base line which was determined without the sample within one hour. After sudden application of steady shear, Z-force grows and reaches a steady state. The Z-force overshoot is not clear, but seems to be larger at larger shear rate generally. When shear deformation stops, the Z-force relaxes to the original base line again.

The second category contains uncoated CaCO_3 filled PS ($d_p = 0.5, 0.07 \mu\text{m}$) and CB filled PS ($\phi = 0.3$). The Z-force of these compounds does not relax to the base line completely within one hour before shear flow. The values of Z-force at the shear time zero are dependent upon the sample insertion procedure. Since the sample insertion procedure is a manual process, these Z-force values are not always the same. The Z-force value at time zero is larger when the particle size of filler is smaller in case of uncoated CaCO_3 filled PS melts. The CB filled PS

possesses a much smaller value of Z-force at time zero than uncoated CaCO_3 filled PS ($d_p = 0.5, 0.07 \mu\text{m}$). After the sudden application of shear deformation, Z-force behaviors of these uncoated CaCO_3 filled PS are very different from the responses of the samples belonging to the first category. They may not possess the steady state, but Z-forces decrease roughly exponentially. When the Z-force of these samples approaches roughly constant value, the samples have come out from the cone-plate test section or exhibited secondary flow effect. After the shear flow stops, the Z-force decreases and approaches a certain positive value, but does not relax to the sample-free base line. The CB filled PS melt ($\phi = 0.3$) shows a similar response to the first category. It possesses a steady state. After the shear flow stops, Z-force relaxes fairly close to the base line compared to the other two compounds in this category.

Coated CaCO_3 filled PS ($d_p = 0.5, 0.07 \mu\text{m}$) melts belong to the third category. The Z-force behavior of this category is more complex. After completing the sample insertion procedure, the Z-force increases at first, and then it decreases again. The Z-force does not approach a certain constant value within one hour. After the sudden application of shear flow, the Z-force decreases and reaches to almost zero.

The Z-force behavior has been investigated also for samples which have experienced much shorter relaxation or aging periods than one hour, but less than five minutes after the sample insertion procedure (Figure IV.36, p. 114). The behavior of the Z-force of the latter experiment is different from the former one. In the case of coated CaCO_3 ($d_p = 0.5 \mu\text{m}$) dilled PS melt, when the shear deformation was applied to these samples, Z-force decreased at first and then seems to reach a constant value. The Z-force of coated CaCO_3 ($d_p = 0.07 \mu\text{m}$) filled PS melt which has aging periods of less than five minutes increased after the sudden application of shear flow, and then reached a constant value. However, the Z-force behavior of the samples whose aging periods are less than five minutes is abnormal after stopping the shear deformation. The Z-force decreases a little in a short time, and then it increases again. This Z-force growth in a static condition is similar to the Z-force growth in an aging period of other samples.

D.2 Discussion

The Z-force behavior of small particle filled polymer melts is more complex than pure polymer melts. These complex results may be related to some particular properties of filled compounds, such as the yield stress and the high viscosity.

In Table IV.6, the yield stresses have been mentioned for the compounds which were categorized into three groups

Table IV.6

Classification of Transient Z-force Behavior
in Yield Stress in Shear Flow

Category	Sample	Volume Content (-)	Average Particle Size (μm)	Yield Stress in Shear Flow ($\times 10^{-3}$ Pa)
1st	PS	0.0	-	0.0
	Uncoated CaCO_3/PS	0.3	17	0.1
	Uncoated CaCO_3/PS	0.3	3	1.6
	Coated CaCO_3/PS	0.3	17	<0.1
	Coated CaCO_3/PS	0.3	3	<0.1
	CB/PS	0.2	0.045	1.3
2nd	Uncoated CaCO_3/PS	0.3	0.5	9
	Uncoated CaCO_3/PS	0.3	0.07	38
	CB/PS	0.3	0.045	8.8
3rd	Coated CaCO_3/PS	0.3	0.5	0.16
	Coated CaCO_3/PS	0.3	0.07	1.0

in Section D.1. The pure melt and compounds which have yield stresses less than $\sim 2 \times 10^3$ Pa belong to the first category. The compounds which have yield stresses larger than $\sim 9 \times 10^3$ Pa belong to the second category. The large yield stresses may be one reason why the Z-force does not relax completely within the aging period (one hour) before shear deformation.

It was observed that the samples come out from the cone-plate test section during the shear deformations. This may be related to the secondary flow. This effect may be regarded as a reason for the continuous decrease of Z-force during the deformation. The sample coming out during deformation may be more rapid in the compounds which contain the very small particles, and Z-force decrease during deformation is more noticeable in these systems.

The abnormal Z-force behavior of coated CaCO_3 ($d_p = 0.5, 0.07 \mu\text{m}$) filled compounds is mysterious. It seems difficult to explain why Z-force increases and then decreases during the aging period of one hour. The compounds which contain small coated CaCO_3 particles ($d_p = 0.5, 0.07 \mu\text{m}$) show this abnormal behavior, but the compounds containing larger particles do not. The abnormal Z-force behavior may occur when the amount of the stearic acid which the compounds contain is large. If it is assumed that the amount of stearic acid is proportional to the surface area of CaCO_3 particle, the smaller coated CaCO_3

particle filled systems contain much more stearic acid. The mechanism of this abnormal Z-force behavior, however, is not clear yet.

E. Steady State First Normal Stress Difference

E.1 Results

Figures IV.41 to IV.43 show the first normal stress difference as a function of shear stress. These samples mentioned in the figures show almost complete Z-force relaxation within the aging period of one hour before shear deformation begins.

Figure IV.41 shows the first normal stresses decrease at the fixed shear stress with decreasing average particle diameter of uncoated CaCO_3 . The first normal stress difference of coated CaCO_3 filled PS melt is not very dependent upon the average particle diameter (Figure IV.42). Figure IV.43 shows the effect of loading level of CB in PS. The first normal stress difference at the fixed shear stress decreases with increasing loading level of filler.

E.2 Discussion

The first normal stress difference at the fixed shear stress of CaCO_3 filled PS compounds decreases with stearic acid surface treatment on CaCO_3 particles. This result is the same as that found by Tanaka and White (150). The first normal stress difference at the fixed shear stress

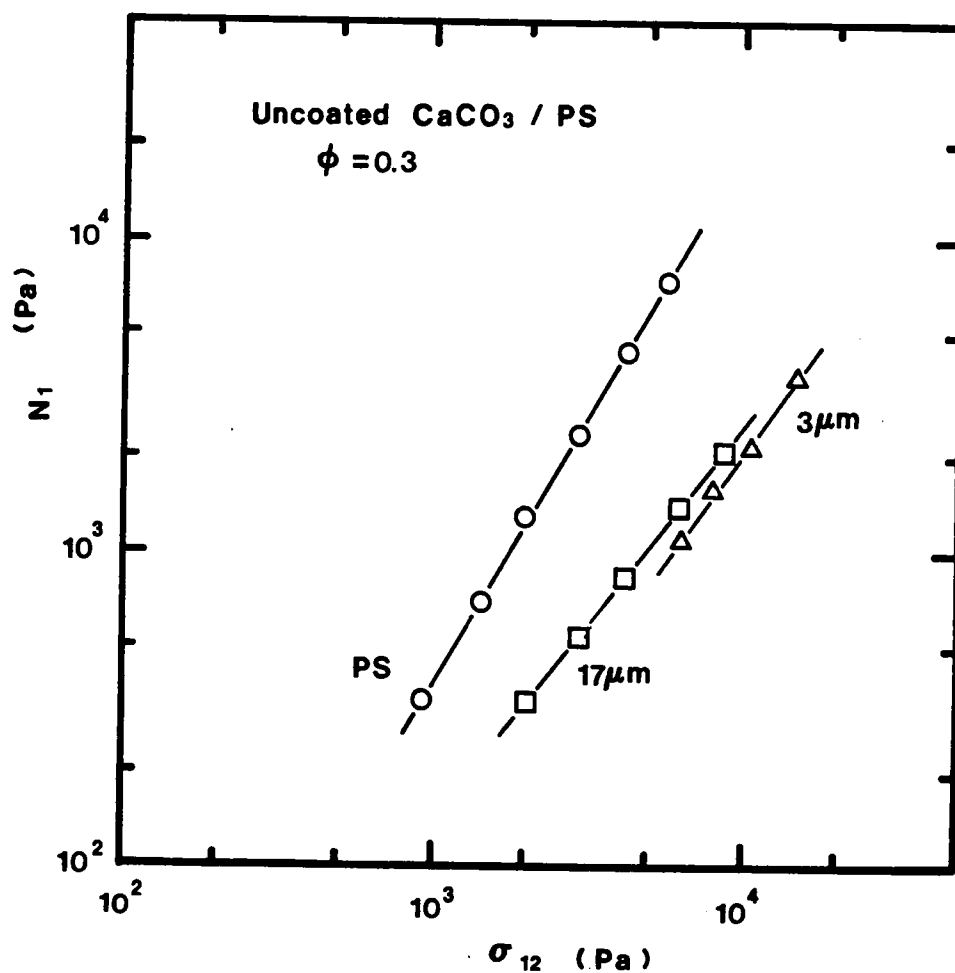


Figure IV.41. First normal stress difference as a function of shear stress for uncoated CaCO_3 filled PS at 180°C .

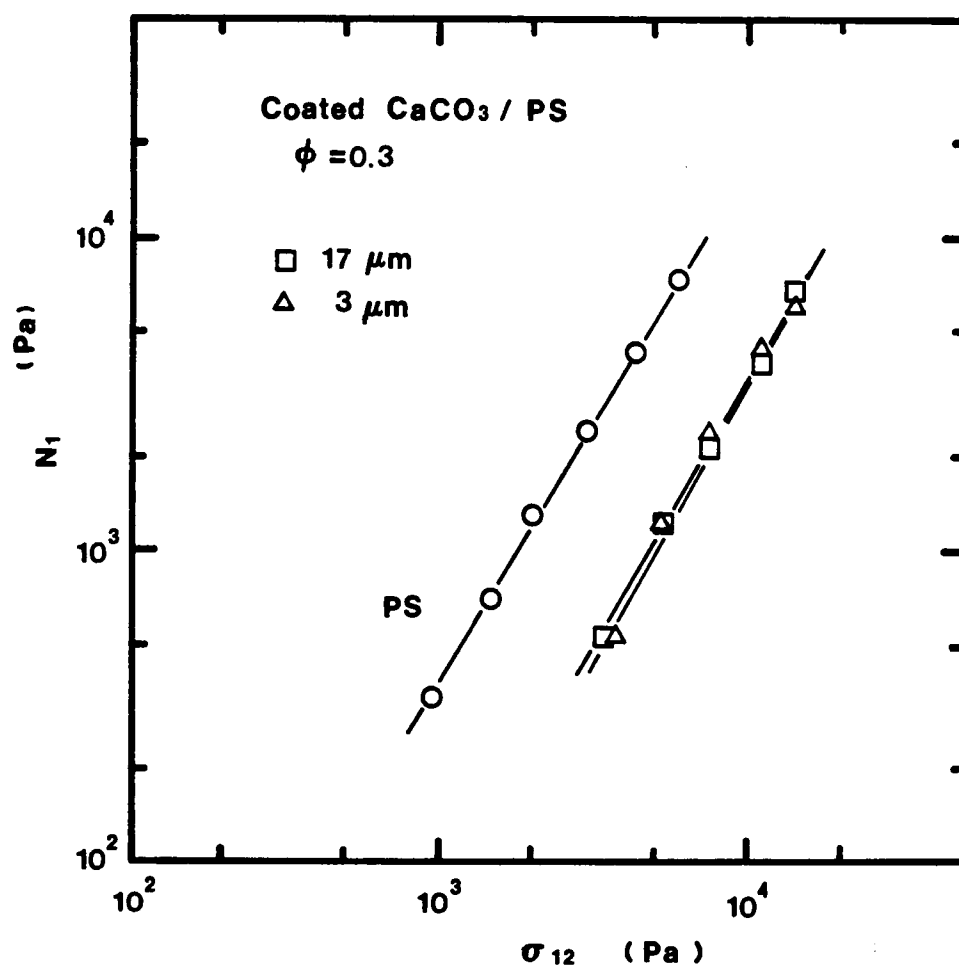


Figure IV.42. First normal stress difference as a function of shear stress for coated CaCO_3 filled PS at 180°C .

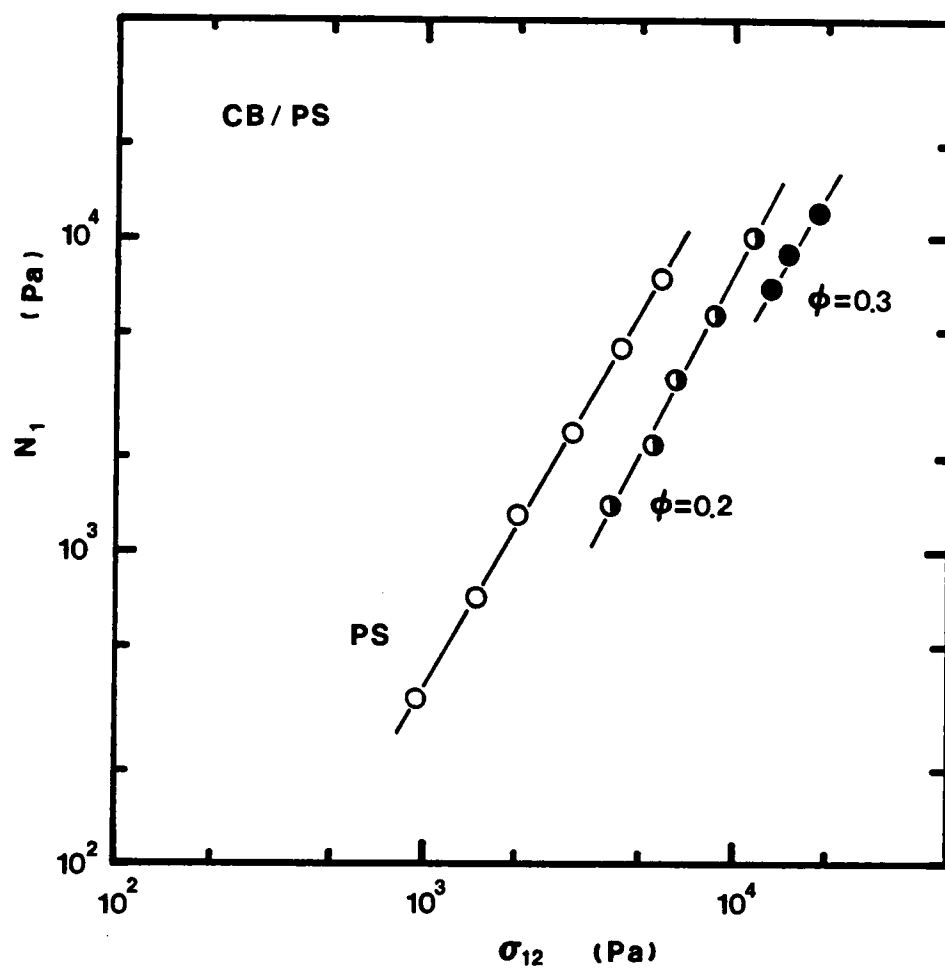


Figure IV.43. First normal stress difference as a function of shear stress for CB filled PS at 180°C.

of CB filled PS compounds decreases with increasing volume content of the filler. This result is the same as that found by Lobe and White (91) and by Tanaka and White (150).

CHAPTER V

EXPERIMENTAL STUDIES ON ELONGATIONAL FLOW

Experimental studies of the rheological behavior in elongational flow are presented in this chapter. The elongational viscosity χ and elongation to break L_B/L_0 are considered.

A. Transient Elongational Viscosity

A.1 Results

Figures V.1 to V.21 show the transient elongational viscosity, $\chi(E,t)$ for PS and for particle filled PS samples. The elongational viscosity of the pure PS sample increases to a steady state. In the case of the small particle filled PS, the elongational viscosity grows much more rapidly at the very beginning of the deformation. It later grows more gradually and approaches, and would appear to achieve, a steady state.

A.2 Discussion

The transient elongational viscosity of the PS melt is similar to that reported by various earlier researchers (73, 90, 148, 167). The transient data for the filled melts is similar to that reported by Lobe and White (91) and Tanaka and White (150).

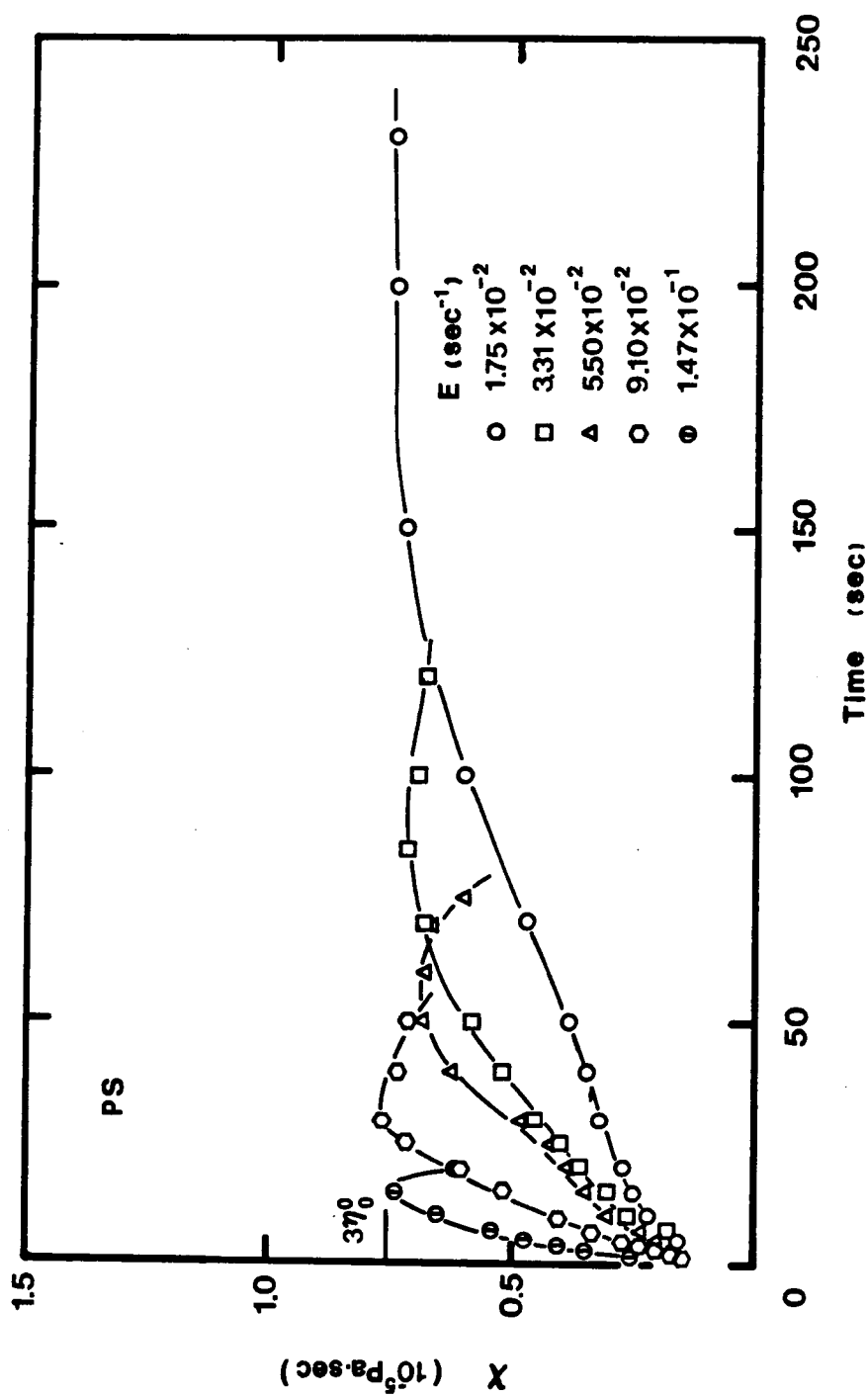


Figure V.1. Transient elongational viscosity at various elongational rates for PS at 180°C.

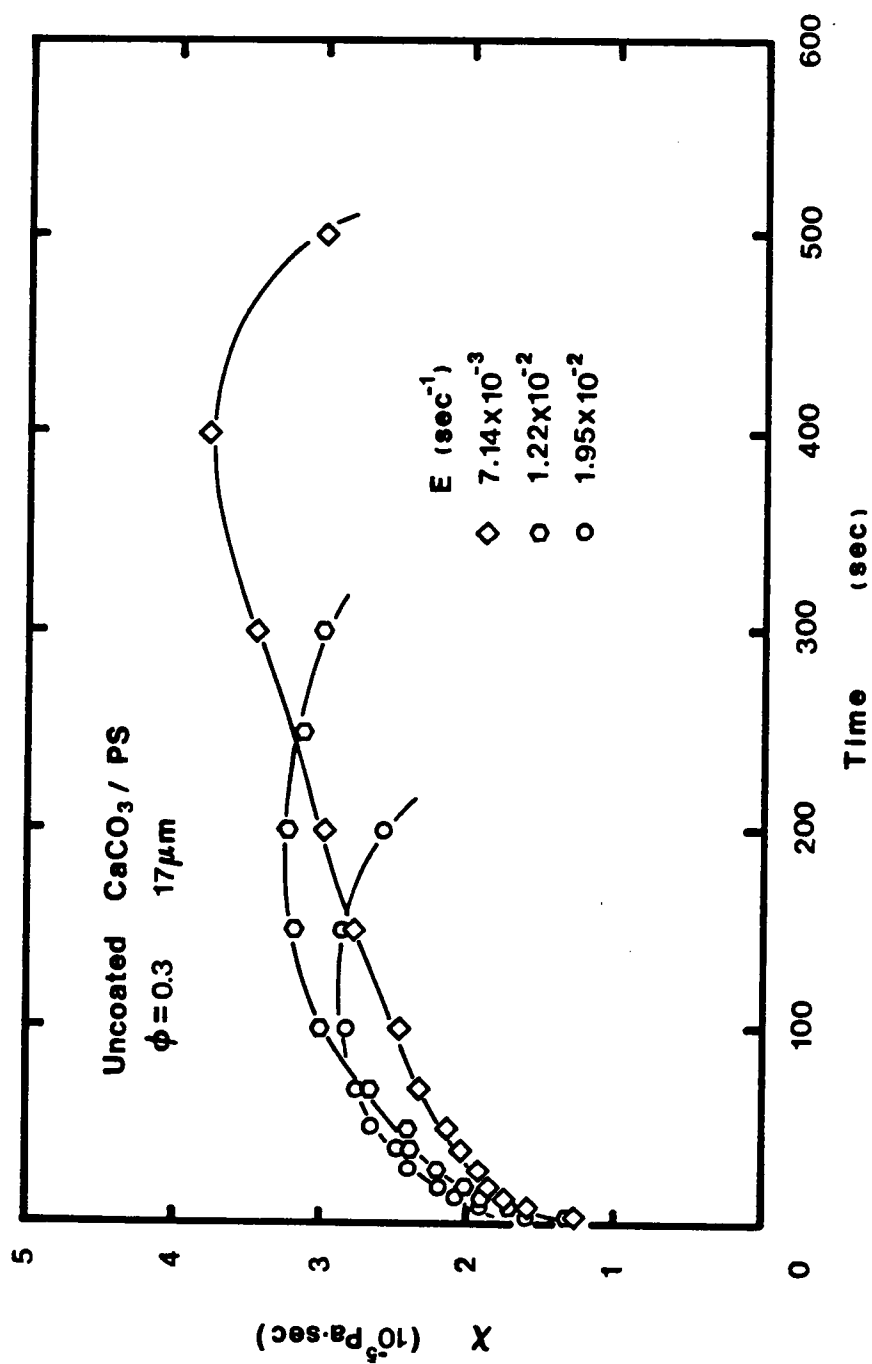


Figure V.2. Transient elongational viscosity at low elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 17 \mu\text{m}$) at 180°C .

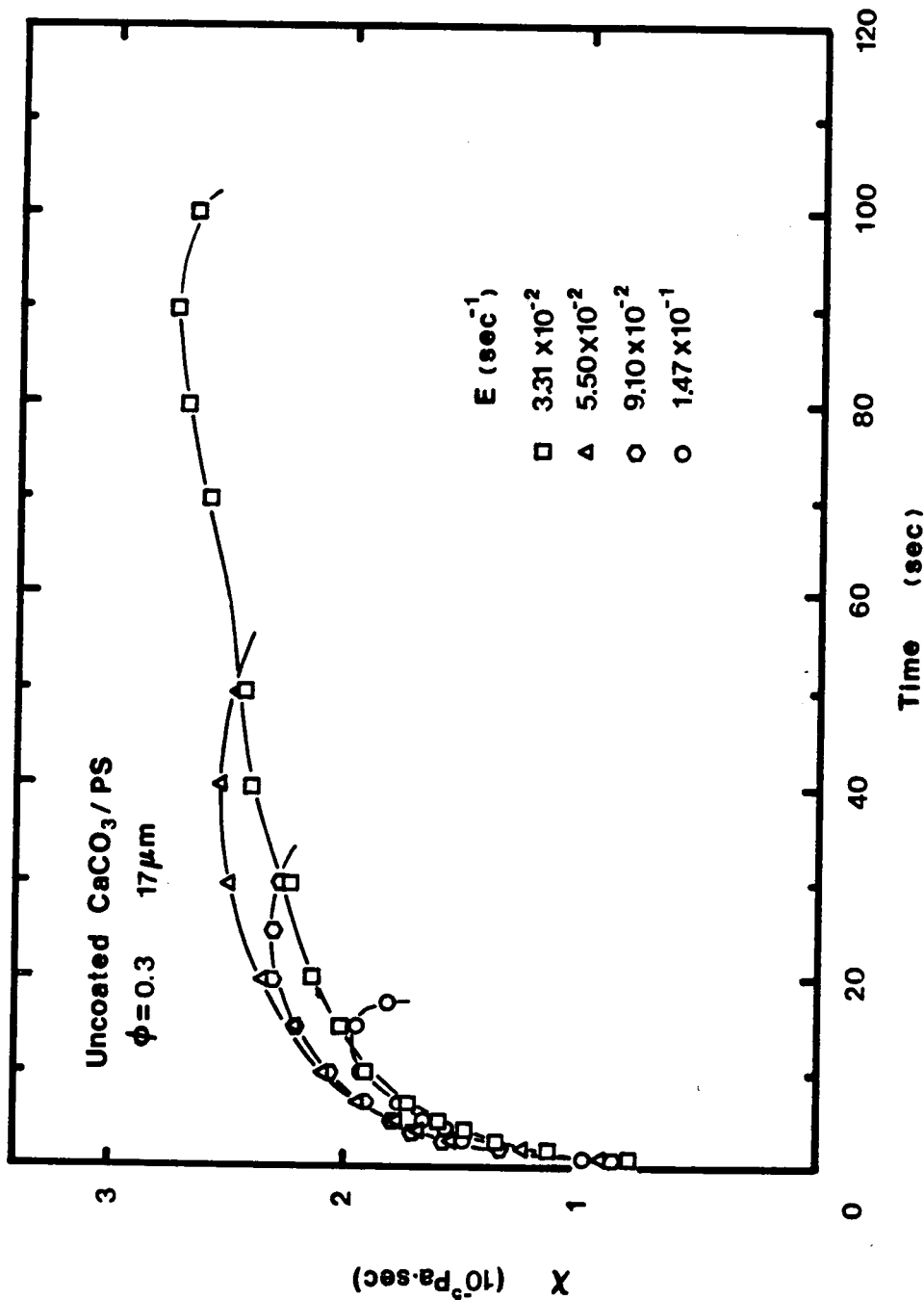


Figure V.3. Transient elongational viscosity at high elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 17\mu\text{m}$) at 180°C .

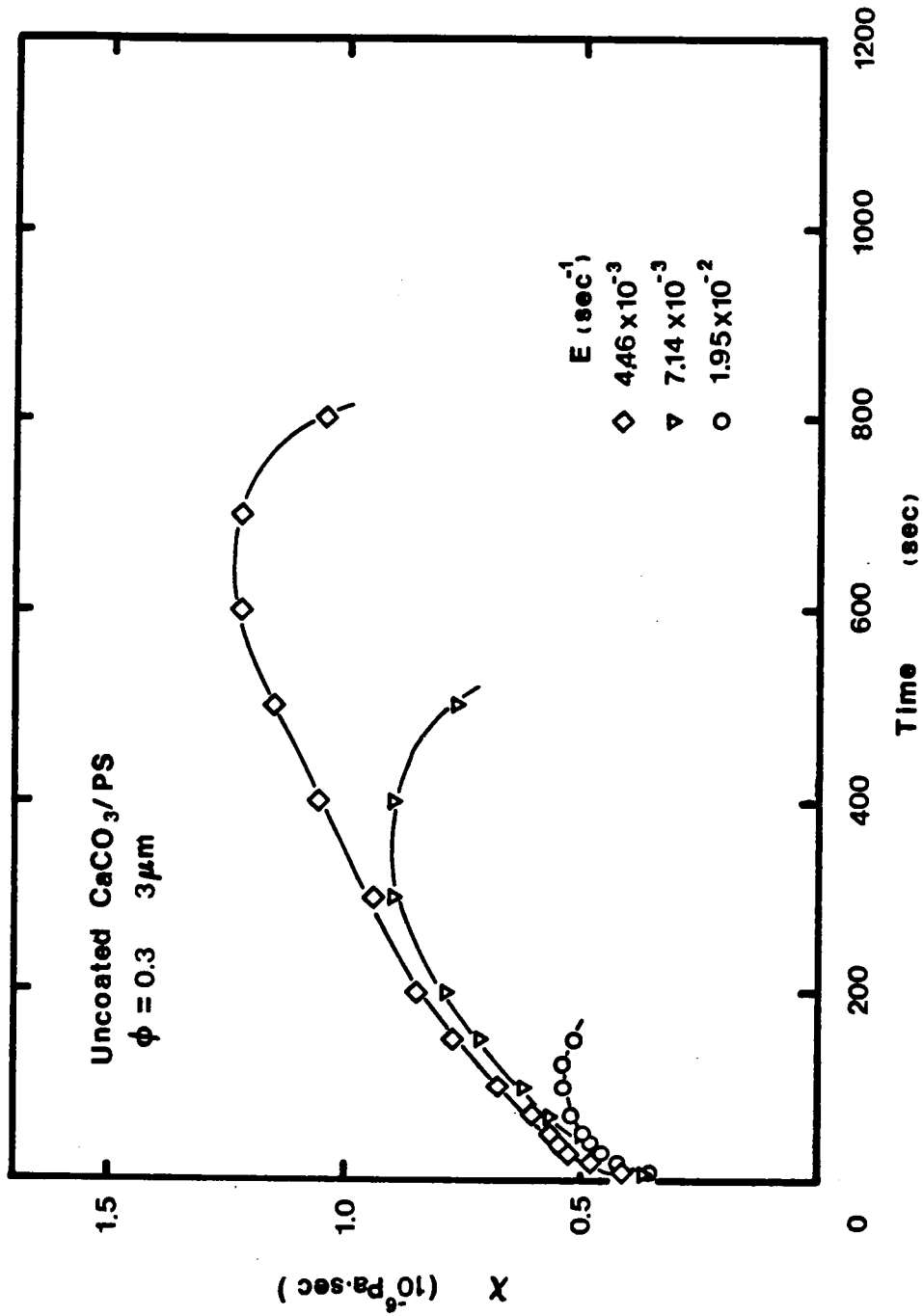


Figure V.4. Transient elongational viscosity at low elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 3\mu\text{m}$) at 180°C .

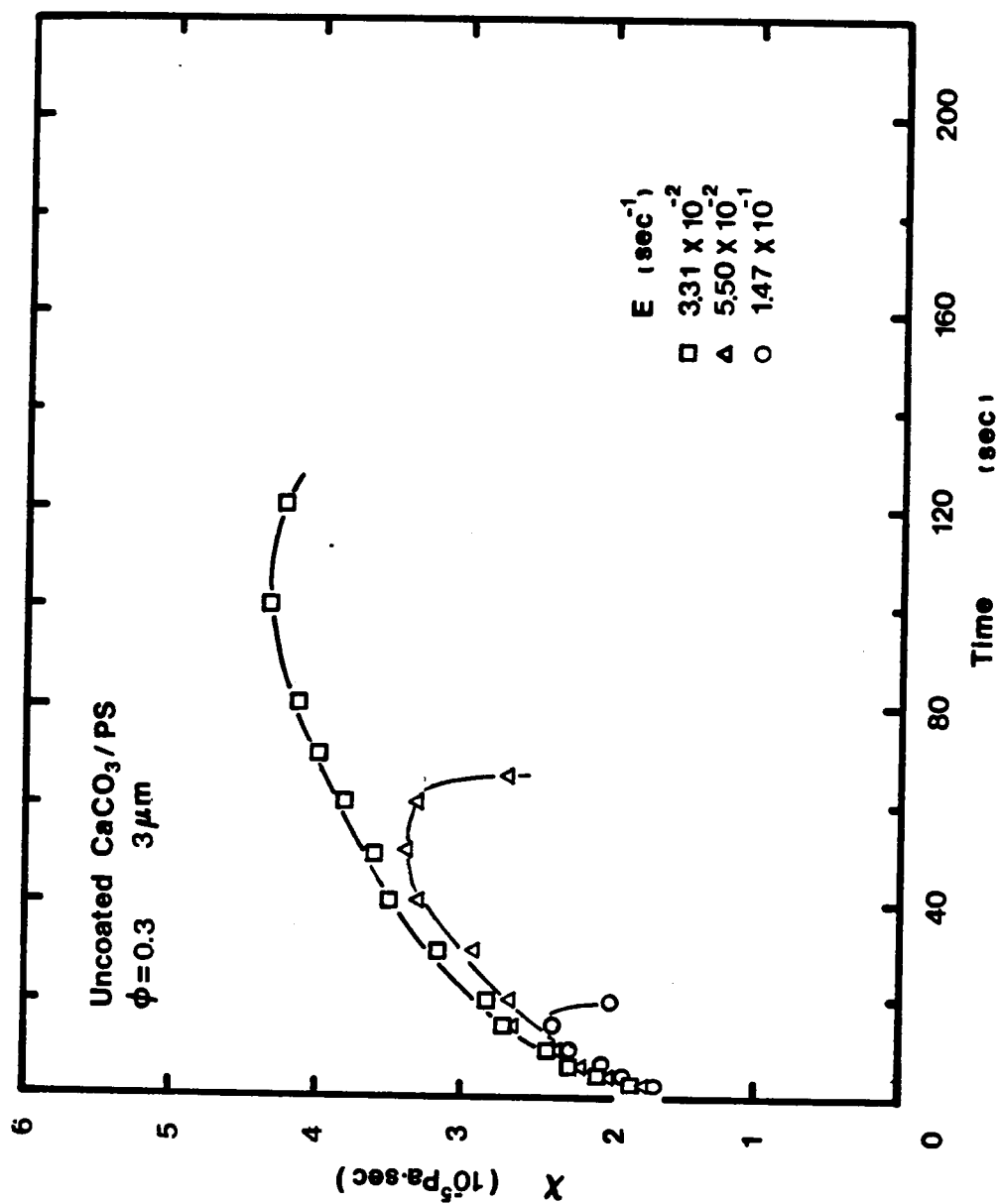


Figure V.5. Transient elongational viscosity at high elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 3 \mu\text{m}$) at 180°C .

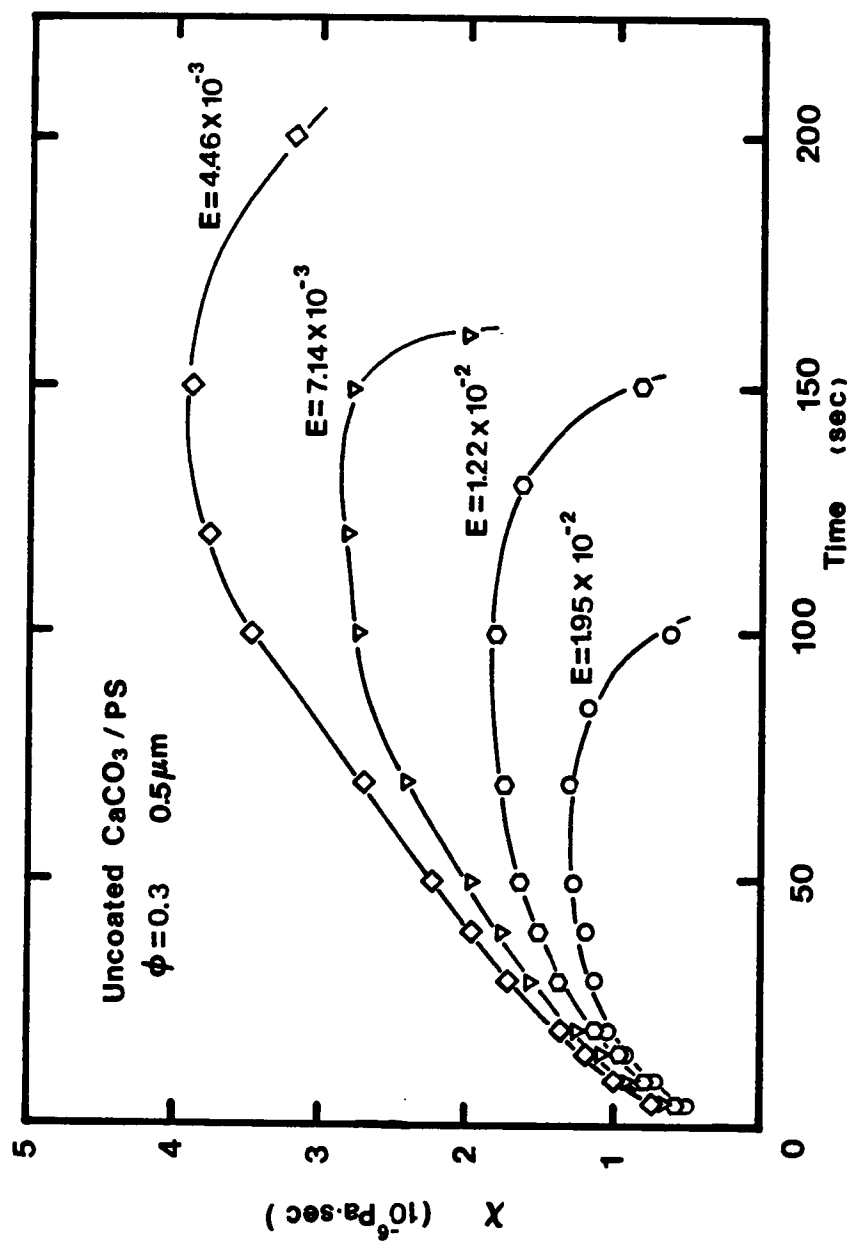


Figure V.6. Transient elongational viscosity at low elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 0.5 \mu\text{m}$) at 180°C .

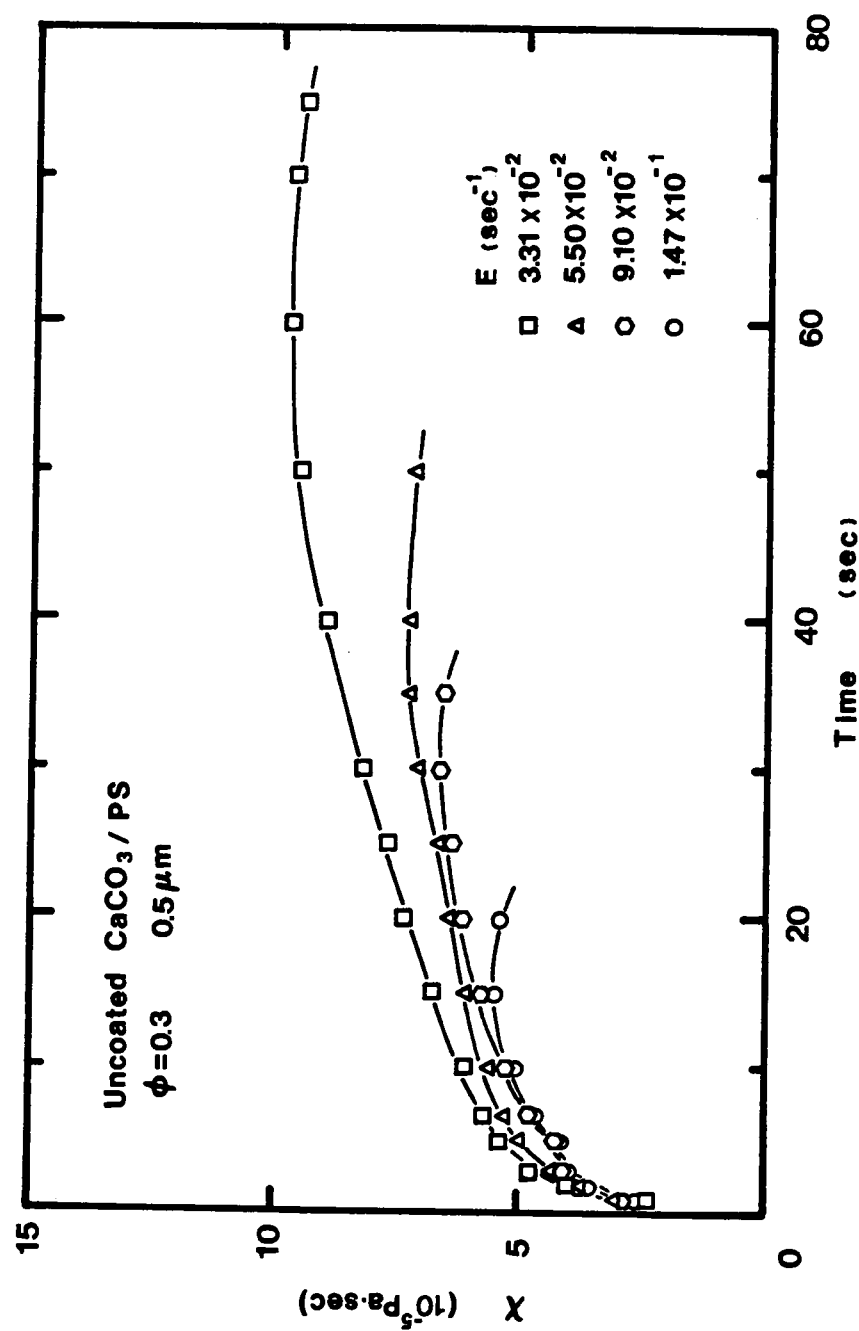


Figure V.7. Transient elongational viscosity at high elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.5 \mu\text{m}$) at 180°C .

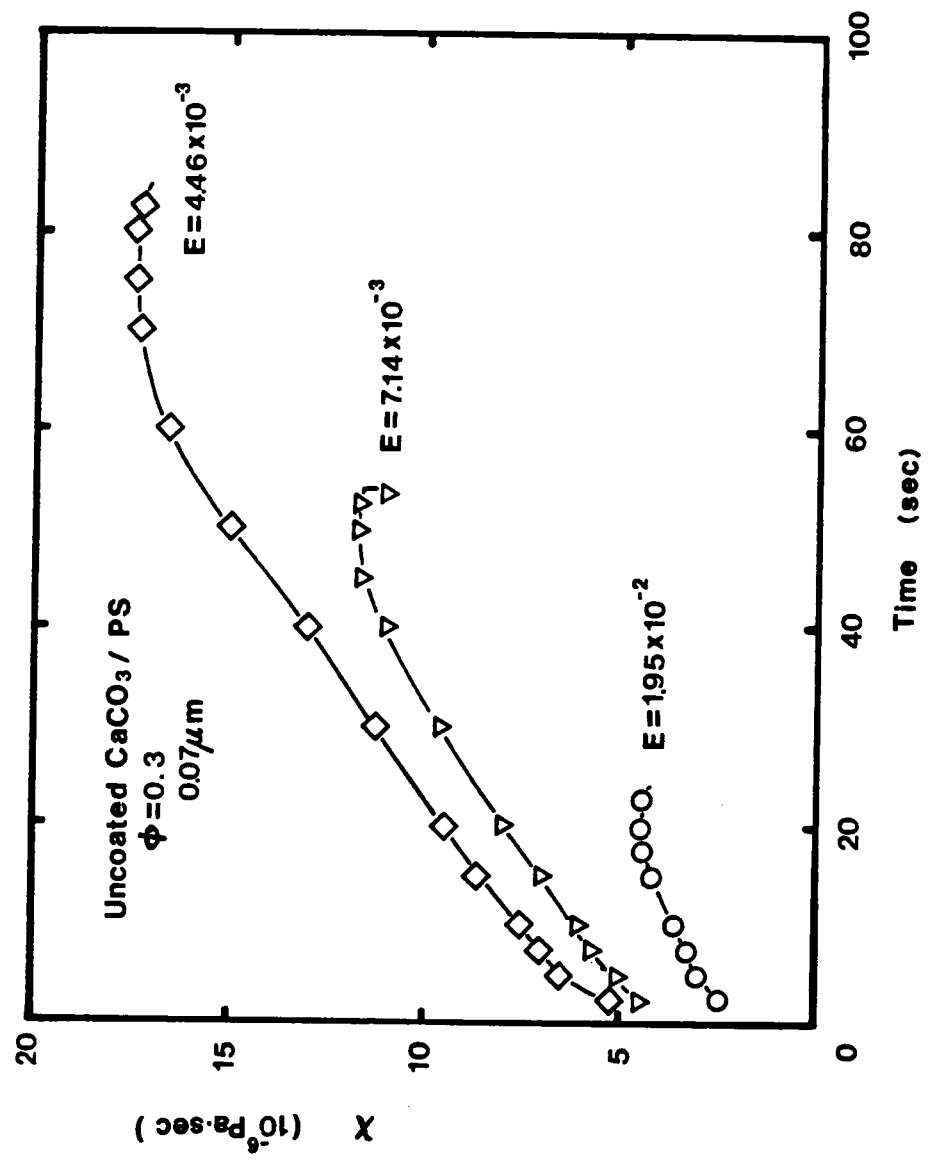


Figure V.8. Transient elongational viscosity at low elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.07 \mu\text{m}$) at 180°C .

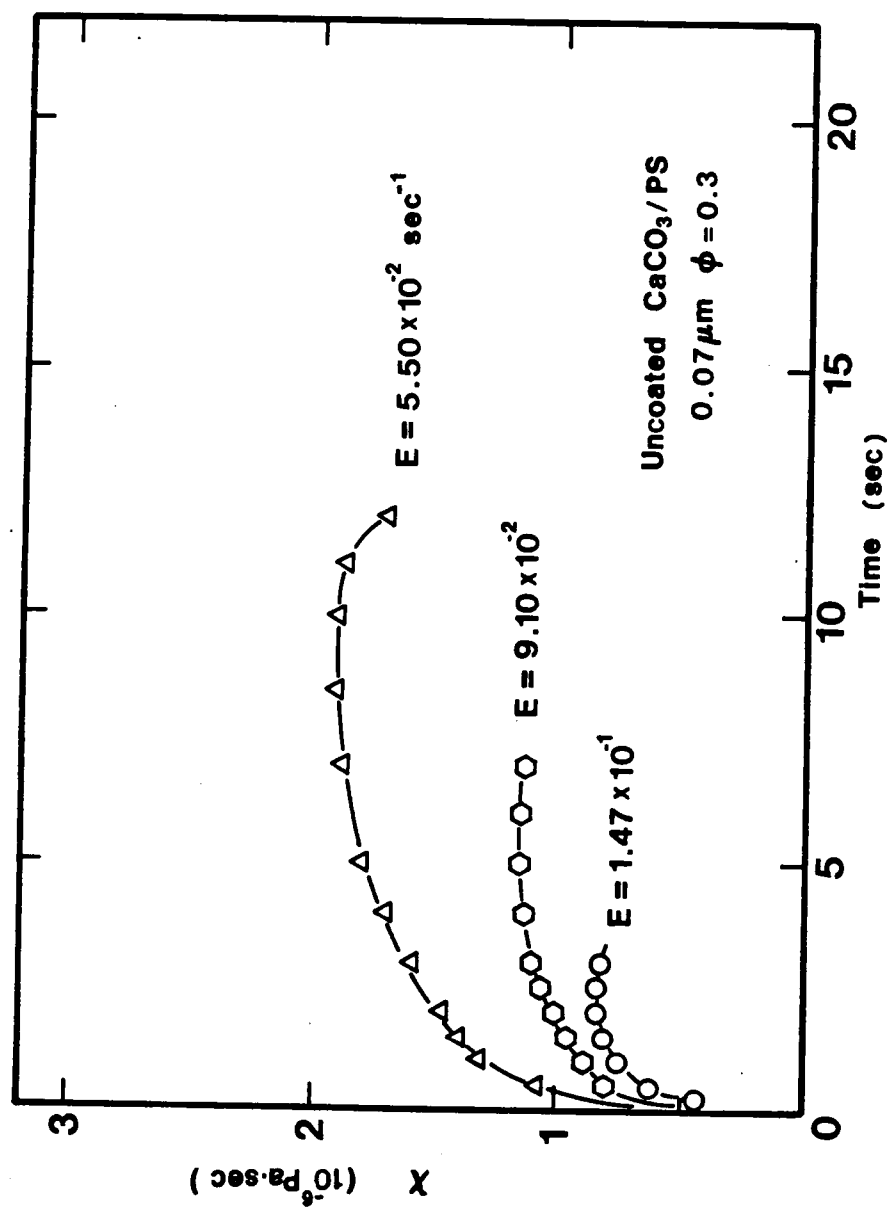


Figure V.9. Transient elongational viscosity at high elongational rates for uncoated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.07 \mu\text{m}$) at 180°C .

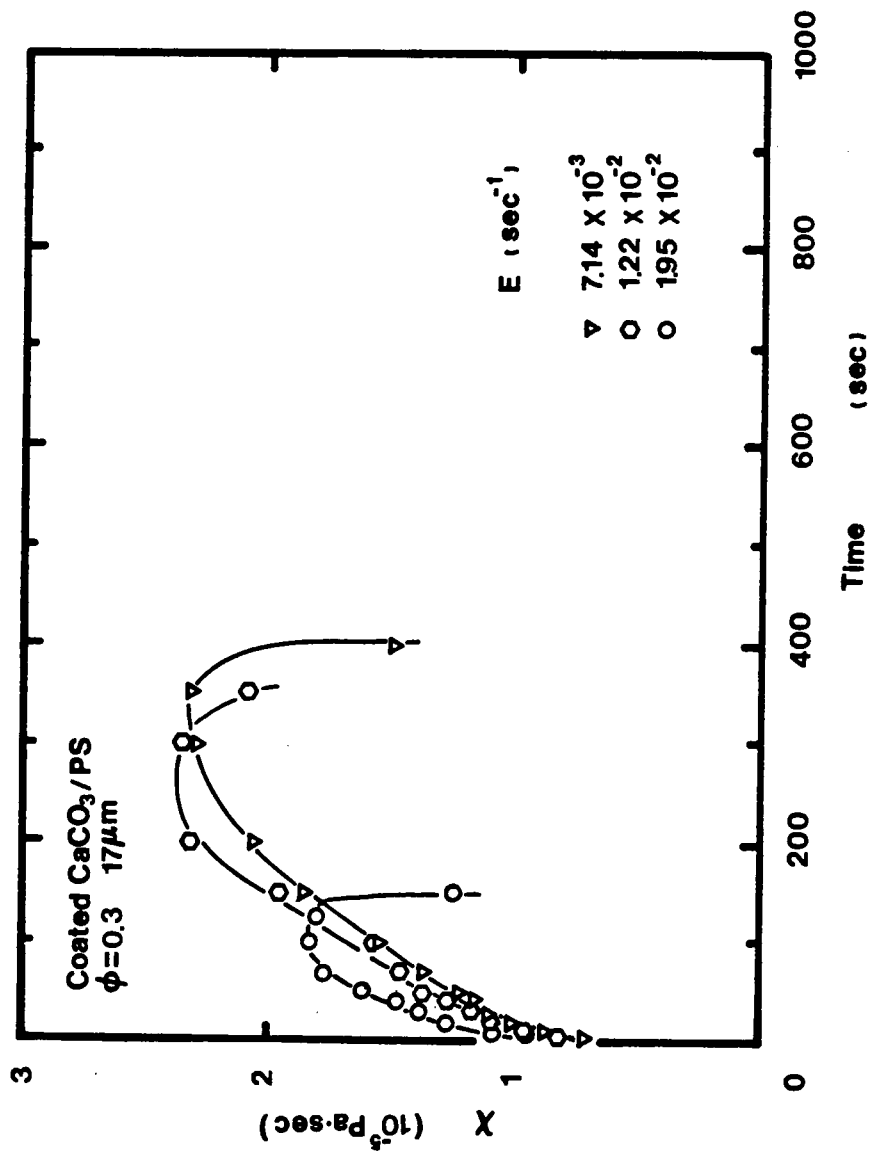


Figure V.10. Transient elongational viscosity at low elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 17 \mu\text{m}$) at 180°C .

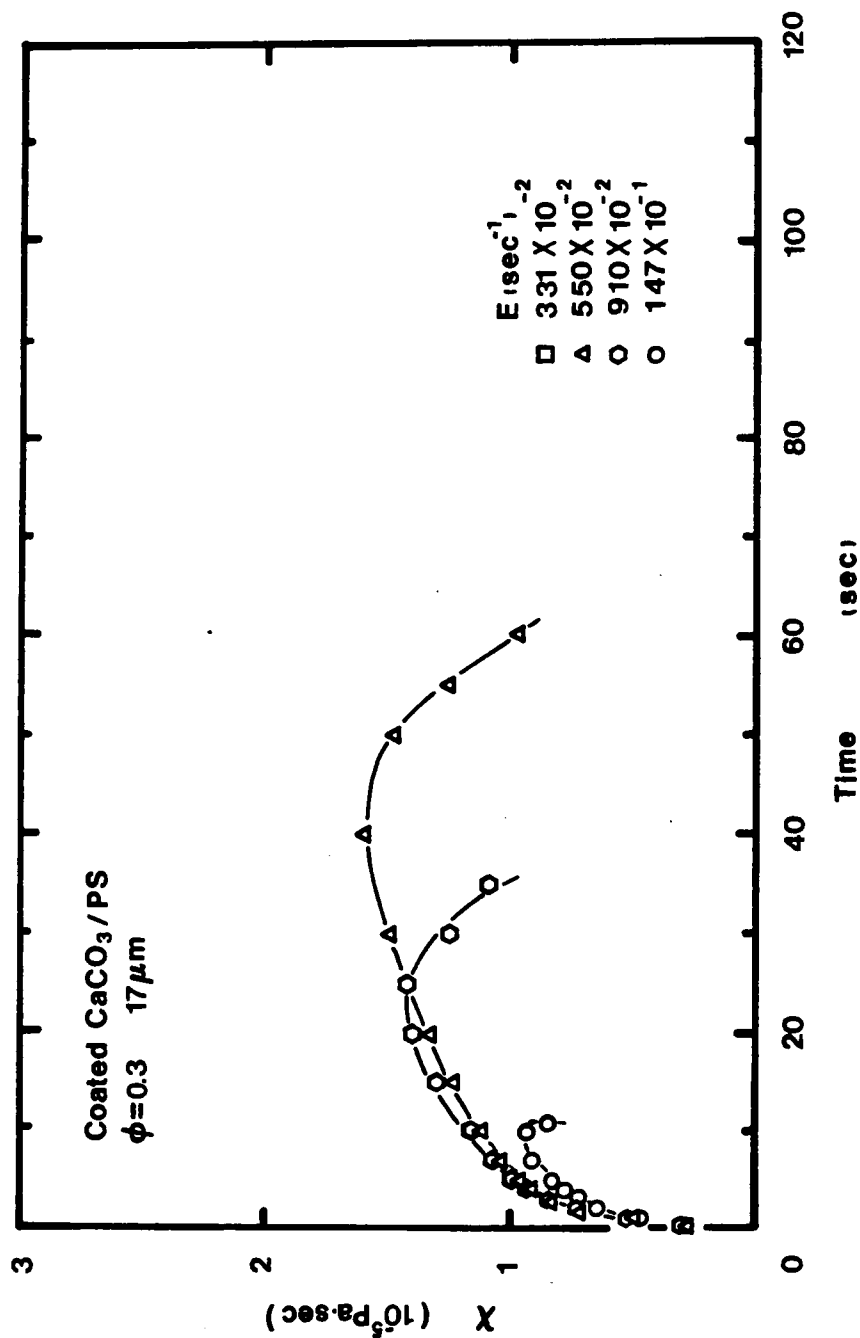


Figure V.11. Transient elongational viscosity at high elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 17 \mu\text{m}$) at 180°C .

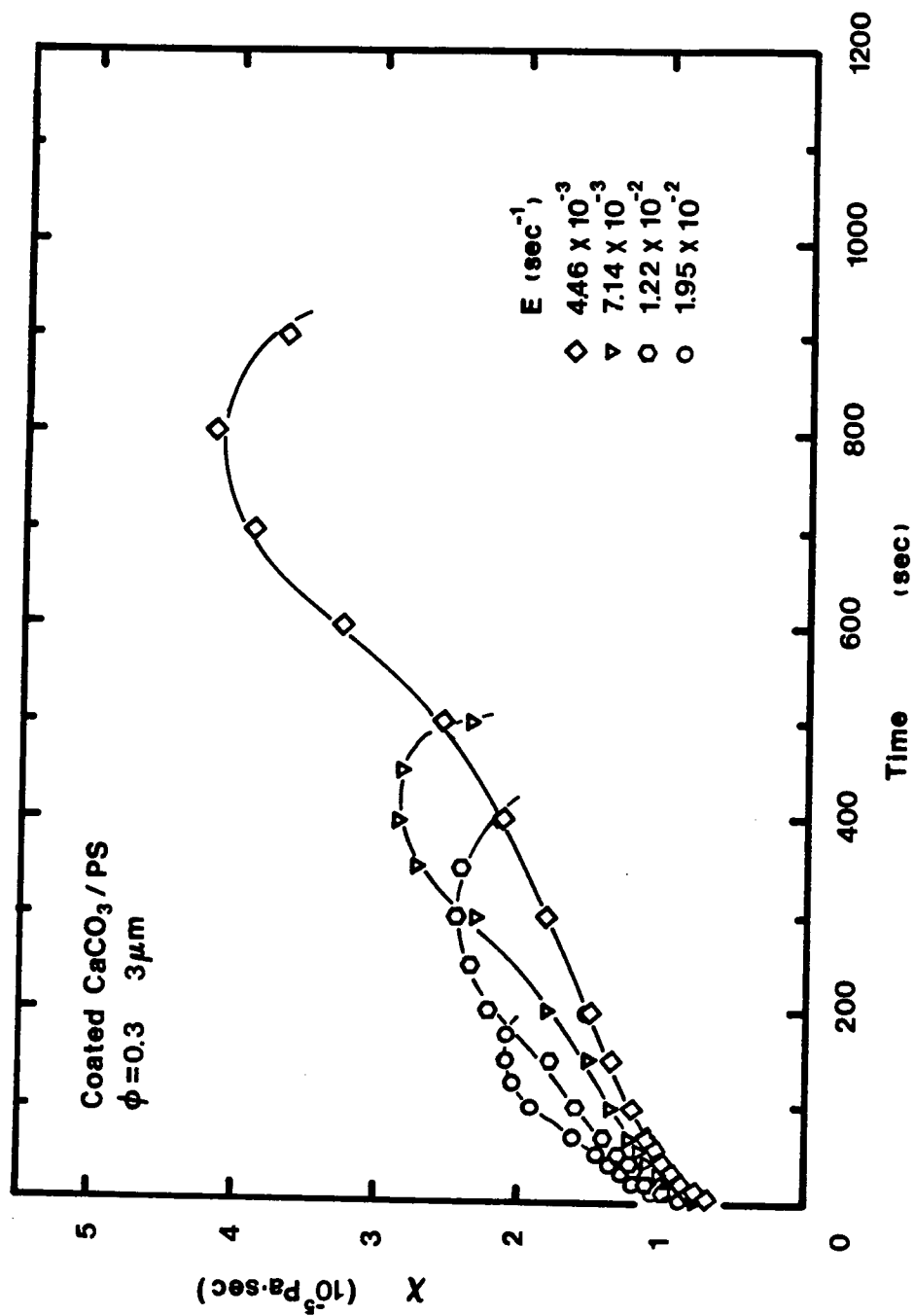


Figure V.12. Transient elongational viscosity at low elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $d_p = 3\mu\text{m}$) at 180°C .

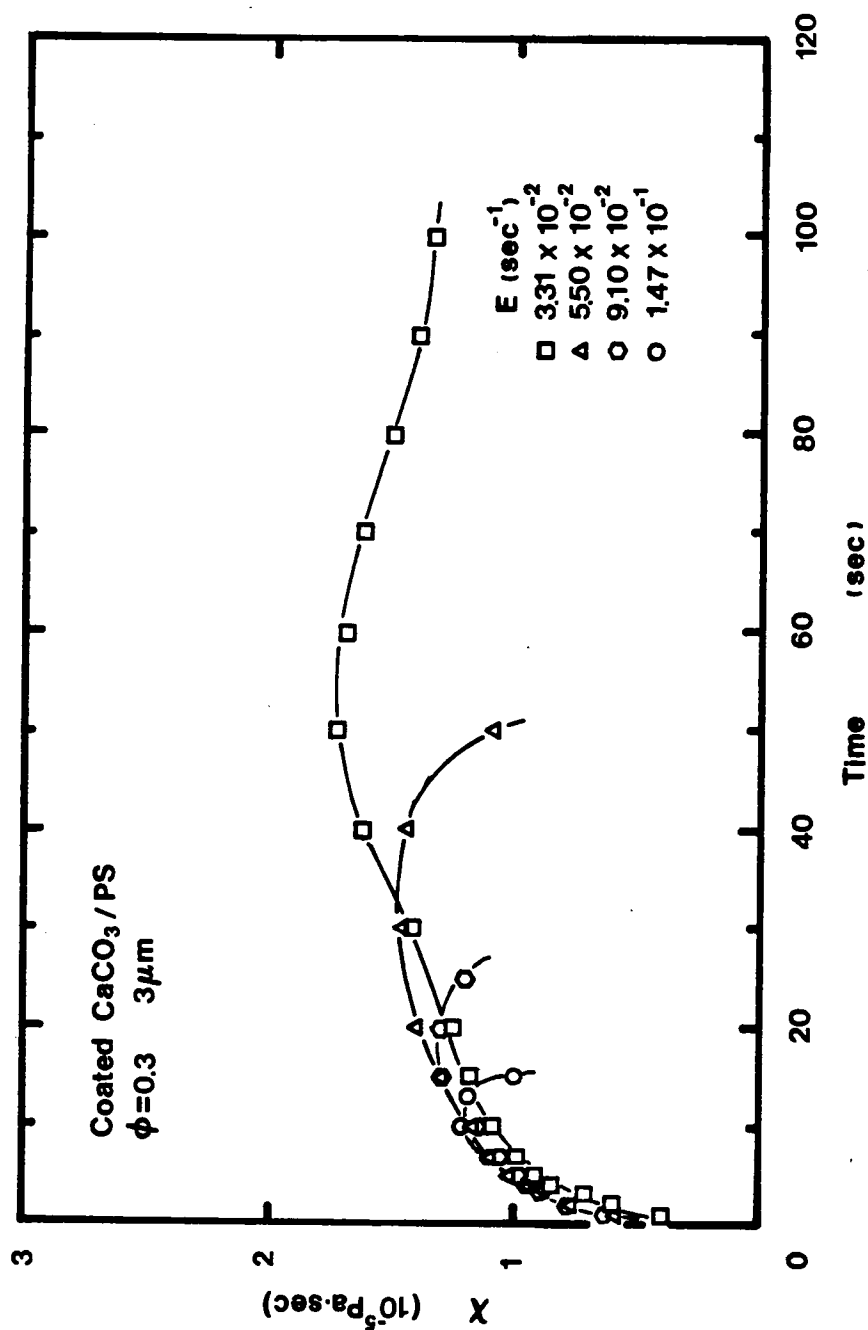


Figure V.13. Transient elongational viscosity at high elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 3\mu\text{m}$) at 180°C .

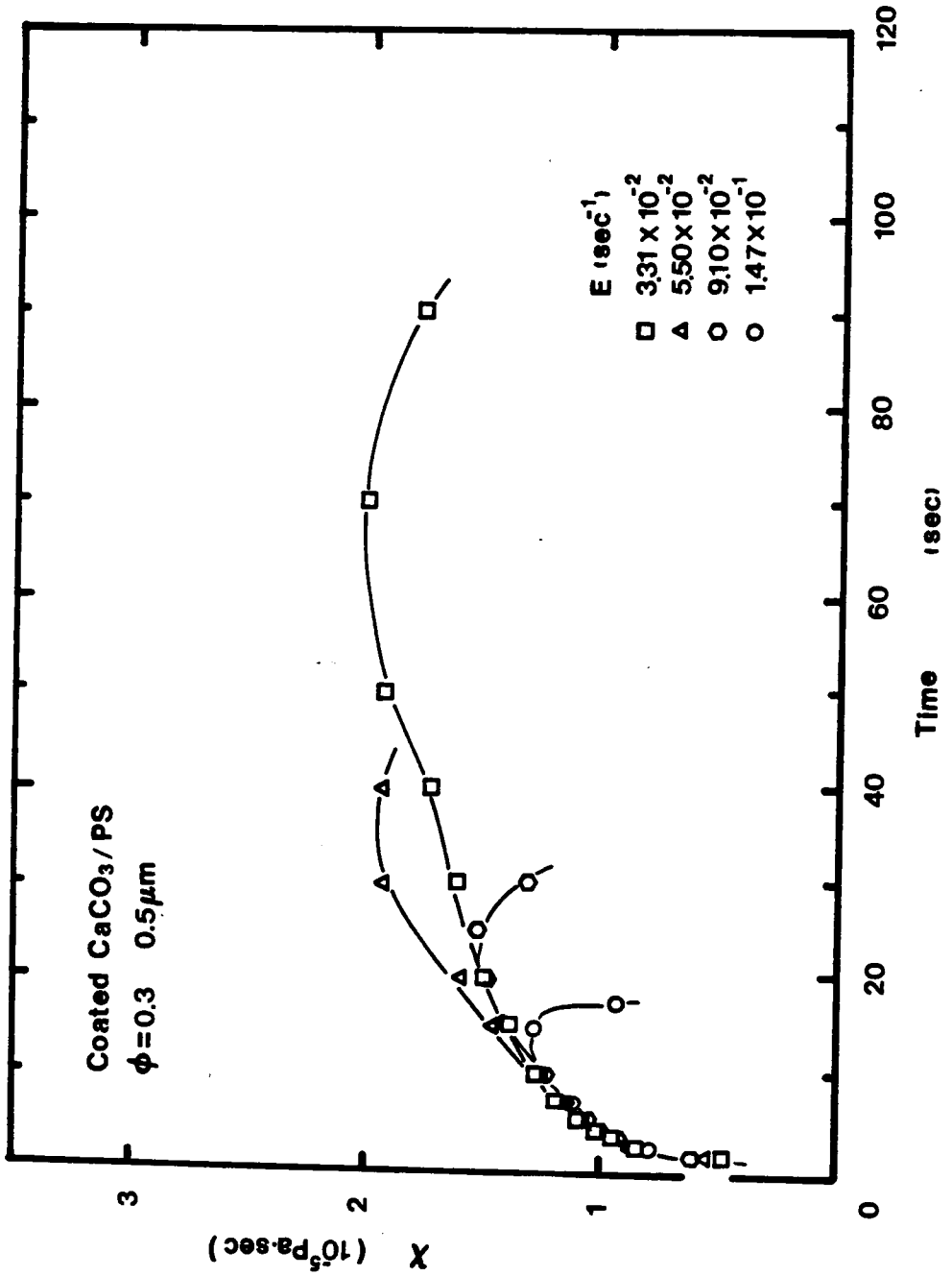


Figure V.14. Transient elongational viscosity at low elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.5 \mu\text{m}$) at 180°C .

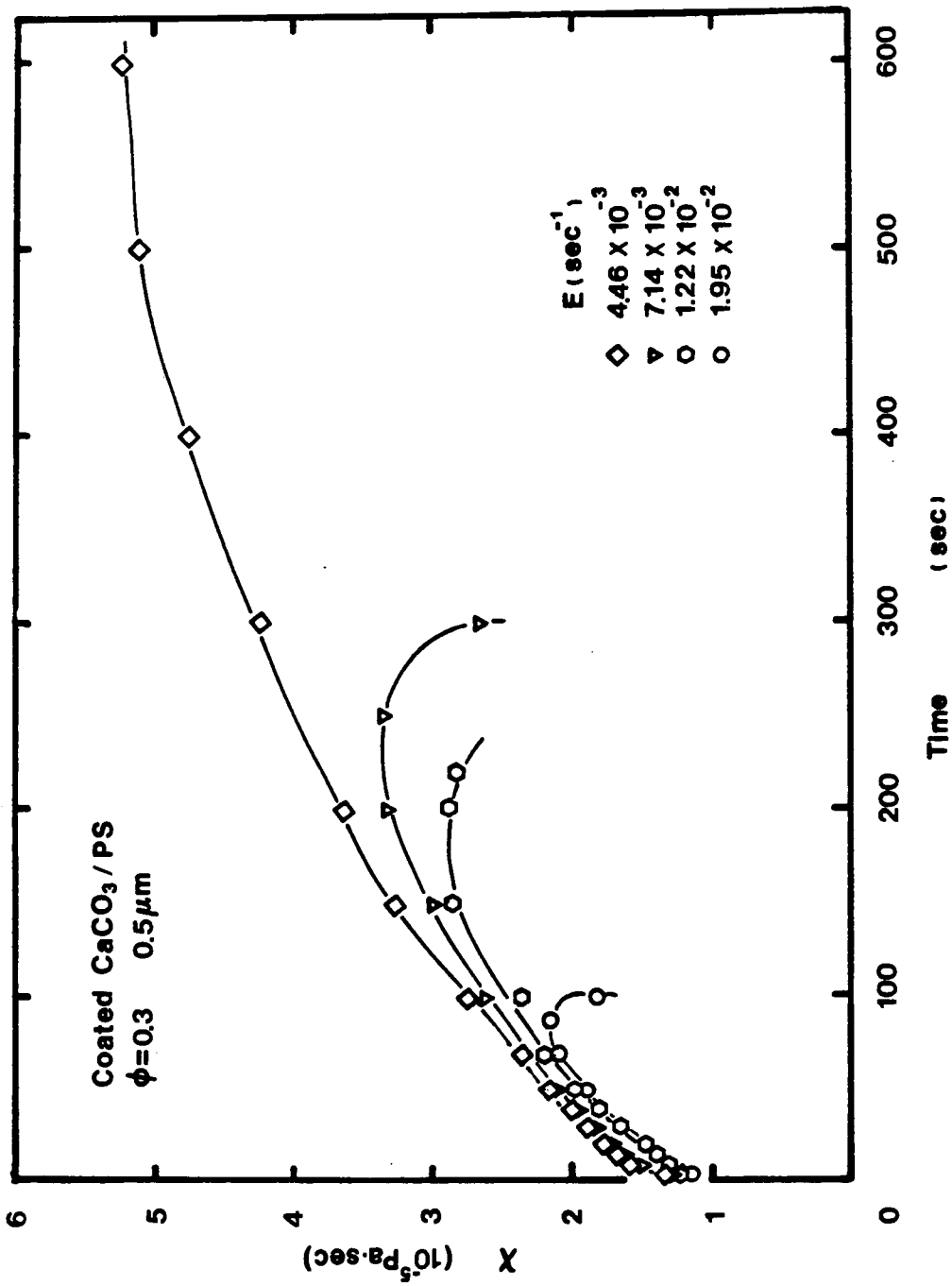


Figure V.15. Transient elongational viscosity at high elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.5 \mu\text{m}$) at 180°C .

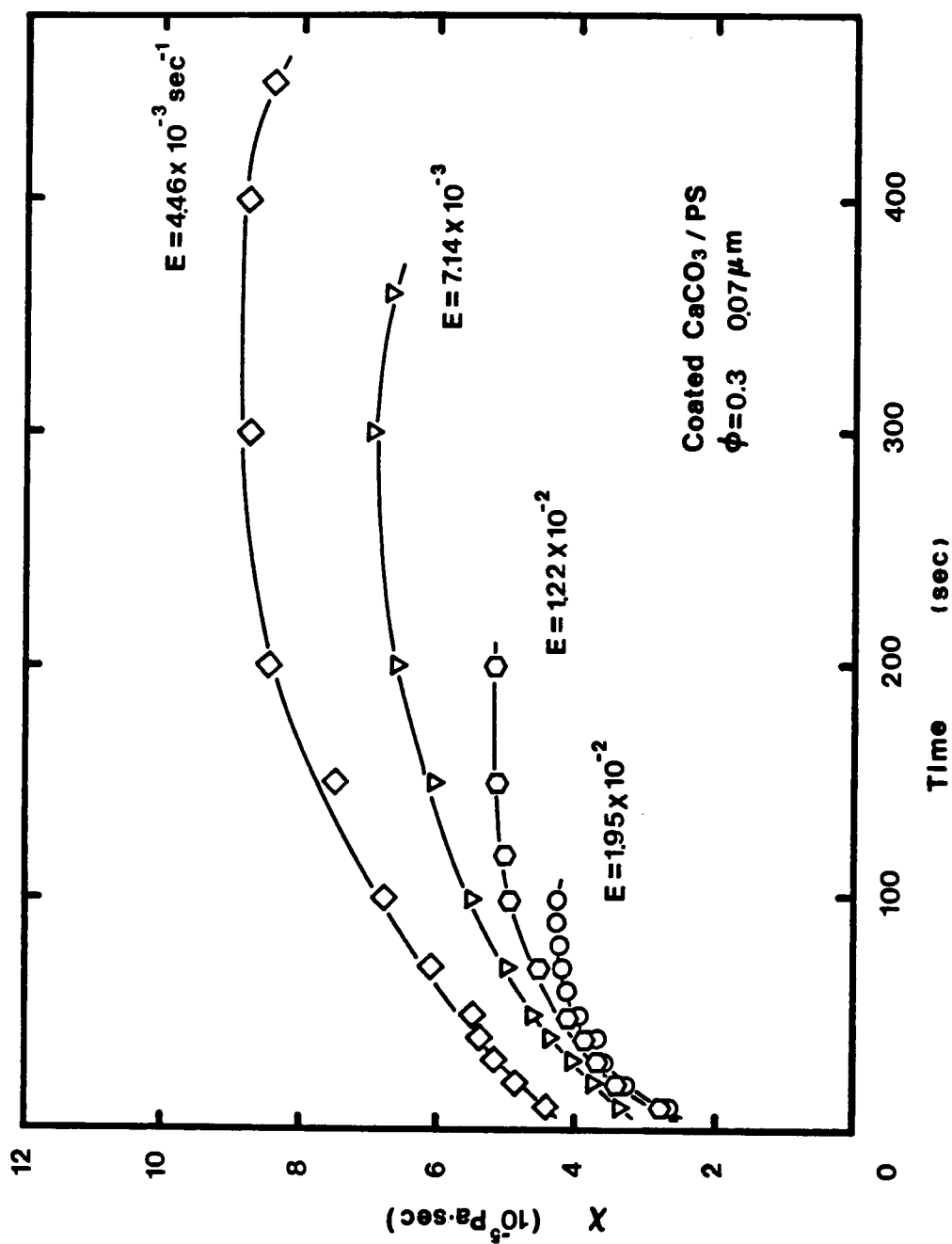


Figure V.16. Transient elongational viscosity at low elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.07 \mu\text{m}$) at 180°C .

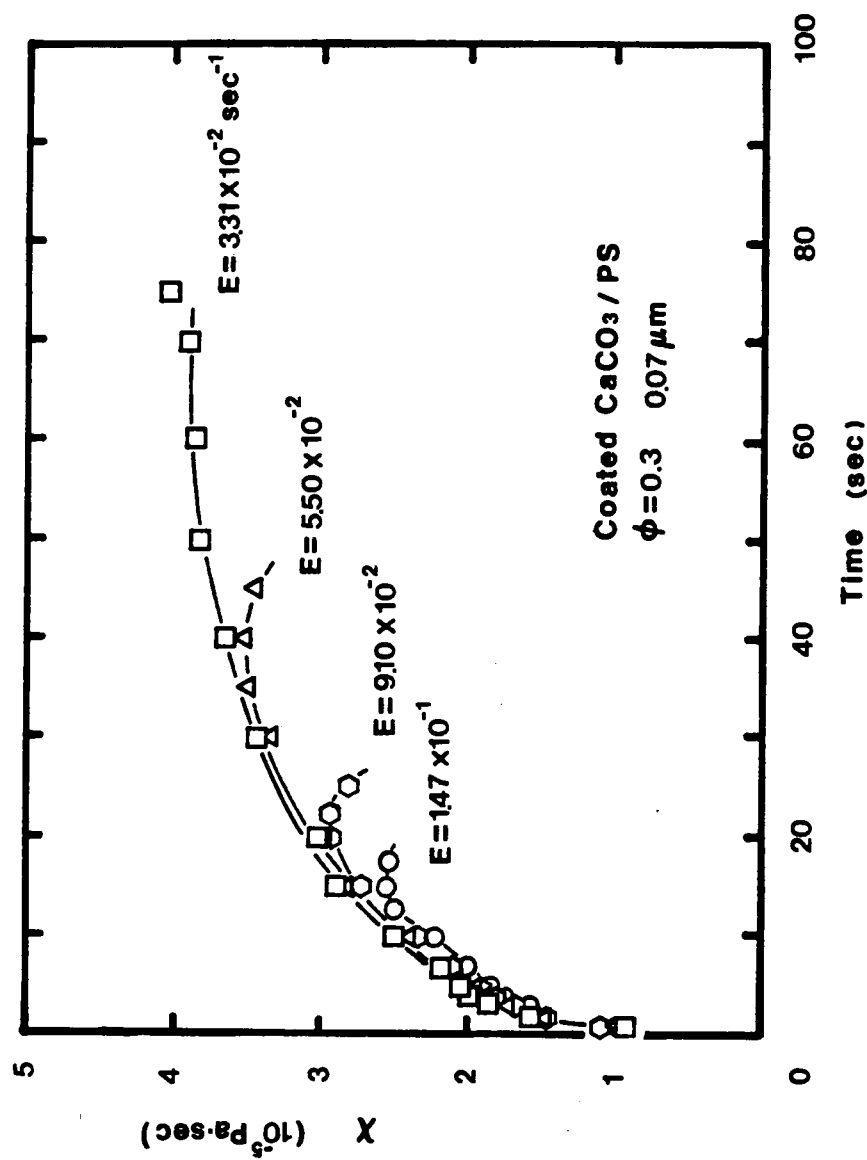


Figure V.17. Transient elongational viscosity at high elongational rates for coated CaCO_3 filled PS ($\phi = 0.3$, $dp = 0.07 \mu\text{m}$) at 180°C .

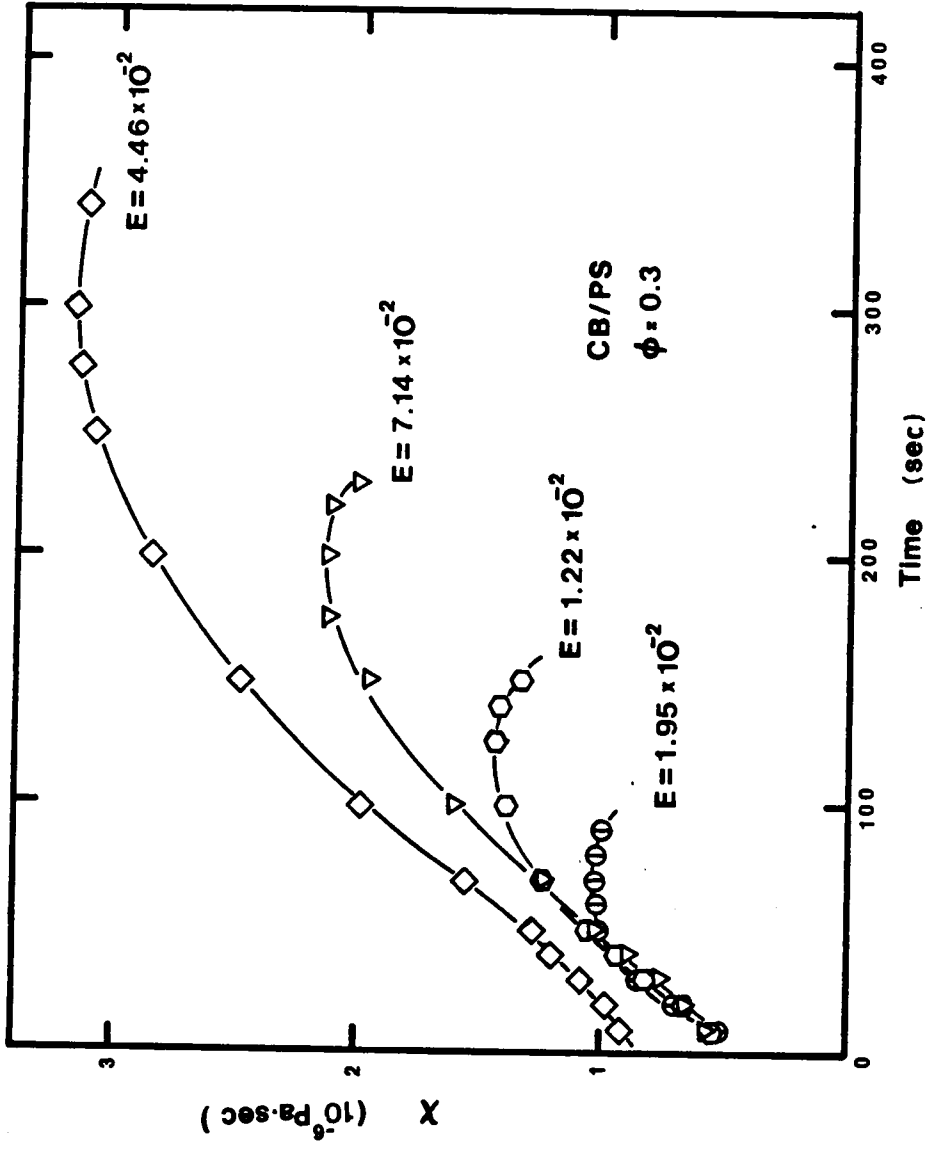


Figure V.18. Transient elongational viscosity at low elongational rates for CB filled PS ($\phi = 0.3$, $dp = 0.045 \text{ } \mu\text{m}$) at 180°C .

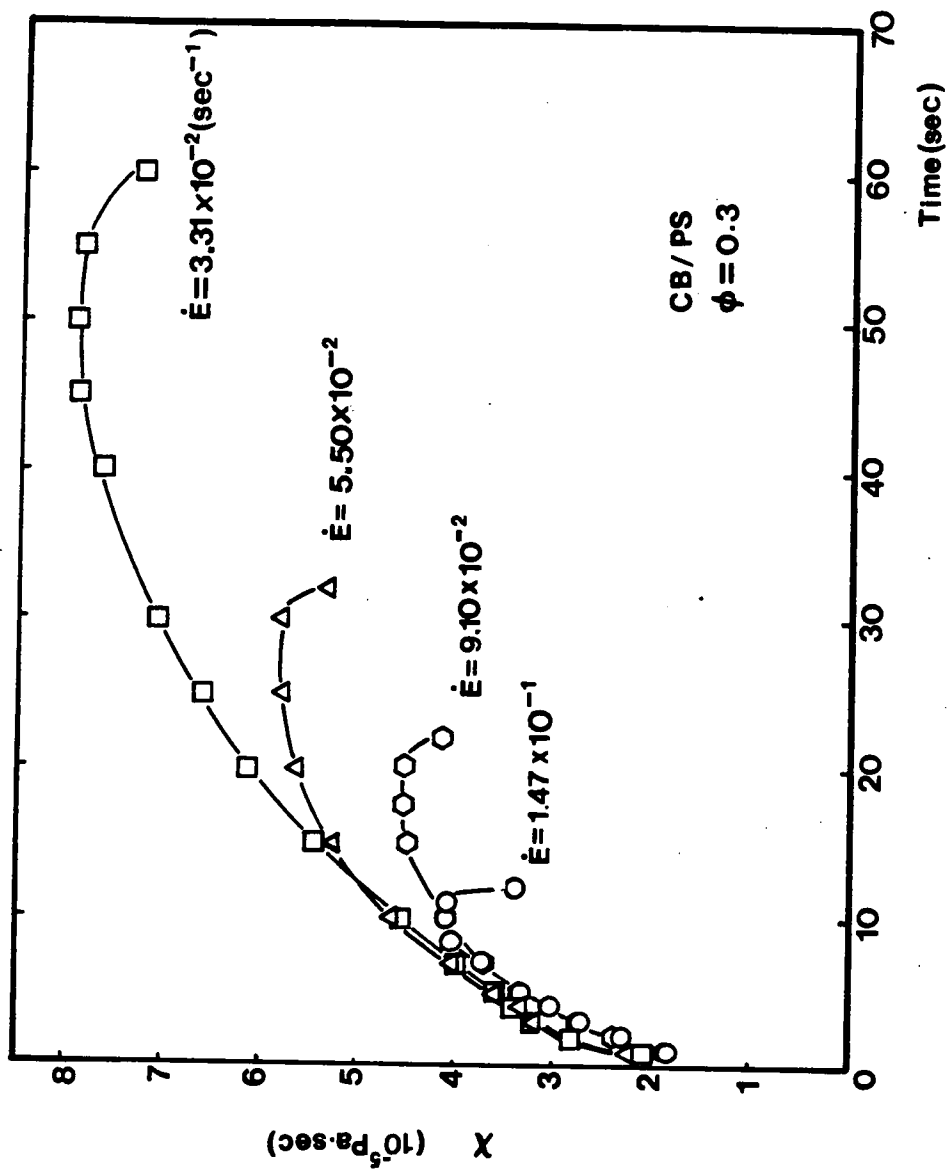


Figure V.19. Transient elongational viscosity at high elongational rates for CB filled PS ($\phi = 0.3$, $dp = 0.045 \text{ }\mu\text{m}$) at 180°C .

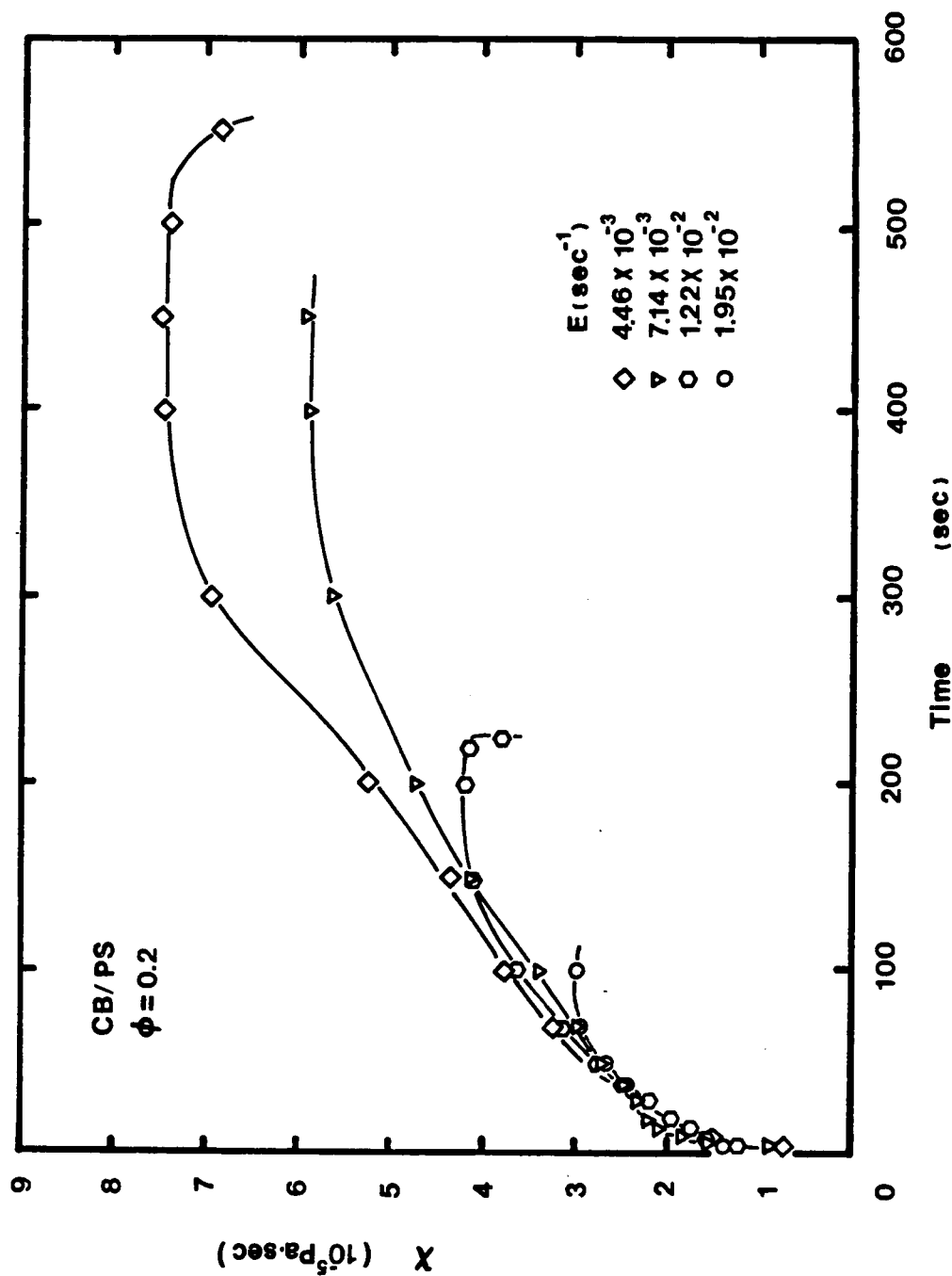


Figure V.20. Transient elongational viscosity at low elongational rates for CB filled PS ($\phi = 0.2$, $dp = 0.045 \mu\text{m}$) at 180°C .

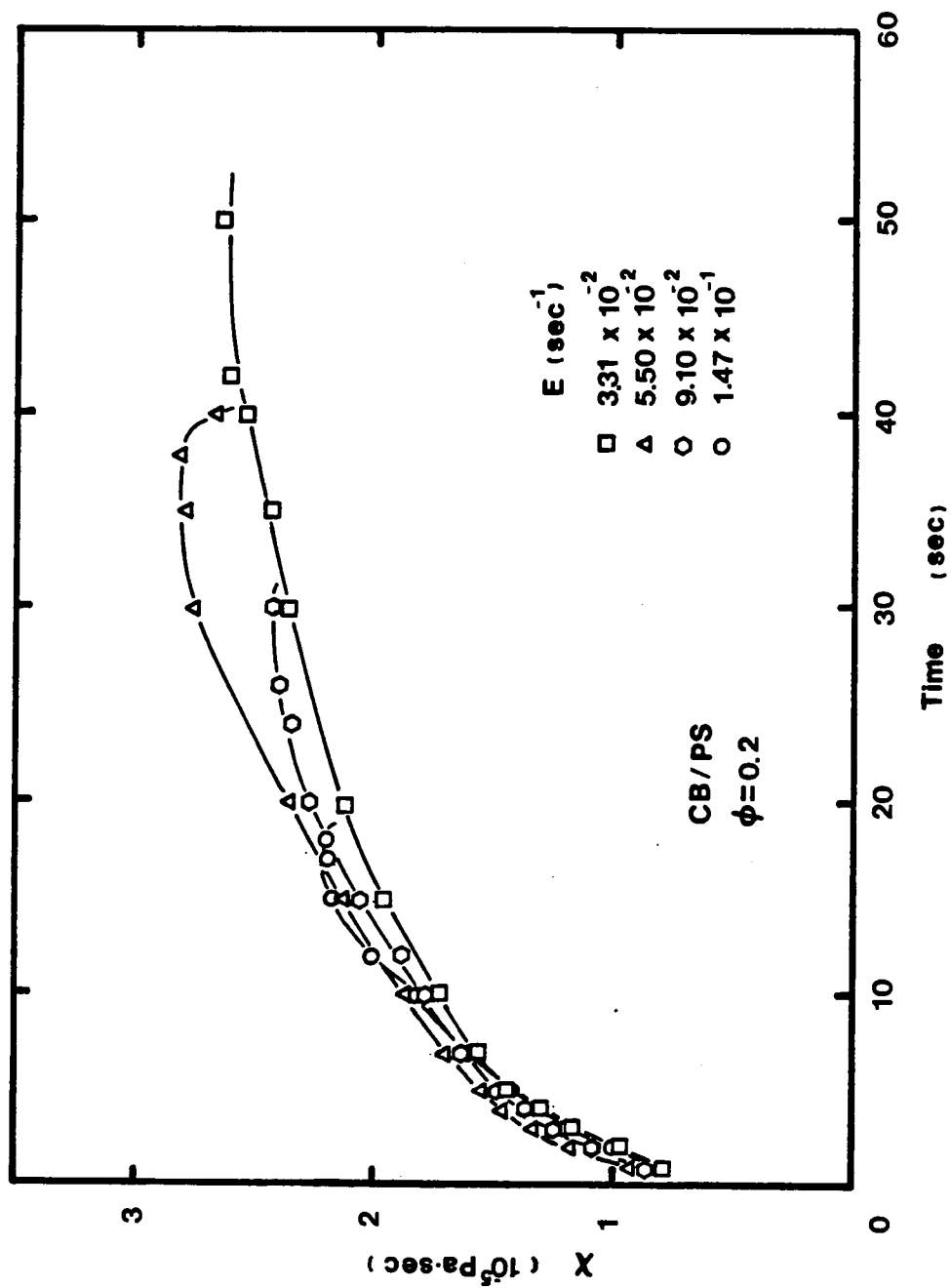


Figure V.21. Transient elongational viscosity at high elongational rates for CB filled PS ($\phi = 0.2$, $dp = 0.045 \text{ } \mu\text{m}$) at 180°C .

The sudden increase of the elongational viscosity of small particle filled systems at the beginning of deformation may be related to the yield stress of the system. Both transient and steady state elongational viscosities of most filled PS samples are fairly reproducible. Some samples, containing larger CaCO_3 particles, show poorer reproducibility.

B. Steady State Elongational Viscosity

B.1 Results

The steady state elongational viscosities are plotted as a function of elongational rate in Figures V.22 to V.24. Figure V.22 shows the steady state elongational viscosities of polystyrene and uncoated CaCO_3 filled PS systems. The steady state elongational viscosity increases with decreasing average particle diameter especially at low elongational rates. The data is a strong decreasing function of the stretch rate.

Figure V.23 shows the behavior of coated CaCO_3 filled PS systems. The steady state values increase with decreasing average particle diameters in this case also, and they are always smaller than those of uncoated CaCO_3 filled PS of the same average particle diameter. The three largest particle diameter filled compounds do not show remarkable differences among them in their steady state elongational viscosities.

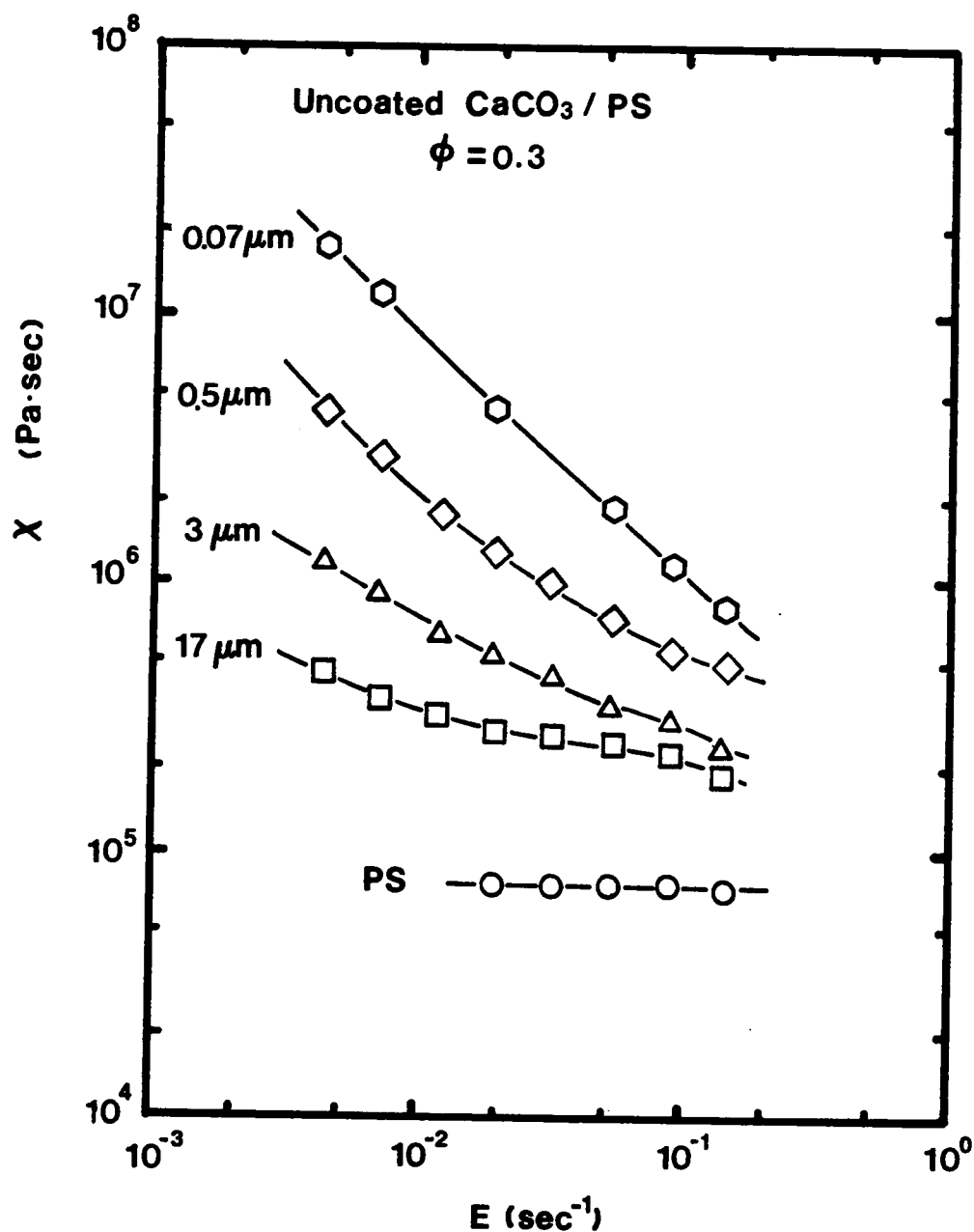


Figure V.22. Steady state elongational viscosity of uncoated CaCO_3 filled PS as a function of elongational rates at 180°C .

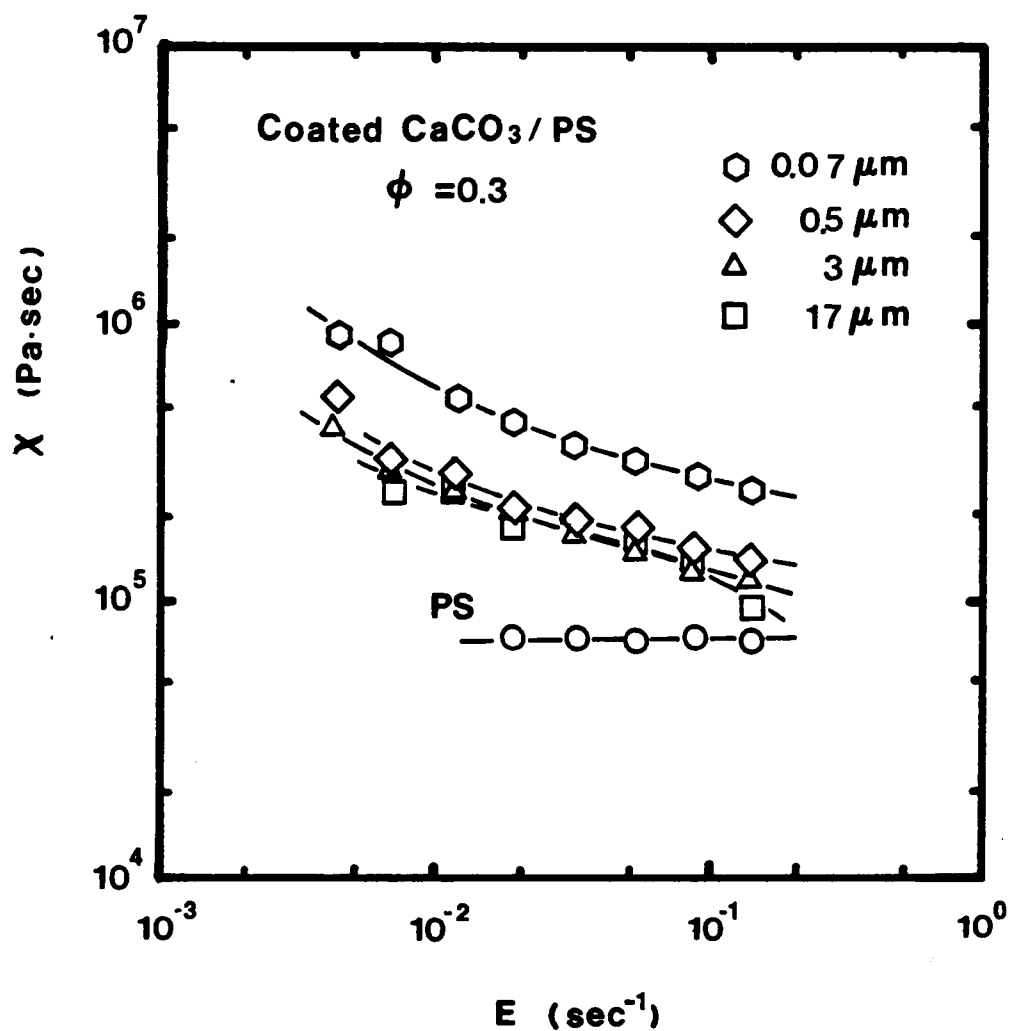


Figure V.23. Steady state elongational viscosity of coated CaCO_3 filled PS as a function of elongational rates at 180°C .

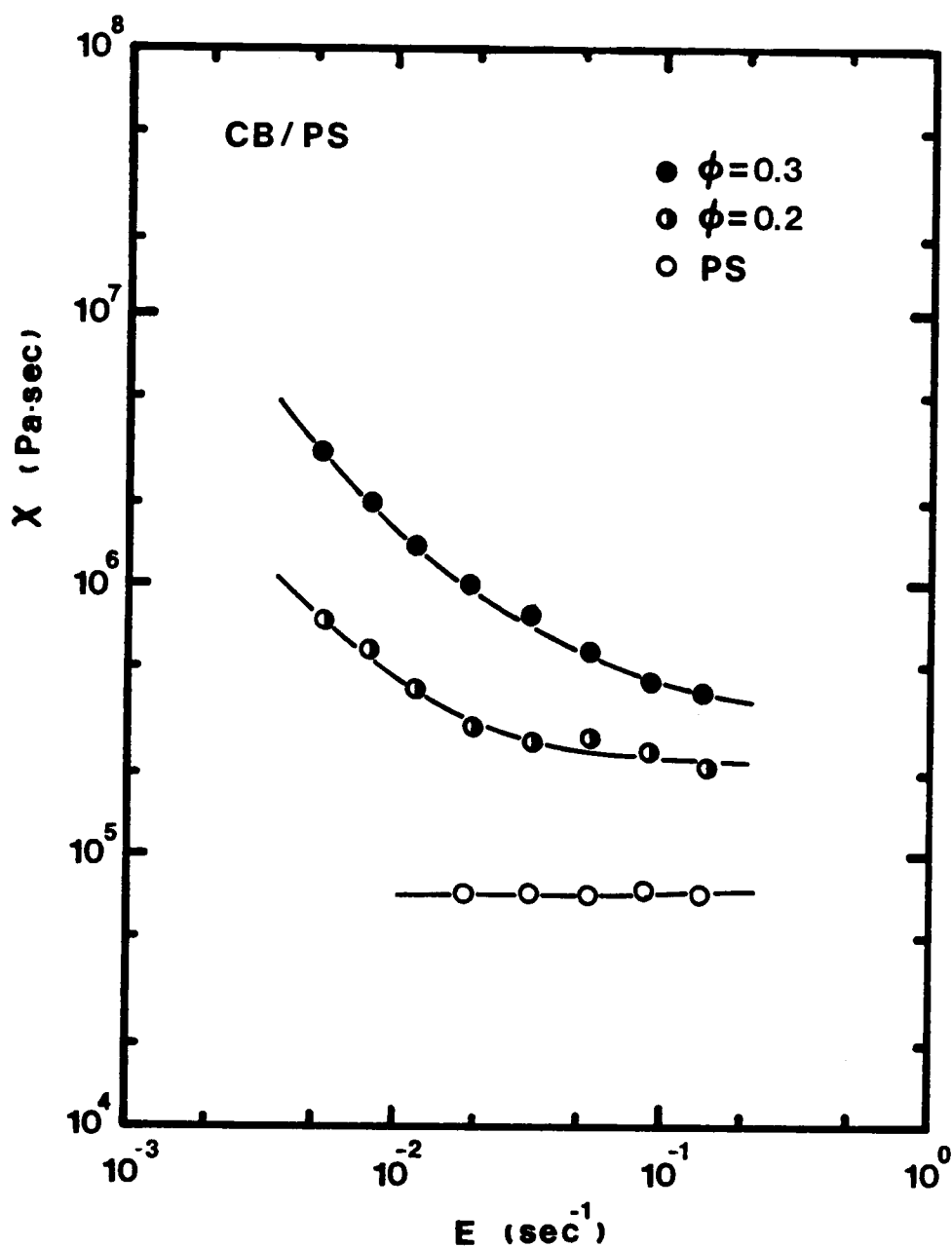


Figure V.24. Steady state elongational viscosity of CB filled PS as a function of elongational rates at 180°C.

Figure V.24 shows CB filled PS systems with different loading levels of filler. The steady state values increase with increasing loading levels of filler and again are decreasing functions of the stretch rate.

B.2 Discussion

Figures V.25 to V.27 contain plots of steady state elongational viscosity as a function of tensile stress σ_{11} . The elongational viscosity of PS which is constant and independent of the stretch rate, is close to three times the zero shear viscosity, that is, $3 \eta_0$. Uncoated CaCO_3 filled PS melts tend to infinite values at finite tensile stress (Figure V.25). Similar behavior is observed by Tanaka and White (150) for a CaCO_3/PS compound. This indicates a yield stress during elongational flow. Small particle filled PS compounds show clear and large yield stresses. The yield stress decreases with increasing particle size of filler.

Figure V.26 shows data for the coated CaCO_3 filled PS. The stearic acid surface treatment on CaCO_3 particles reduces the tendency to yield stresses in the systems. The tendency towards yield stresses is not as distinctive as in the uncoated CaCO_3 filled compounds. Again, it increases with decreasing particle size. Stearic acid may make an electric barrier on the surface of the calcium carbonate particle which has a dipole-dipole mechanism. This may be a reason for viscosity and yield stress reduction.

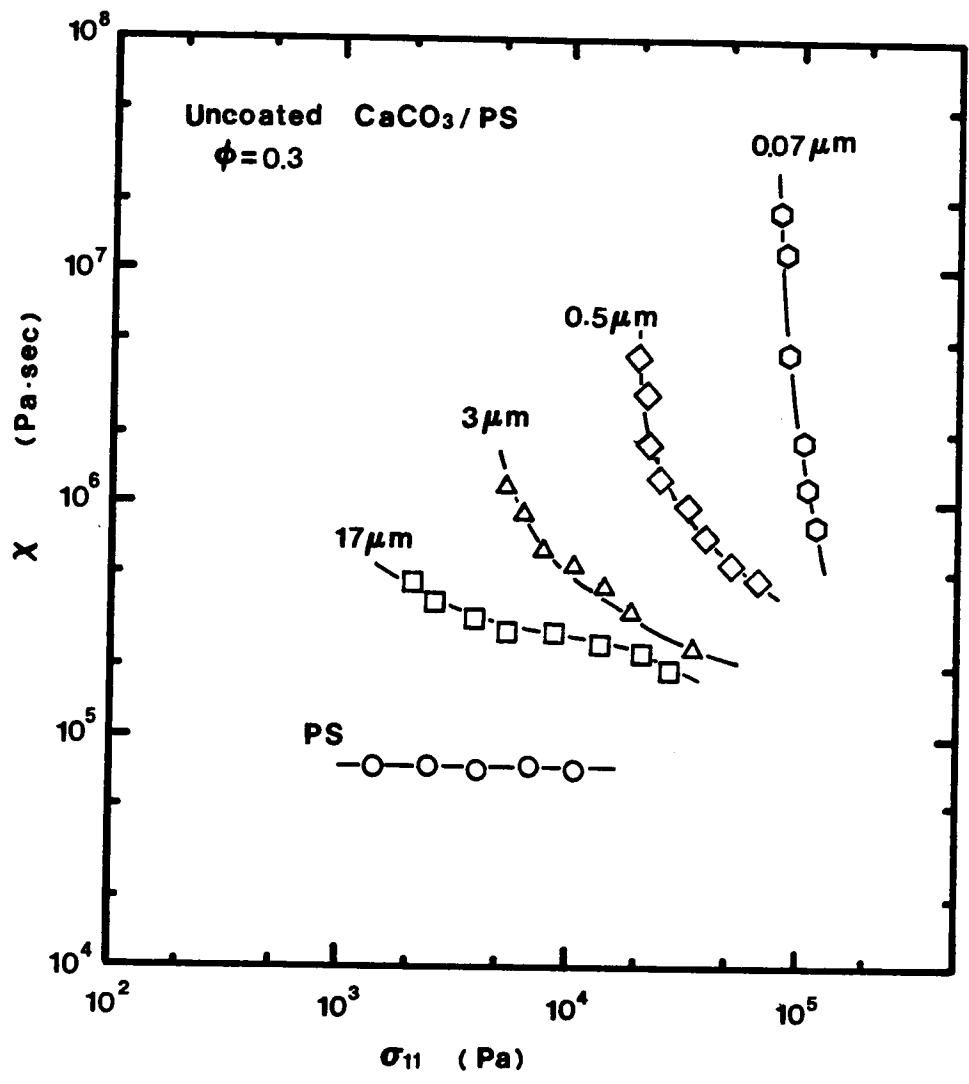


Figure V.25. Steady state elongational viscosity of uncoated CaCO_3 filled PS as a function of tensile stress.

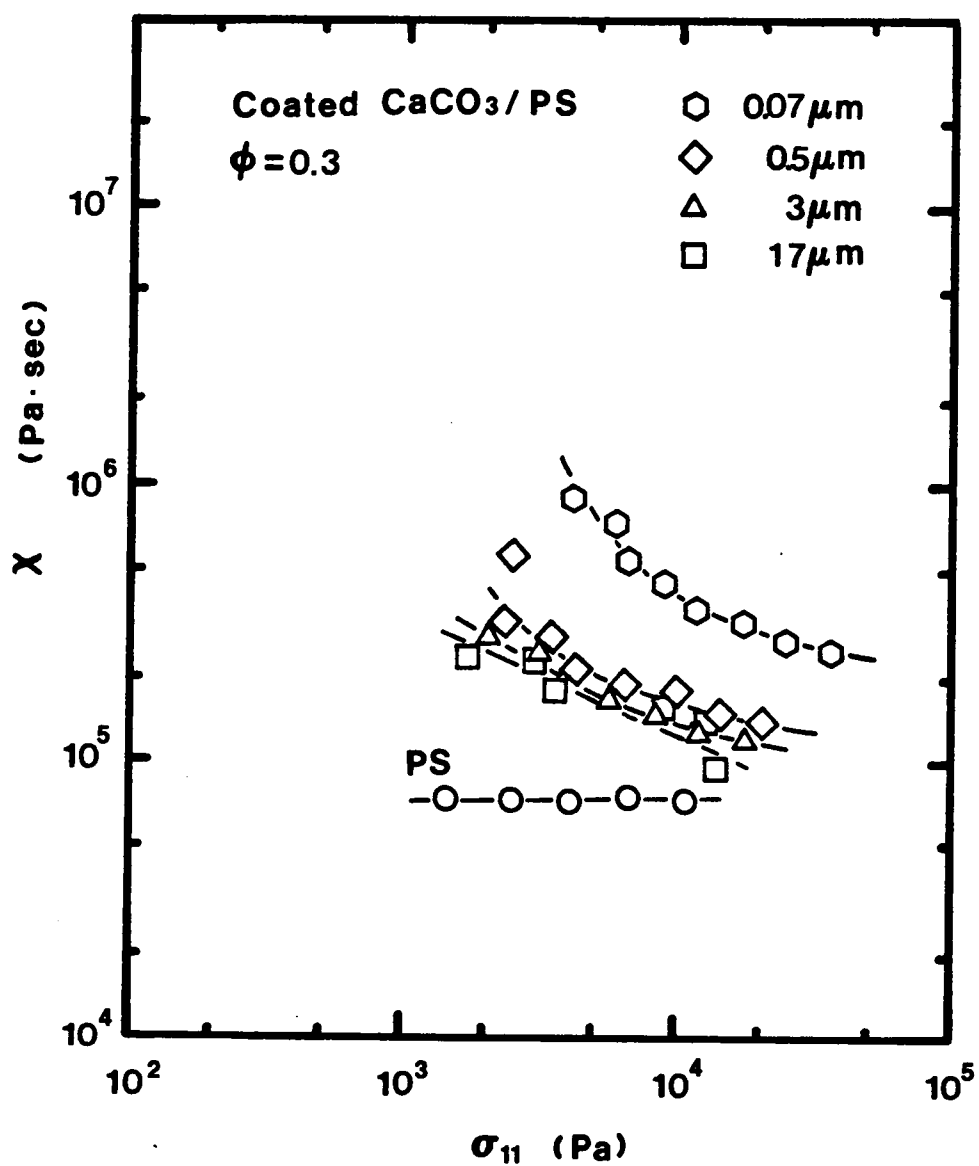


Figure V.26. Steady state elongational viscosity of coated CaCO_3 filled PS as a function of tensile stress.

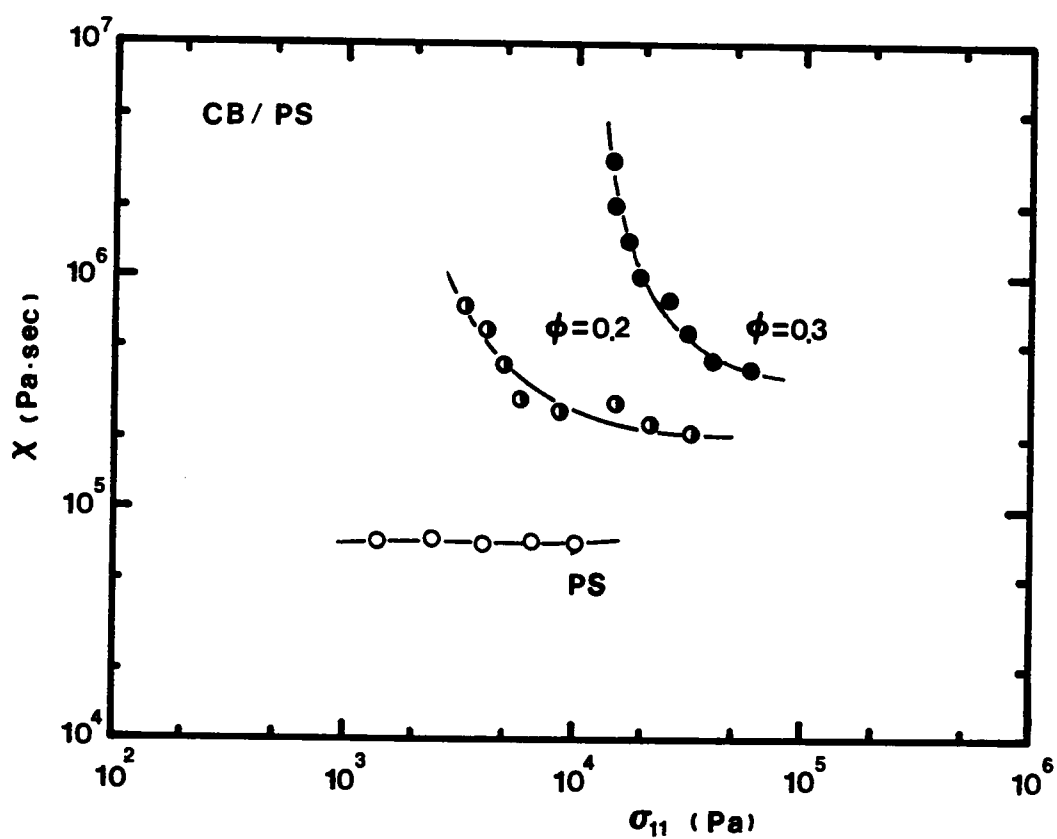


Figure V.27. Steady state elongational viscosity of CB filled PS as a function of tensile stress.

The yield stresses of the compounds in elongated flow are summarized in Table V.1. Where comparison is possible, the data agree reasonably well with the literature on the same uncoated 0.5 μm diameter particle system as studied by Tanaka and White (150)--we obtain a yield value of $9 \sim 10 \times 10^3$ Pa as opposed to $9 \sim 12 \times 10^3$ by those authors.

C. Elongation to Break

C.1 Results

Figures V.28 to V.30 plot elongation to break as a function of elongational rate. The elongation to break tends to decrease with addition of filler. The elongation to break decreases with decreasing average particle diameter of fillers for both uncoated and coated CaCO_3 filled PS melts generally (Figures V.28 and V.29). The elongation to break increases with stearic acid surface treatment of CaCO_3 especially for the relatively small particle filled compounds. The elongation to break reduces with increasing volume content of CB (Figure V.30).

The elongation to break of relatively small uncoated CaCO_3 filled PS melts and 30 vol% CB filled PS melts tend to decrease with increasing elongational rate. Other systems show almost constant or slightly increasing tendencies with decreasing elongational rates.

For both uncoated and coated CaCO_3 filled PS melts, the compounds which have average particle diameters of

Table V.1

Elongational Yield Stresses

Filler	Particle Size (μm)	Matrix	Temperature ($^{\circ}\text{C}$)	Loading (vol%)	$Y_S \times 10^{-3}$	$Y_e \times 10^{-3}$ (Pa)	Y_e/Y_S^{**}	References
CB	0.019	PS	170	20	12	(~11)	1.5 (1.6)	Lobe and White (91)
CB	0.019	PS	170	25	60	(60)	1.2 (1.2)	Lobe and White (91)
CB	0.045	PS	180	20	2.5	(1.3)	-	Tanaka and White (150)
CB	0.045	PS	180	20	~2	(1.3)	-	The Present Work
CB	0.045	PS	180	30	10	(9.2)	1.7 (1.8)	Tanaka and White (150)
CB	0.045	PS	180	30	9	(8.8)	1.7 (1.7)	The Present Work
TiO ₂	0.18	PS	180	20	~1	(0.4)	-	Tanaka and White (150)
TiO ₂	0.18	PS	180	30	2.2	(1.8)	1.8 (2.2)	Tanaka and White (150)
Uncoated CaCO ₃	0.07	PS	180	30	40	(38)	1.8 (1.8)	The Present Work
Uncoated CaCO ₃	0.5	PS	180	30	12	(9)	1.8 (2.4)	Tanaka and White (150)
Uncoated CaCO ₃	0.5	PS	180	30	10	(9)	1.5 ((1.7)	The Present Work
Uncoated CaCO ₃	3	PS	180	30	~1.5	(1.6)	-	The Present Work
Uncoated CaCO ₃	17	PS	180	30	-	(0.1)	-	The Present Work
Coated CaCO ₃	0.07	PS	180	30	-	(1.0)	-	The Present Work
Coated CaCO ₃	0.5	PS	180	30	0.4	(0.16)	1.8 (4.4)	Tanaka and White (150)
Coated CaCO ₃	0.5	PS	180	30	-	(0.16)	-	The Present Work
Coated CaCO ₃	3	PS	180	30	-	(<0.1)	-	The Present Work
Coated CaCO ₃	17	PS	180	30	-	(<0.1)	-	The Present Work

*Values with parentheses are estimated from Casson's plot; values without parentheses are estimated from η versus σ_{12} plot by each author.

**Calculated with Y_S from Casson's plot.

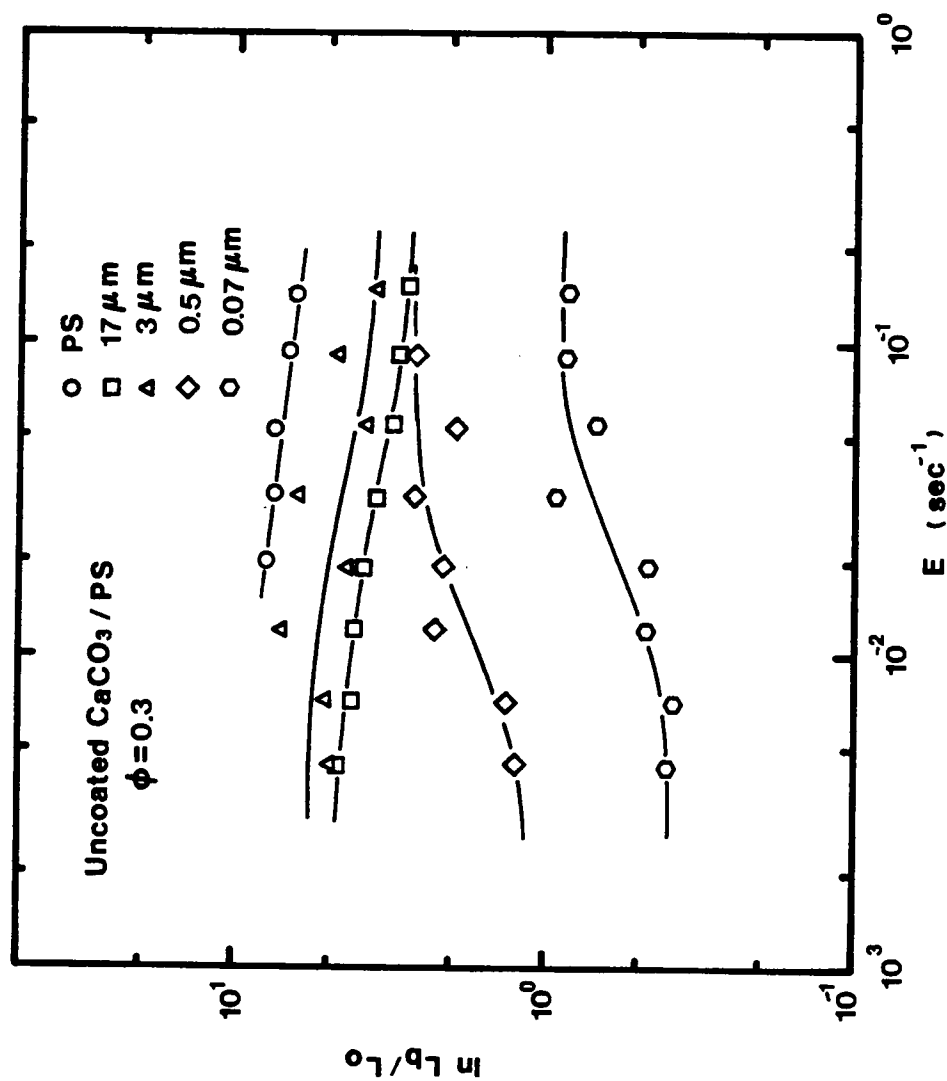


Figure V.28. Elongation to break as a function of elongational rate for uncoated CaCO_3 filled PS at 180°C .

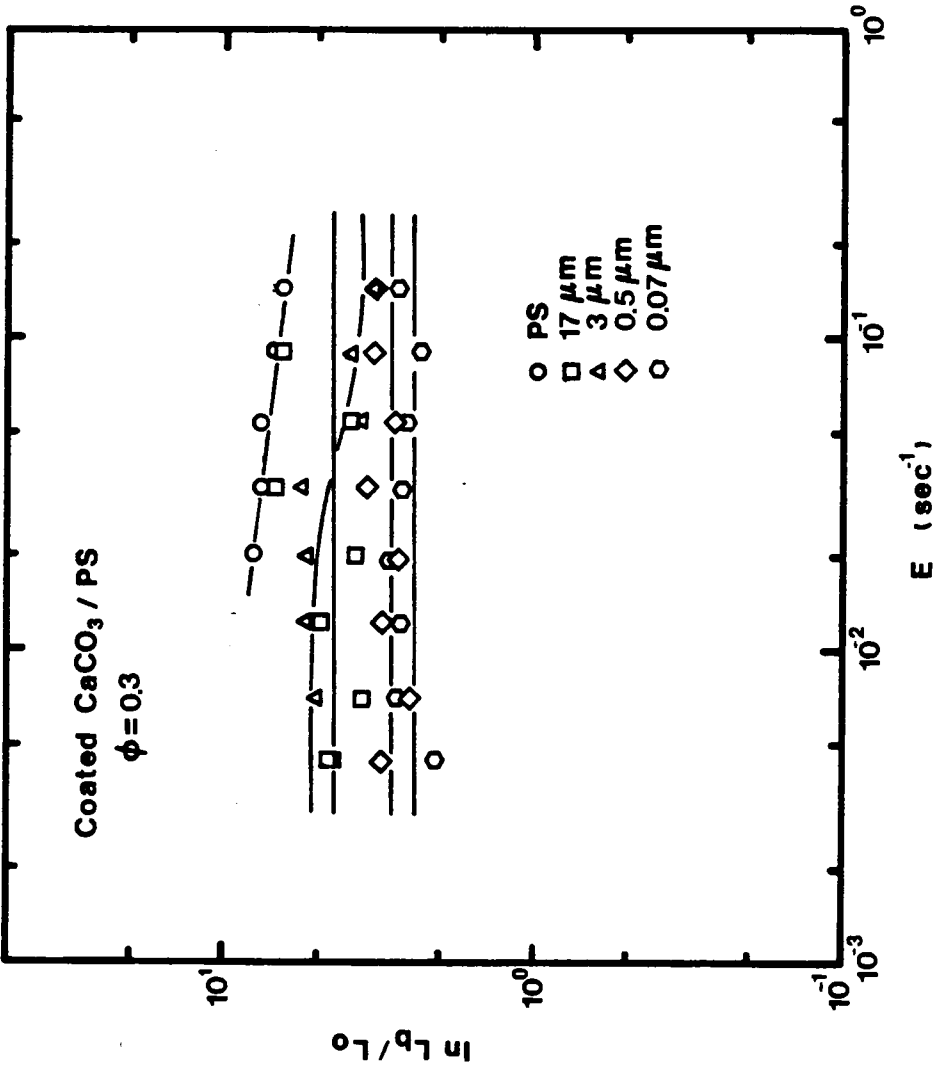


Figure V.29. Elongation to break as a function of elongational rate for coated CaCO_3 filled PS at 180°C .

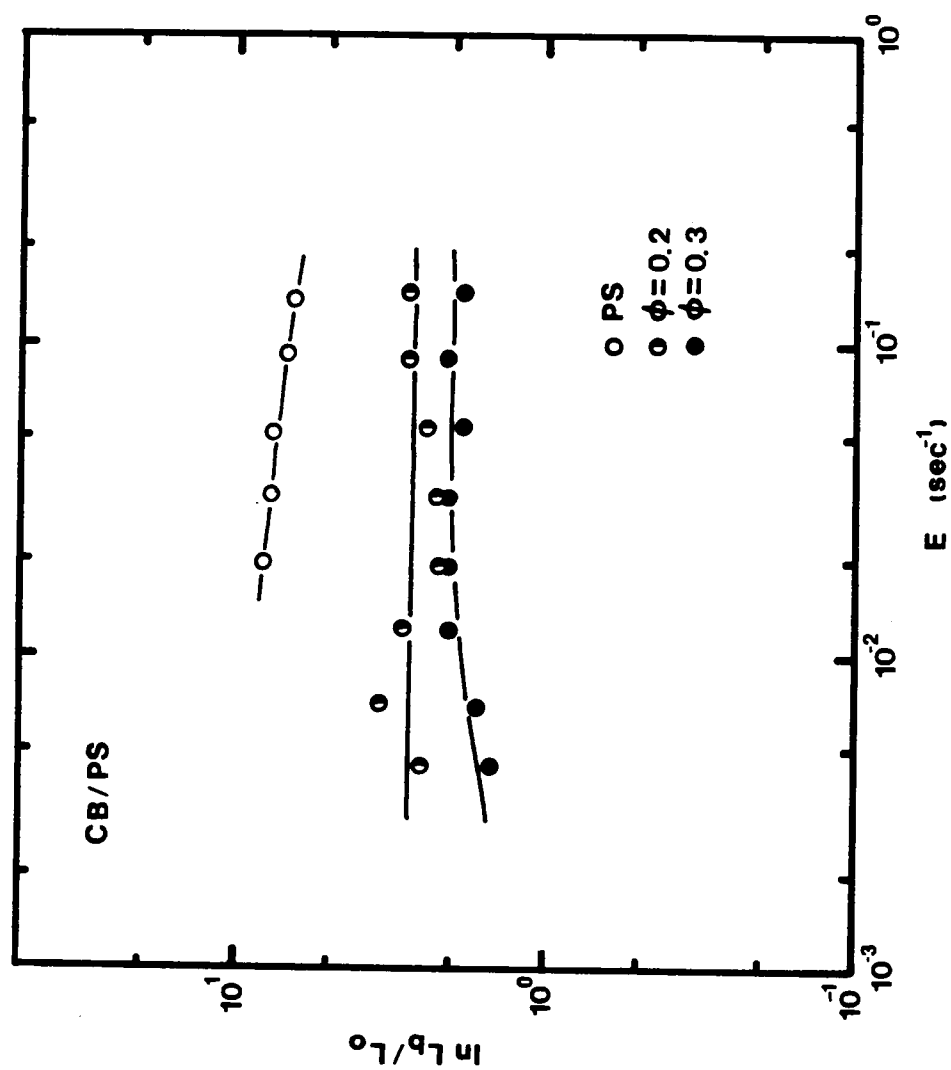


Figure V.30. Elongation to break as a function of elongational rate for CB filled PS at 180°C .

17 μm and 3 μm show almost the same elongation to break. The elongation to break of 3 μm particle filled compounds may be slightly larger than 17 μm particle filled compounds.

C.2 Discussion

A mechanism for the short elongation to break of filled polymer melts has been proposed by White and Tanaka (177). They attribute this behavior to ductile failure induced by a decreasing elongational viscosity function associated with the yield value. It could also be associated with poor dispersion.

The elongation to break obtained in this present work is compared with the data obtained by Tanaka (177) in Table V.2. The elongations to break obtained in the present work is always larger than Tanaka's data. The samples which have larger elongational viscosity show larger ratios of $\ln (L_B/L_O)_{\text{present}}$ to $\ln (L_B/L_O)_{\text{Tanaka}}$ generally. Uncoated CaCO_3 filled PS exhibits a four times larger value than Tanaka's. On the other hand, pure PS shows only 1.1 times larger value than Tanaka's. This is probably due to the better sample clamping method and better temperature uniformity and perhaps better dispersion.

Table V.2

Elongation to Break, Comparison between Present Data and Tanaka's Data

Samples	Average Particle Size (μm)	Volume Content (-)	$\ln(L_B/L_0)$ by Tanaka	$\ln(L_B/L_0)$ Present Work	$\frac{\ln(L_B/L_0)_{\text{present}}}{\ln(L_B/L_0)_{\text{Tanaka}}}$
PS	-	-	6.5	7.2	1.1
Uncoated CaCO_3/PS	0.5	0.3	0.5	2	4
Coated CaCO_3/PS	0.5	0.3	1.5	3	2
CB/PS	0.045	0.3	1	1.8	1.8
CB/PS	0.045	0.2	2	2.5	1.3

CHAPTER VI

COMPARISON OF STEADY SHEAR FLOW AND ELONGATIONAL FLOW EXPERIMENTAL DATA WITH RHEOLOGICAL THEORY

A. Introduction

In this chapter a comparison of experimental data and rheological theories is presented. The rheological behavior of unfilled PS is interpreted in terms of a viscoelastic fluid model. A new theory for a viscoelastic plastic thixotropic fluid is proposed. Experimental data for small particle filled PS compounds are interpreted in terms of this theory.

B. Rheological Theory for Unfilled Systems

Single integral constitutive equations successfully describe the non-linear viscoelastic properties of unfilled polymer melts and elastomers. The general form of the single integral constitutive equation is

$$\underline{\sigma} = -p\underline{I} + \int_0^\infty [m_1(z)\underline{c}^{-1} - m_2(z)\underline{c}]dz \quad [\text{VI.1}]$$

$$\text{where } z = t - s \quad [\text{VI.2}]$$

Here z is a running back time, t is the present time, s is a past time, $m_1(z)$ and $m_2(z)$ are memory functions and $\underline{c}^{-1}$

and $\underline{c}$ are Finger and Cauchy deformation tensors respectively. There are various forms of memory functions. The Bogue-White model is one of the most widely and successfully used memory functions. The memory functions of the Bogue-White model have the forms of Equations II.31 and II.33. In these formulations, memory functions are considered to be dependent upon the average invariants of the rate of deformation tensor $\underline{d}$. This model has been successfully applied in the description of non-linear viscoelastic phenomena of polymer melts and elastomers by Middleman (105), Chen and Bogue (26), Furuta, Lobe and White (91), Ide and White (72), Toki (154) and Montes (109).

We shall use memory functions of the Bogue-White type. We shall consider both the case where the relaxation time depends upon instantaneous and time averaged rate of deformation invariants. Specifically,

$$m_1(z) = \sum_{i=1}^n \frac{G_i^0}{\tau_{i \text{ eff}}^0} e^{-\frac{z}{\tau_{i \text{ eff}}^0}} \quad [\text{VI.3}]$$

where

$$\tau_{i \text{ eff}}^0 = \frac{\tau_{0 \text{ } i}^0}{1 + a \tau_{0 \text{ } i}^0 \text{II}_d^{1/2}} \quad [\text{VI.4}]$$

or

$$\tau_{i \text{ eff}} = \frac{\tau_{0 \text{ } i}^0}{1 + a \tau_{0 \text{ } i}^0 \text{II}_d^{1/2}} \quad [\text{VI.5}]$$

Here superscript "o" denotes an unfilled system and subscript "o" denotes the zero shear condition. We shall also take

$$m_2(z) = 0 \quad [\text{VI.6}]$$

B.1 Application to Steady Shear Flow

The velocity field for simple shear flow can be expressed as

$$\underline{V} = \dot{\gamma} x_2 \underline{e}_1 + 0 \underline{e}_2 + 0 \underline{e}_3 \quad [\text{VI.7}]$$

where subscript 1 and 2 denote flow direction and normal direction respectively.

The deformation rate tensor can be written as

$$d = \frac{1}{2} \begin{vmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad [\text{VI.8}]$$

where

$$\dot{\gamma} = \frac{\partial V_1}{\partial x_2} \quad [\text{VI.9}]$$

The Finger deformation tensor for a simple shear flow initiated at time zero is

$$t > z > 0, \underline{c}^{-1} = \begin{vmatrix} 1 + \dot{\gamma} z & \dot{\gamma} z & 0 \\ \dot{\gamma} z & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad [\text{VI.10}]$$

For future reference, we note that:

$$\bar{\zeta}^{-1} = \begin{vmatrix} \frac{2}{3} \dot{\gamma}^2 z^2 & \dot{\gamma} z & 0 \\ \dot{\gamma} z & -\frac{1}{3} \dot{\gamma}^2 z^2 & 0 \\ 0 & 0 & -\frac{1}{3} \dot{\gamma}^2 z^2 \end{vmatrix} \quad [\text{VI.11}]$$

For $z > t$, Equations VI.9 and VI.10 remain valid with z equal to t .

The second invariants of the deformation rate tensor is

$$\begin{aligned} II_d^{1/2} &= \dot{\gamma} \quad \text{for } 0 < z < t \\ II_d^{1/2} &= 0 \quad \text{for } t < z < \infty \end{aligned} \quad [\text{VI.12}]$$

The transient shear viscosity expression obtained with Equation VI.4 is

$$\begin{aligned} \eta_{12}(t) = \frac{\sigma_{12}(t)}{\dot{\gamma}} &= \sum_{i=1}^n G_i^0 [\tau_i^0 \text{ eff} - e^{-\frac{t}{\tau_i^0 \text{ eff}}} \cdot (t + \tau_i^0 \text{ eff}) \\ &\quad + t \cdot e^{-\frac{t}{\tau_i^0 \text{ eff}}}] \end{aligned} \quad [\text{VI.13}]$$

for the transient state, and

$$\eta_{12} = \lim_{t \rightarrow \infty} \eta_{12}(t) = \sum_{i=1}^n G_i^0 \text{ eff} = \frac{\sum_{i=1}^n G_i^0 \tau_i^0}{1 + a \tau_i^0 \dot{\gamma}} \quad [\text{VI.14}]$$

for the steady state.

The steady state first normal stress difference is given by

$$N_1 = 2 \left(\sum_{i=1}^n G_i^0 \tau_{i \text{ eff}}^2 \right) \dot{\gamma}^2 \quad [\text{VI.15}]$$

On the other hand, the transient shear viscosity expression obtained from the original Bogue-White model with Equation VI.5 (Equations II.31 to II.33) is (105, 107, 154)

$$\eta(t) = \sum_{i=1}^n G_i^0 \tau_{i \text{ eff}}^0 \left[1 - e^{-\frac{t}{\tau_{i \text{ eff}}^0}} + \left(\frac{t}{\tau_{i \text{ eff}}^0} \right)^2 a \dot{\gamma} \cdot \tau_{i \text{ eff}}^0 e^{-a \dot{\gamma} t} \cdot \text{EI} \left(\frac{t}{\tau_{i \text{ eff}}^0} \right) \right] \quad [\text{VI.16}]$$

where $\text{EI}(x)$ is the exponential integral defined as

$$\text{EI}(x) = \int_x^\infty e^{-\beta} d \ln \beta \approx \frac{e^{-x}}{x} \quad [\text{VI.17}]$$

The expressions for steady state shear viscosity and first normal stress difference are the same as Equations VI.14 and VI.15 respectively.

B.2 Application to Elongational Flow

The velocity field for elongational flow is

$$\underline{v} = Ex_1 \underline{e}_1 - \frac{1}{2} Ex_2 \underline{e}_2 - \frac{1}{2} Ex_3 \underline{e}_3 \quad [\text{VI.18}]$$

where subscript 1 denotes the stretching direction, 2 and 3 denote the normal direction.

The deformation rate tensor can be written as

$$\underline{d} = \frac{1}{2} \begin{vmatrix} 2E & 0 & 0 \\ 0 & -E & 0 \\ 0 & 0 & -E \end{vmatrix} \quad [\text{VI.19}]$$

The Finger deformation tensor for elongational deformation between present time t and past time s is

$$\underline{c}^{-1} = \begin{vmatrix} e^{2EZ} & 0 & 0 \\ 0 & e^{-EZ} & 0 \\ 0 & 0 & e^{-EZ} \end{vmatrix} \quad [\text{VI.20}]$$

For future reference, we note that:

$$\underline{c}^{-1} = \frac{1}{3} \begin{vmatrix} 2(e^{2EZ} - e^{-EZ}) & 0 & 0 \\ 0 & -e^{2EZ} + e^{-EZ} & 0 \\ 0 & 0 & -e^{2EZ} + e^{-EZ} \end{vmatrix} \quad [\text{VI.21}]$$

The second invariants of the deformation rate tensor are (see Equation VI.7)

$$II_d^{1/2} = \sqrt{3}E \quad \text{for } 0 < Z < t \quad [\text{VI.22}]$$

$$II_d^{1/2} = 0 \quad \text{for } t < Z < \infty$$

The tensile stress acting on the filament is

$$\frac{F(t)}{A(t)} = \sigma_{11}(t) \quad [\text{VI.23}]$$

The transient elongational viscosity for a deformation induced at time zero is

$$\begin{aligned} \chi(t) = \frac{\sigma_{11}(t)}{E} = \frac{1}{E} \sum_{i=1}^n G_i^0 & \left[\frac{1}{2E\tau_{i \text{ eff}}^0 - 1} (e^{\frac{(2E\tau_{i \text{ eff}}^0 - 1)t}{\tau_{i \text{ eff}}^0}} - 1) \right. \\ & + \frac{1}{E\tau_{i \text{ eff}}^0 + 1} (e^{-\frac{(E\tau_{i \text{ eff}}^0 + 1)t}{\tau_{i \text{ eff}}^0}} - 1) \\ & \left. + e^{-\frac{t}{\tau_{i \text{ eff}}^0}} (e^{2Et} - e^{-Et}) \right] \end{aligned} \quad [\text{VI.24}]$$

The steady state elongational viscosity is

$$\chi = \lim_{t \rightarrow \infty} \chi(t) = \sum_{i=1}^n \frac{3\tau_{i \text{ eff}}^0 G_i^0}{(1 - 2E\tau_{i \text{ eff}}^0)(1 + E\tau_{i \text{ eff}}^0)} \quad [\text{VI.25}]$$

when

$$E < \frac{1}{2\tau_{\text{max eff}}} \quad [\text{VI.26}]$$

is satisfied.

On the other hand, the transient elongational viscosity expression obtained from the original Bogue-White model, Equations II.31 to II.33, is

$$\begin{aligned}
\chi(t) = & \frac{1}{E} \sum G_i^0 \left[\frac{1}{2E\tau_{i\text{eff}}^0 - 1} \left(e^{\frac{(2E\tau_{i\text{eff}}^0 - 1)t}{\tau_{i\text{eff}}^0}} - 1 \right) \right. \\
& + \frac{1}{E\tau_{i\text{eff}}^0 + 1} \left(e^{-\frac{(E\tau_{i\text{eff}}^0 + 1)t}{\tau_{i\text{eff}}^0}} - 1 \right) \\
& + \left(e^{\frac{t}{\tau_{oi}^0}} + \sqrt{3}aEtEI\left(\frac{t}{\tau_{oi}^0}\right) \right) \cdot \left(e^{(2 - \sqrt{3}a)Et} \right. \\
& \left. \left. - e^{-(1 + \sqrt{3}a)Et} \right) \right] \quad \text{[VI.27]}
\end{aligned}$$

The steady state form is the same as Equation VI.25.

C. Comparison of Theory and Experimental Data for Unfilled System

C.1 Evaluation of Material Constants for Unfilled System

C.1.a Procedures to evaluate material constants. We shall presume a single exponential term. The material constants we need to obtain for the unfilled system are G^0 , τ_0^0 and a . The procedure to evaluate these material constants is discussed here.

In a single-element Maxwell model, τ^0 is equal to a characteristic relaxation time, $\bar{\tau}^0$ defined by

$$\bar{\tau}^0 = \frac{N_1}{2\eta\dot{\gamma}^2} = \frac{\bar{\tau}_0^0}{1 + a\bar{\tau}_0^0\dot{\gamma}} \quad \text{[VI.28.a]}$$

or

$$\frac{1}{\bar{\tau}^0} = \frac{1}{\bar{\tau}_0^0} + a\dot{\gamma} \quad [\text{VI.28.b}]$$

where $\bar{\tau}^0$ is a zero shear characteristic relaxation time of an unfilled system. Also we may write

$$\eta^0 = \bar{\tau}^0 G^0 = \frac{\bar{\tau}_0^0}{1 + a \bar{\tau}_0^0 \dot{\gamma}} G^0 = \frac{\eta_0^0}{1 + a \bar{\tau}_0^0 \dot{\gamma}} \quad [\text{VI.29.a}]$$

or

$$\frac{1}{\eta^0} = \frac{1}{\eta_0^0} + \frac{a\bar{\tau}_0^0}{\eta_0^0} \dot{\gamma} \quad [\text{VI.29.b}]$$

where η_0^0 is a zero shear viscosity of an unfilled system.

$\bar{\tau}_0^0$ and G^0 appearing in these equations satisfy

$$\eta_0^0 = \bar{\tau}_0^0 G^0 \quad [\text{VI.30}]$$

We are able to obtain the material constants for an unfilled system using Equations VI.28 to VI.30.

Procedures for obtaining the material constants G^0 , a and τ_0^0 are as follows:

(1) Using Equation VI.28.b:

Plot $1/\bar{\tau}^0$ versus $\dot{\gamma}$ and then obtain $1/\bar{\tau}_0^0$ and "a" from an intersection at $\dot{\gamma} = 0$ and a slope of the plot.

(2) Using Equation VI.29.b:

Plot $1/\eta^0$ versus $\dot{\gamma}$, and then obtain $1/\eta_0^0$ and $a\bar{\tau}_0^0/\eta_0^0$ from an intersection at $\dot{\gamma} = 0$ and a slope of the plot.

Equate "a" value using $\bar{\tau}_0^0$ obtained in (1) or evaluate $\bar{\tau}_0^0$ using "a" value obtained in (1).

(3) Using Equation VI.30:

Evaluate G^0 using $\bar{\tau}_0^0$ and η_0^0 obtained in (1) and/or (2). Following these procedures (1) to (3), we obtain three sets of material constants (a , τ_0^0 , G^0).

C.1.b Values of material constants. We evaluate the material constants following procedures (1) to (3) in this section. Figure VI.1 shows the plots of $1/\bar{\tau}^0$ and $1/\eta^0$ versus $\dot{\gamma}$.

- (1) From $1/\bar{\tau}^0$ versus $\dot{\gamma}$ plot (Equation VI.28.b), $\bar{\tau}^0 = 5.4$ sec and $a = 1.2$ were obtained from an intersection and a slope. $(\bar{\tau}_0^0; a) = (5.4; 1.2)$ was evaluated.
- (2) From $1/\eta^0$ versus $\dot{\gamma}$ plot (Equation VI.29.b), $\eta_0^0 = 2.6 \times 10^4 \text{ Pa}\cdot\text{sec}$ and $a\bar{\tau}_0^0 = 2.1$ sec were obtained. Using $\bar{\tau}_0^0 = 5.4$ sec obtained in (1), we get $a = 0.4$. Using $a = 1.2$ obtained in (1), we get $\bar{\tau}_0^0 = 1.8$ sec. $(\bar{\tau}_0^0; a) = (5.4; 0.4)$ and $(1.8; 1.2)$ were evaluated.
- (3) Using $\eta_0^0 = 2.6 \times 10^4 \text{ Pa}\cdot\text{sec}$, G^0 is calculated for each set of $(\bar{\tau}_0^0; a)$ from Equation VI.30.

$$\begin{aligned}
 (\bar{\tau}_0^0; a; G^0) &= (5.4; 1.2; 4.8 \times 10^3) \\
 &= (5.4; 0.4; 4.8 \times 10^3) \\
 &= (1.8; 1.2; 1.4 \times 10^4)
 \end{aligned}$$
 were obtained.

These values are summarized in Table VI.1. A set number is given to each set for convenience in the next section.

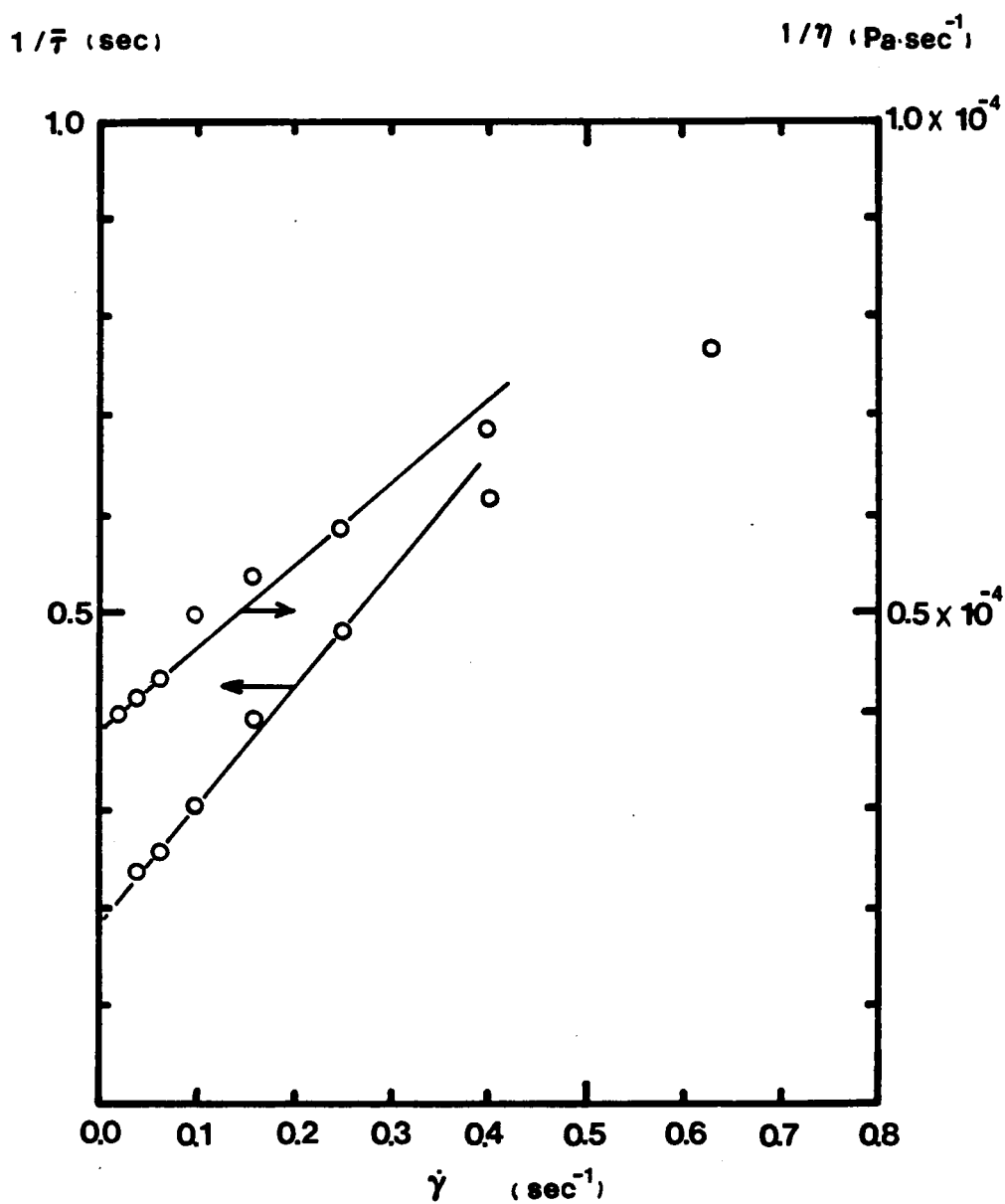


Figure VI.1. $1/\bar{\tau}^0$ and $1/\eta$ as a function of shear rate for PS.

Table VI.1

Values of Material Constants Obtained by Applying
Equations VI.28.b, VI.29.b, and VI.30

Procedure	$\tau_0^0 (= \overline{\tau}_0^0)$ (sec)	a (-)	G^0 (Pa)	Number
"a" and " τ_0^0 " are obtained in pro- cedure (1)	5.4	1.2	4.8×10^3	1
" τ_0^0 " obtained in (1) was used to find "a" in (2)	5.4	0.4	4.8×10^3	2
"a" obtained in (1) was used to find " τ_0^0 " in (2)	1.8	1.2	1.4×10^4	3

$\eta_0^0 = 2.6 \times 10^4$ Pa·sec was used to calculate G^0 in
any case.

C.1.c Comparison of theory and experimental data for unfilled system using obtained material constants. In this section, theoretical predictions are compared with experimental data. The material constants which were obtained in Section C.1.b of this chapter are used (see Table VI.1). The set of material constants which shows the best fit is determined for each experiment.

C.1.c.1 Transient shear viscosity. Figures VI.2 to VI.7 show the comparison between theory and transient shear viscosity experimental data. Theoretical predictions calculated from the original Bogue-White model (Equation VI.17) were shown in Figures VI.2 to VI.4, and those from the modified Bogue-White model (Equation VI.14) were shown in Figures VI.5 to VI.7 for different sets of material constants which are shown in Table VI.1.

Calculated results from the original Bogue-White model show that the material constants of set number 1 (Figure VI.2) predicts large errors in the steady state as well as transient value, and sets number 2 and number 3 (Figures VI.3 and VI.5) predict reasonably good steady state values but do not show the clear viscosity overshoot as the experimental data. Predictions from the modified Bogue-White model show that set number 1 (Figure VI.5) is not satisfactory for both transient and steady state, and set 3 (Figure VI.7) is satisfactory at the steady state but not for the transient state. Set number 2 yields reasonable

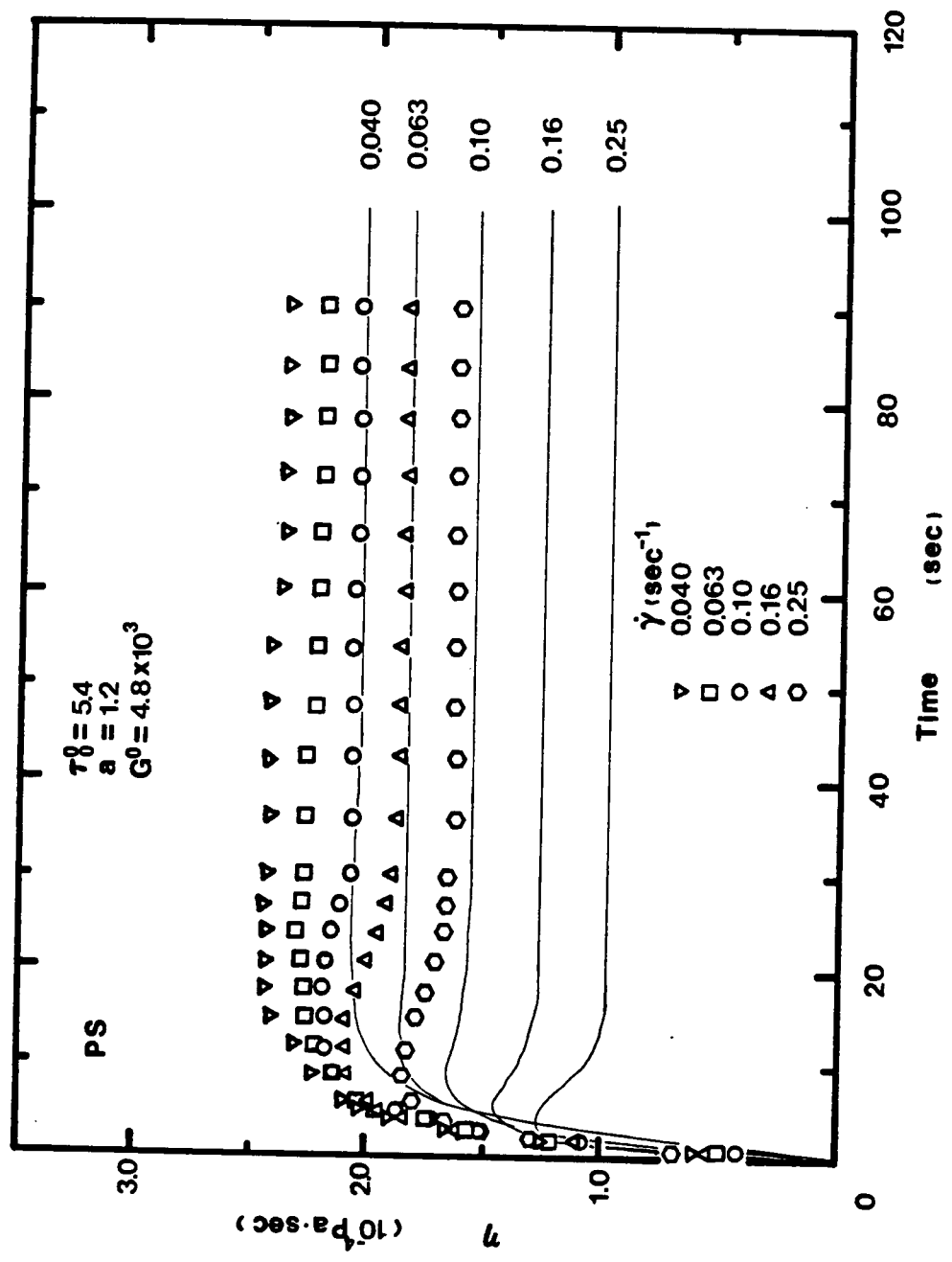


Figure VI.2. Comparison of experimental data with phenomenology theory (original Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 1.

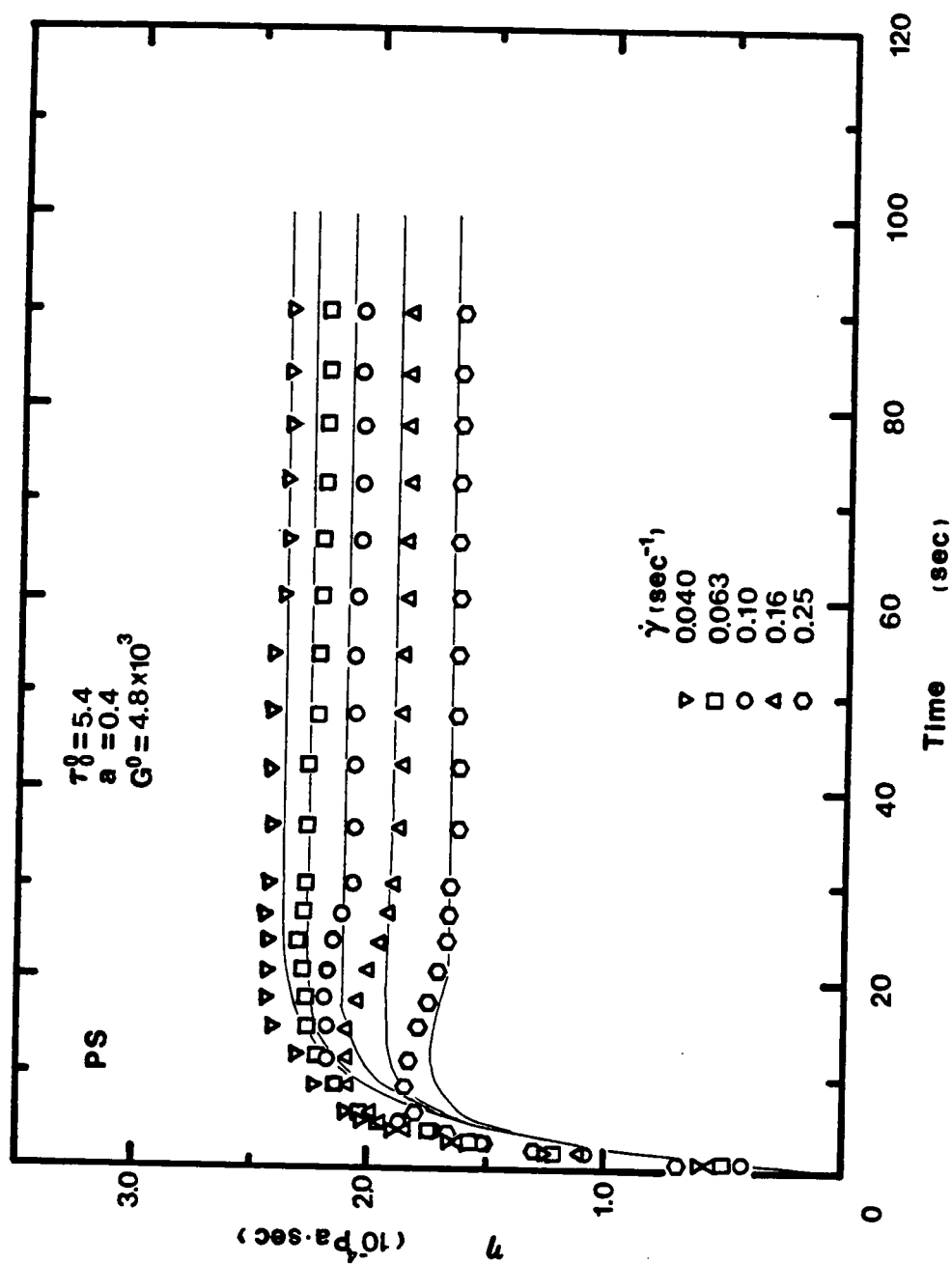


Figure VI.3. Comparison of experimental data with phenomenology theory (original Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 2.

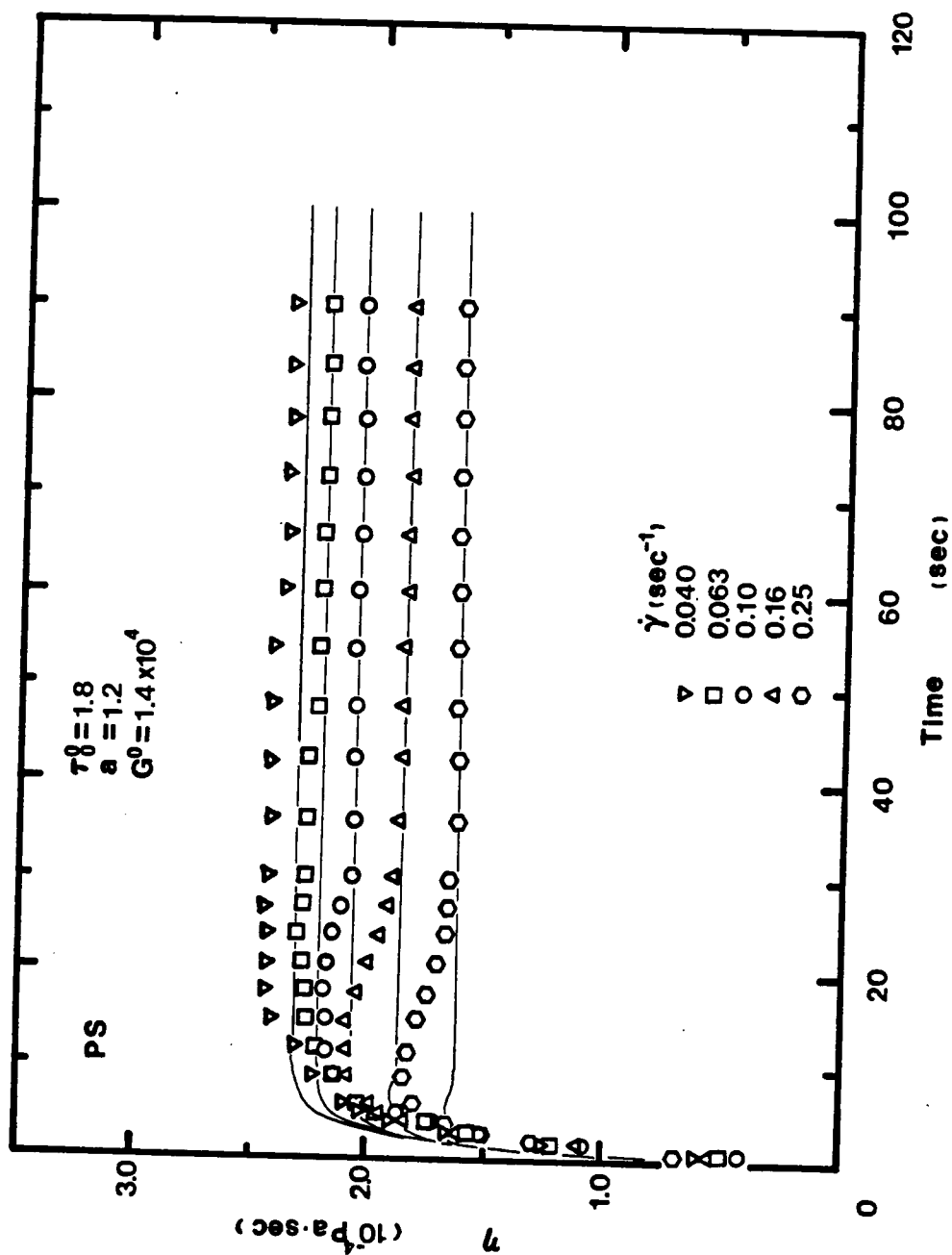


Figure VI.4. Comparison of experimental data with phenomenological theory (original Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 3.

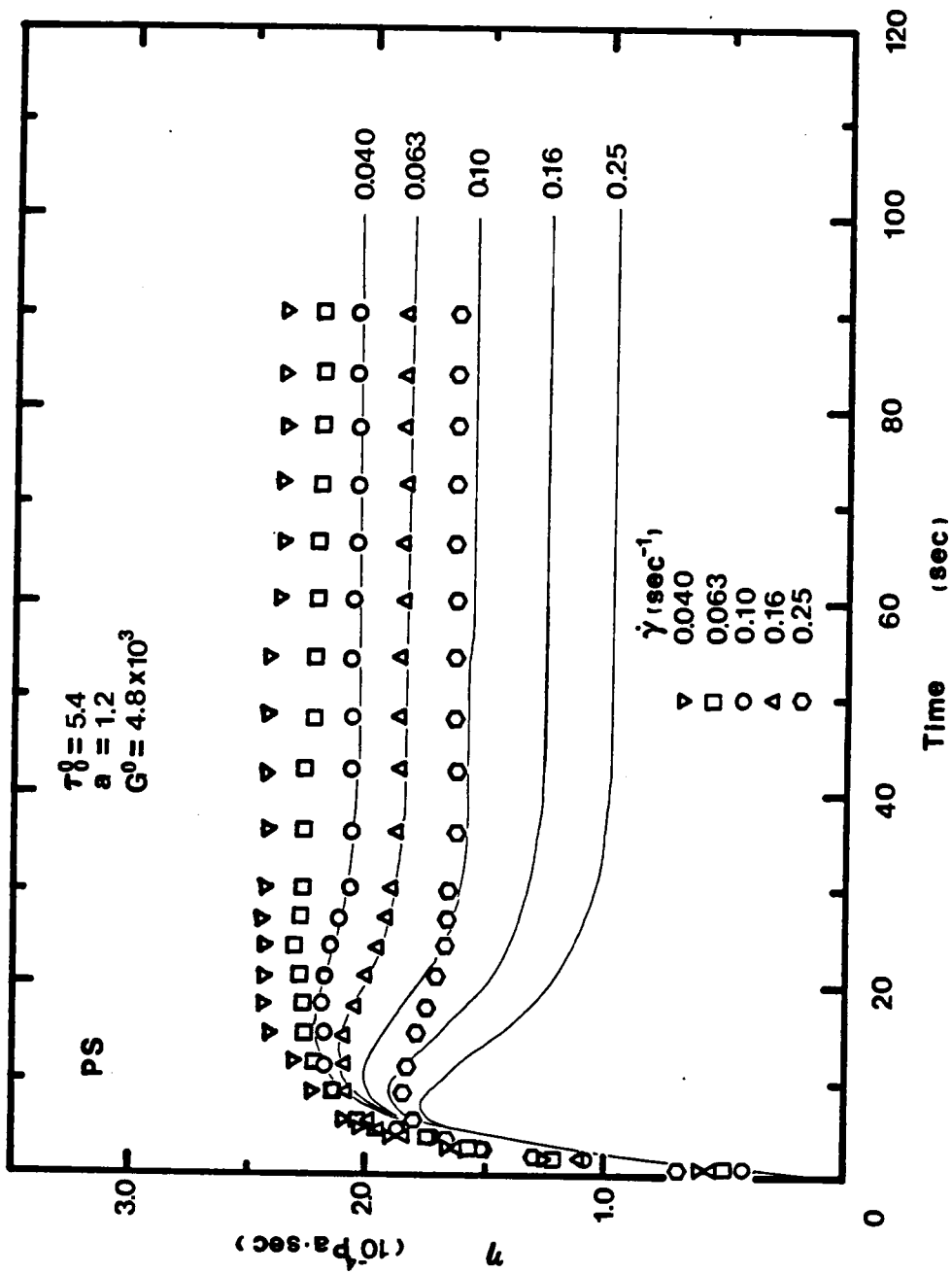


Figure VI.5. Comparison of experimental data with phenomenological theory (modified Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 1.

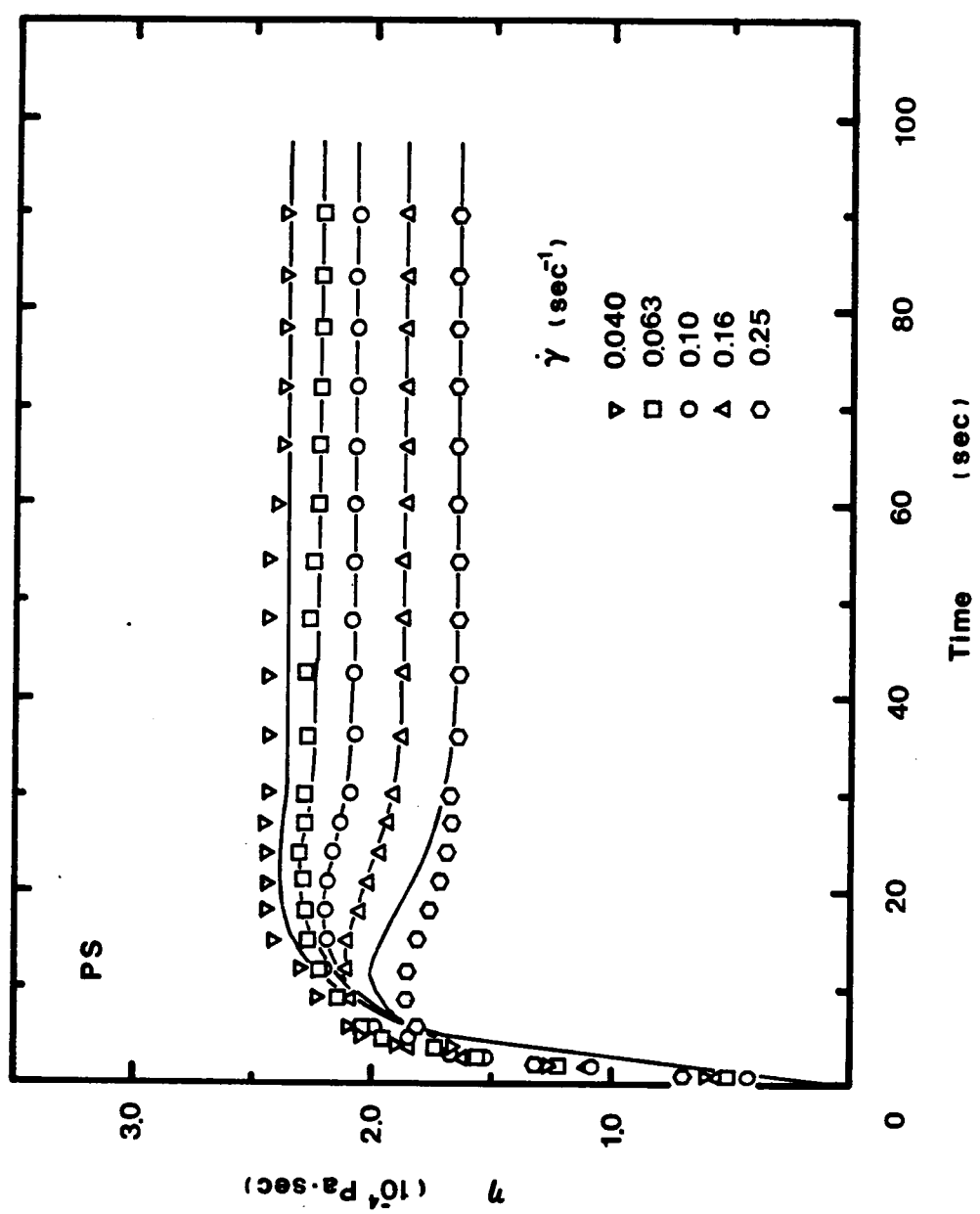


Figure VI.6. Comparison of experimental data with phenomenological theory (modified Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 2.

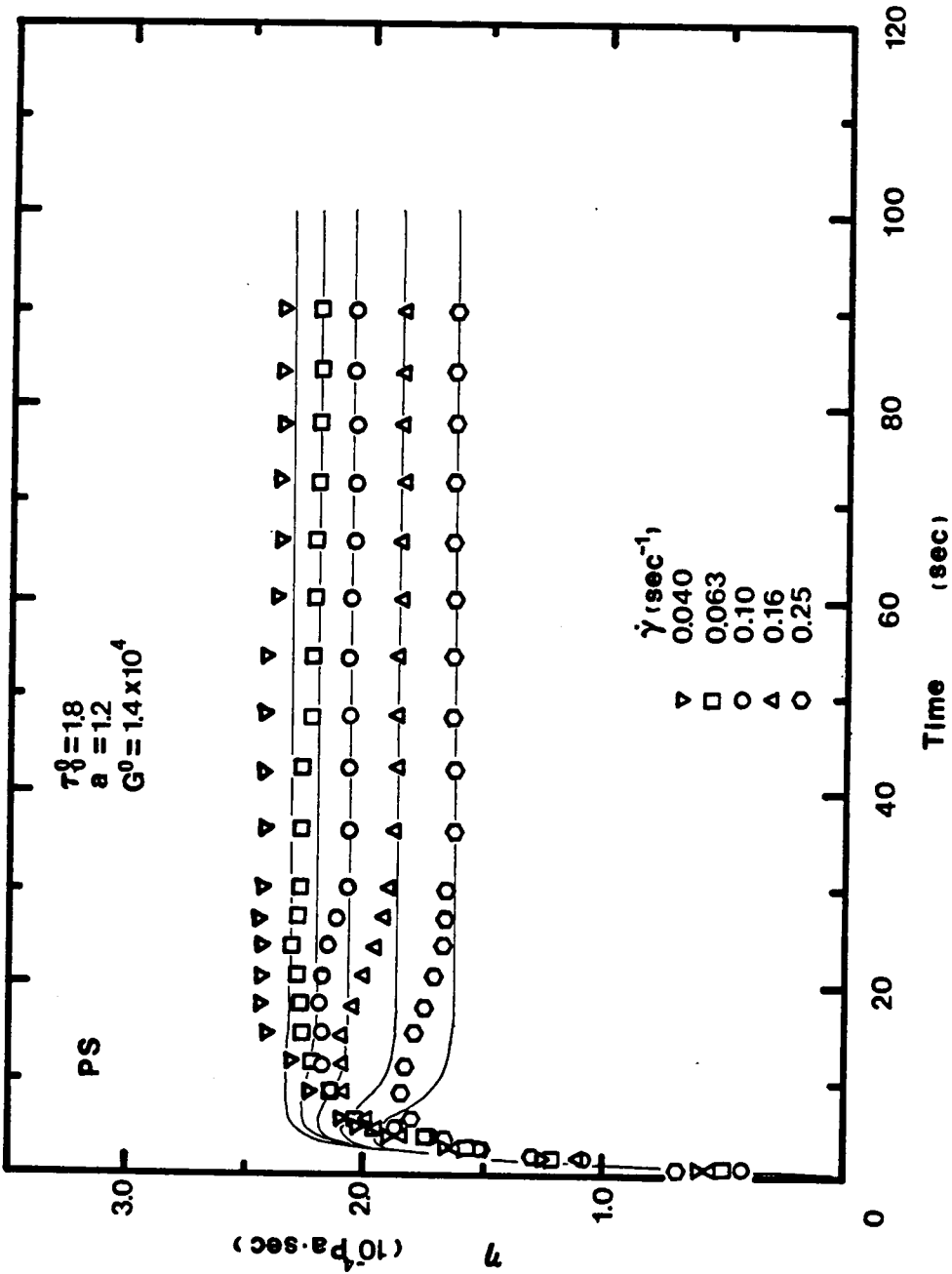


Figure VI.7. Comparison of experimental data with phenomenological theory (modified Bogue-White) for plot of transient shear viscosity of PS with material constants set no. 3.

predictions for both transient and steady state (Figure VI.6).

C.1.c.2 Steady state shear viscosity. The steady state shear viscosity is given by Equation VI.15 in both cases, the original and the modified Bogue-White model. Theoretical predictions calculated with three different sets of material constants are compared with experimental data in Figure VI.8. Predictions with material constants sets number 2 and number 3 are equivalent because sets 2 and 3 yield identical $\tau_0^0 a$ and $\tau_0^0 G^0$ (see Equation VI.15). These sets predict steady state viscosity well. Set number 1 shows a large discrepancy except in the very small shear rate region. Necessary conditions to obtain satisfactory steady shear viscosity are $\tau_0^0 a \approx 2.1$ and $\tau_0^0 G \approx 2.6 \times 10^4$.

C.1.c.3 First normal stress difference. Steady state first normal stress difference is calculated from Equation VI.16 in both original and modified Bogue-White models. Figure VI.9 shows first normal stress difference as a function of shear rate. Predictions with sets number 1 and number 2 exhibit inconsistency at large shear rates. The prediction with set number 3 shows disagreement at any shear rate. The best agreement was obtained using $(\tau_0^0; a; G^0) = (5.4; 0.7; 4.8 \times 10^3)$. Figure VI.10 shows the first normal stress difference as a function of shear stress. Sets 1 and 2 yield identical predictions. They exhibit

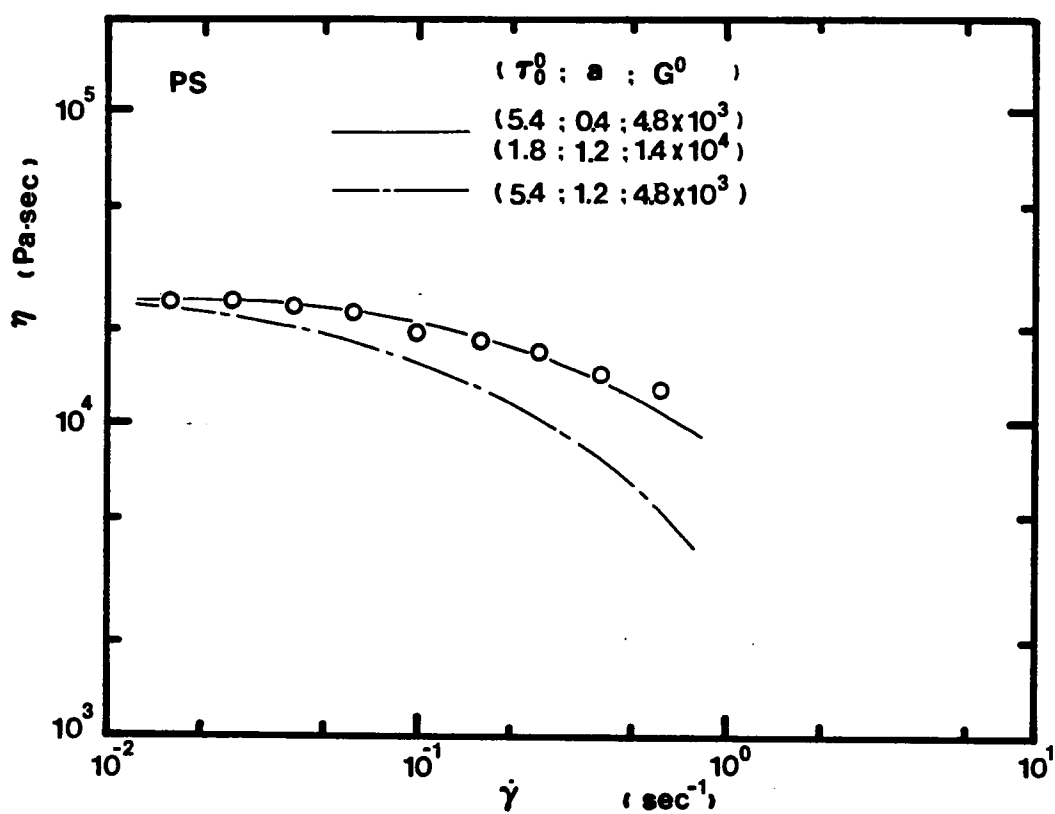


Figure VI.8. Comparison of experimental data with phenomenological theory for plot of steady shear viscosity versus shear rate for PS.

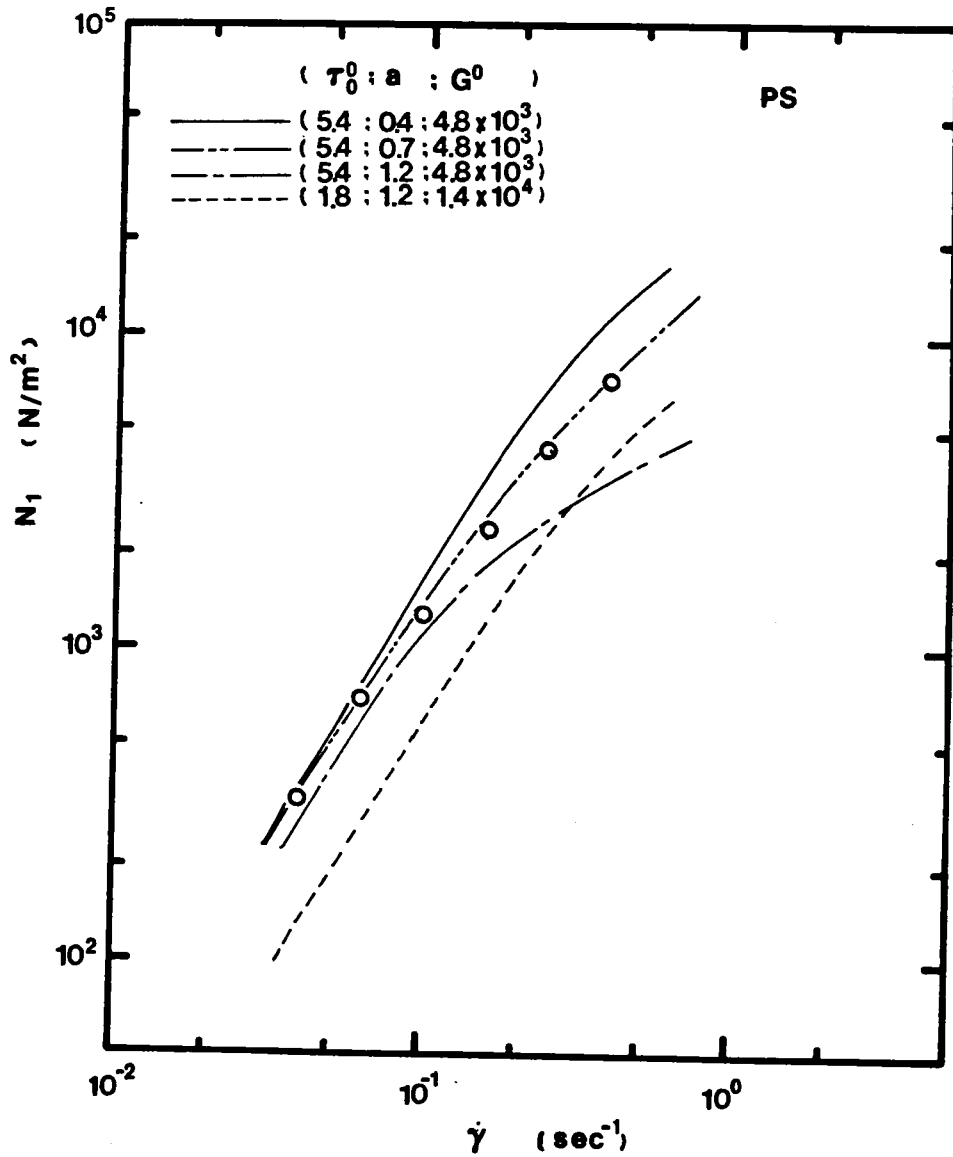


Figure VI.9. Comparison of experimental data with phenomenological theory for plot of first normal stress difference versus shear rate for PS.

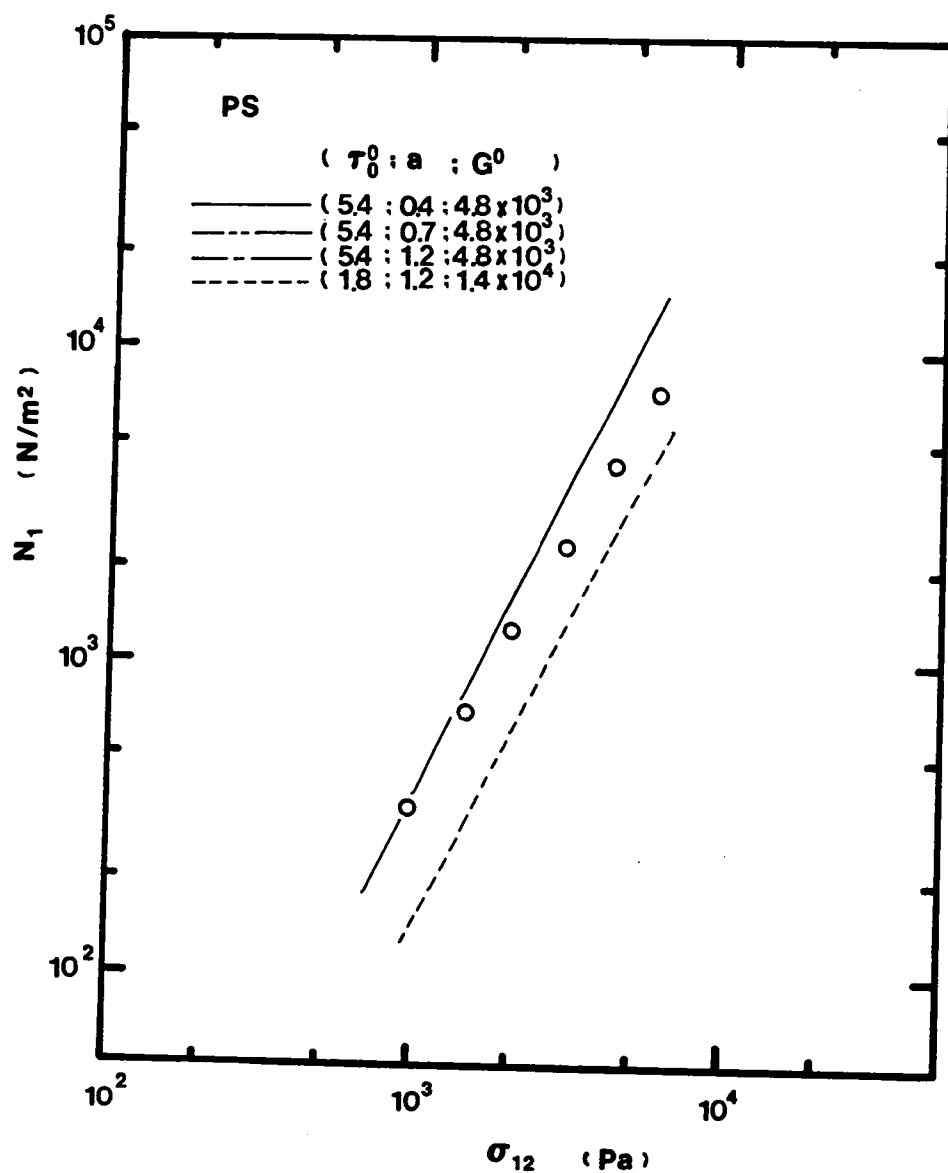


Figure VI.10. Comparison of experimental data with phenomenological theory for plot of first normal stress difference versus shear stress for PS.

discrepancies at large shear stresses because these sets do not satisfy $\tau_{0a}^0 \approx 2.1$ which is necessary to obtain agreement at steady state viscosity.

C.1.c.4 Transient elongational viscosity. Transient elongational viscosity was calculated from Equations VI.28 and VI.25 for the original and modified Bogue-White models respectively. Figures VI.11 and VI.12 represent the comparison between theory and experimental data. Theoretical predictions using three different sets of material constants do not agree with experimental data well in any cases, original and modified Bogue-White models (Figures VI.11 and VI.12 respectively). The predicted elongational viscosity grows more rapidly and reaches a steady state in a shorter period than the experimental. Large effective relaxation time, τ_{eff}^0 , is necessary to obtain slower elongational viscosity build-up. However, large τ_{eff}^0 gives discrepancies at the steady state, that is, steady state reaches infinity. Good agreement between theory and experimental data was not obtained for transient elongational viscosity.

C.1.c.5 Steady state elongational viscosity. The steady state elongational viscosity was calculated from Equation VI.26. Figure VI.13 represents a comparison between predictions and experimental data. The material constants of set number 1 shows finite steady state value

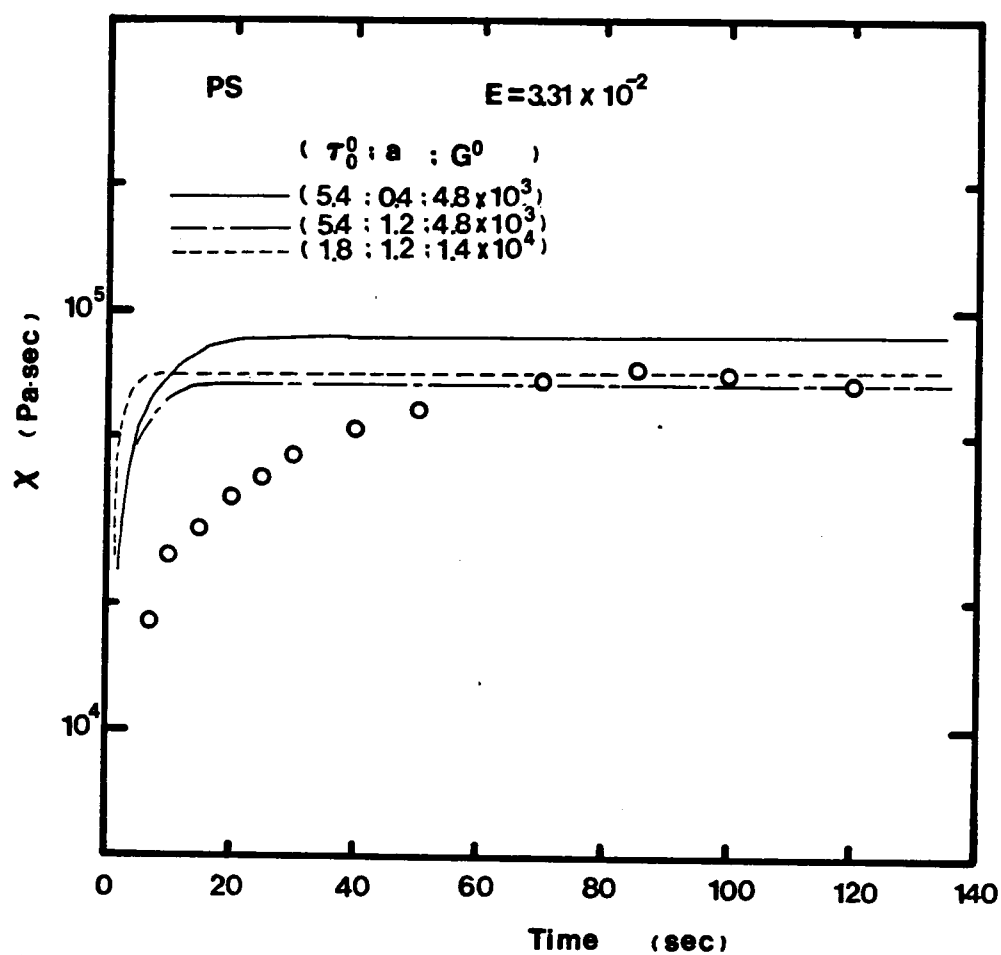
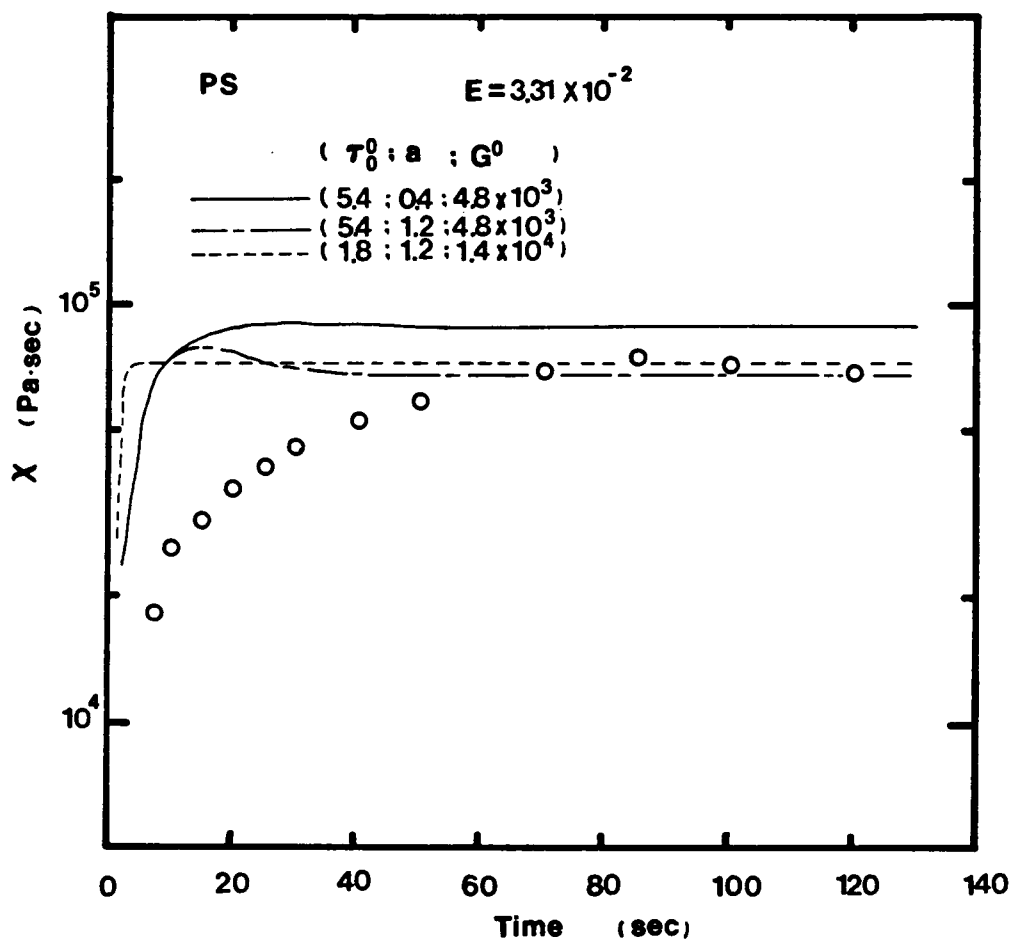


Figure VI.11. Comparison of experimental data with phenomenological theory (original Bogue-White) for plot of transient elongational viscosity of PS.



• Figure VI.12. Comparison of experimental data with phenomenological theory (modified Bogue-White) for plot of transient elongational viscosity of PS.

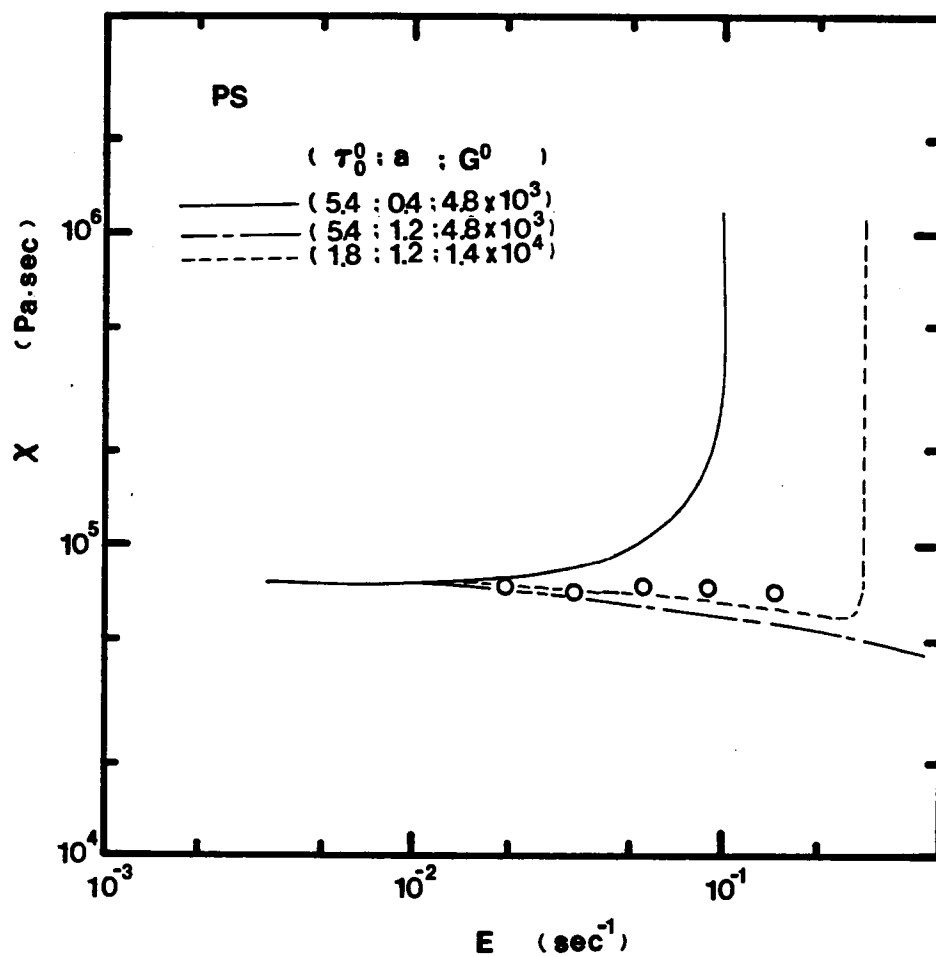


Figure VI.13. Comparison of experimental data with phenomenological theory for plot of steady state elongational viscosity versus elongational rate for PS.

at any elongational rate, because "a" and " τ_0^0 " values of set number 1 satisfies Equation VI.27 at any elongational rate. This may be different from Tanaka (148) and Ide's (73) experimental results which show that the steady state elongational viscosity of PS starts to increase at a finite elongation rate. Predictions for set number 2 approach to infinity at small elongational rates and show large discrepancies from the experimental data in this region, although the prediction agrees with experimental data at very low elongational rates. Set number 3 gives the best agreement among them within the experimental elongational rate region.

The applicability of the set of material constants for each experiment is summarized in Table VI.2.

D. Rheological Theory for Filled Systems

In this section, we develop the theory for the viscoelastic plastic thixotropic fluid on the basis of the theory proposed by White (172).

The stress for a viscoelastic plastic thixotropic fluid can be written as

$$\begin{aligned} \text{tr } \underline{P}^2 < 2Y_1^2, \quad \underline{\sigma} &= -p\underline{I} + G_{11} \underline{\epsilon}^{-1} - G_{12} \underline{\epsilon} \\ \text{tr } \underline{P}^2 > 2Y_1^2, \quad \underline{\sigma} &= -p\underline{I} + \underline{P} \end{aligned} \quad [\text{VI.31}]$$

where White (172) proposed

Table VI.2

Applicability of Material Constants to Each Experiment

$(\tau_0^0; a; G^0)$	Transient Shear Viscosity	Steady State Shear Viscosity	First Normal Stress Difference	Transient Elongational Viscosity	Steady State Elongational Viscosity
(5.4; 1.2; 4.8×10^3) Set Number 1	No	No	Yes (Only at low shear rates)	No	Yes (Only at low elongational rates)
(5.4; 0.4; 4.8×10^3) Set Number 2	Yes (With modified Bogue-White)	Yes	Yes (Only at low shear rates)	No	Yes (Only at very low elongational rates)
1.8; 1.2; 1.4×10^4) Set Number 3	No	Yes	No	No	Yes

$$P(t) = \frac{Y(t, II_d)}{[\frac{1}{2}\text{tr } \underline{\underline{H}}^2(t)]^{1/2}} \underline{\underline{H}}(t) + \underline{\underline{H}}(t) \quad [\text{VI.32}]$$

In these formulations, Y_i denotes an initial yield stress, and $Y(t, II_d)$ denotes the time-deformation rate dependent yield stress. The memory integral, $\underline{\underline{H}}$, for filled systems is defined as

$$\underline{\underline{H}} = \int_0^\infty \frac{G}{\tau_{\text{eff}}} e^{-\frac{z}{\tau_{\text{eff}}}} \underline{\underline{C}}^{-1} dz \quad [\text{VI.33}]$$

where

$$G = f(\phi) \cdot G^o \quad [\text{VI.34}]$$

$$\tau_{\text{eff}} = \tau_{\text{eff}}^o \quad [\text{VI.35}]$$

$$\underline{\underline{C}}^{-1} = \underline{\underline{C}}^{-1} - \frac{1}{3} \text{tr } \underline{\underline{C}}^{-1} \quad [\text{VI.36}]$$

Here superscript "o" again denotes an unfilled system. A function $f(\phi)$ is taken to be equal to the increase in viscosity or modulus due to hydrodynamic effects. It is defined as

$$f(\phi) = \frac{\eta^*(\dot{\gamma})}{\eta^o(\dot{\gamma})} = \frac{\eta(\dot{\gamma}) - Y_{\text{shear}}/\dot{\gamma}}{\eta^o(\dot{\gamma})} \quad [\text{VI.37}]$$

by Tanaka and White (149). Here η without the superscript "o" denotes a viscosity of a filled system and Y_f means the final yield stress.

We sought to formulize a thixotropic yield function to substitute into Equation VI.32. A thixotropic yield

function may be formulized as follows.

- (1) It was assumed that invariants of deformation rate tensor or their function is responsible to the decay of yield stress, that is, $F(I_d, II_d, III_d)$. I_d is zero because of incompressibility. We choose $F(II_d, III_d) = k_1 II_d^{1/2}$ as the simplest form. Here k_1 is a constant.
- (2) It seems reasonable to apply a time dependent memory function to the above-mentioned deformation rate dependence. This makes it possible to weigh events so that the effect of a certain $k_1 II_d^{1/2}$ on the decay of yield stress during deformation is most heavily felt immediately after the occurrence of deformation. The simplest mathematical form of such a memory function is exponential, that is,

$$k_1 II_d^{1/2} e^{-k_2 z} \quad [VI.38]$$

where k_2 is constant and $z = t - s$. This function can be integrated over z from $z = 0$ to $z = \infty$.

$$\int_0^{\infty} k_1 II_d^{1/2} e^{-k_2 z} dz \quad [VI.39]$$

- (3) The simplest mathematical expression would have the form

$$Y(t_1 II_d) = A + \int_0^{\infty} k_1 II_d^{1/2} e^{-k_2 z} dz \quad [VI.40]$$

Assuming a constant deformation rate beginning at time zero, integration yields

$$Y(t, II_d) = A - \left(1 - \frac{k_1}{k_2} II_d^{1/2} e^{-k_2 t}\right) \quad [VI.41]$$

The yield stress must change from an initial value Y_i to the final (steady state) value Y_f . This equation should satisfy:

$$\lim_{t \rightarrow 0} Y(t, II_d) = Y_i \quad [VI.42]$$

$$\lim_{t \rightarrow \infty} Y(t, II_d) = Y_f \quad [VI.43]$$

Therefore, we obtain

$$A = Y_i$$

$$k_2 = \alpha II_d^{1/2} \quad [VI.44]$$

$$k_1 = \alpha(Y_i - Y_f)$$

Substituting this into Equation VI.40, we obtain

$$Y(t, II_d) = Y_i - \int_0^\infty \alpha II_d^{1/2} e^{-\alpha II_d^{1/2} z} dz \cdot (Y_i - Y_f) \quad [VI.45]$$

- (4) According to steady shear experiments, we find the following relation for Y_i

$$Y_i = Y_f + \beta II_d^{1/2} \quad [VI.46]$$

where β is a material constant. We note Y_i does not have a constant value, but is a function of $II_d^{1/2}$. This will be discussed in Section E.1 (Evaluation of Material Constants for Unfilled Systems).

Equations VI.45 and VI.46 are the newly proposed time-deformation rate dependent (thixotropic) yield stress. This formulation contains three material constants, α , β and Y_f . The characteristics of this formulation are illustrated in Figure VI.14. This plot represents the influence of α and $II_d^{1/2}$ values on the decay tendency of yield stress $Y(t, II_d)$. The yield stress decays exponentially from Y_i which is dependent upon $II_d^{1/2}$ to Y_f in any case.

$$\lim_{t \rightarrow 0} Y(t, II_d) = Y_i = Y_f + \beta II_d^{1/2} \quad [VI.47]$$

$$\lim_{t \rightarrow \infty} Y(t, II_d) = Y_f \quad [VI.48]$$

For the same α , the yield value decays more rapidly with a large $II_d^{1/2}$. When $II_d^{1/2}$ remains a constant value, a larger α value gives more rapid decay of the yield value.

A second possible form of the time-deformation rate dependent (thixotropic) yield function has been proposed by Slibar and Paslay (143). We discuss the characteristics of their formulation as a comparison. Their formulation is

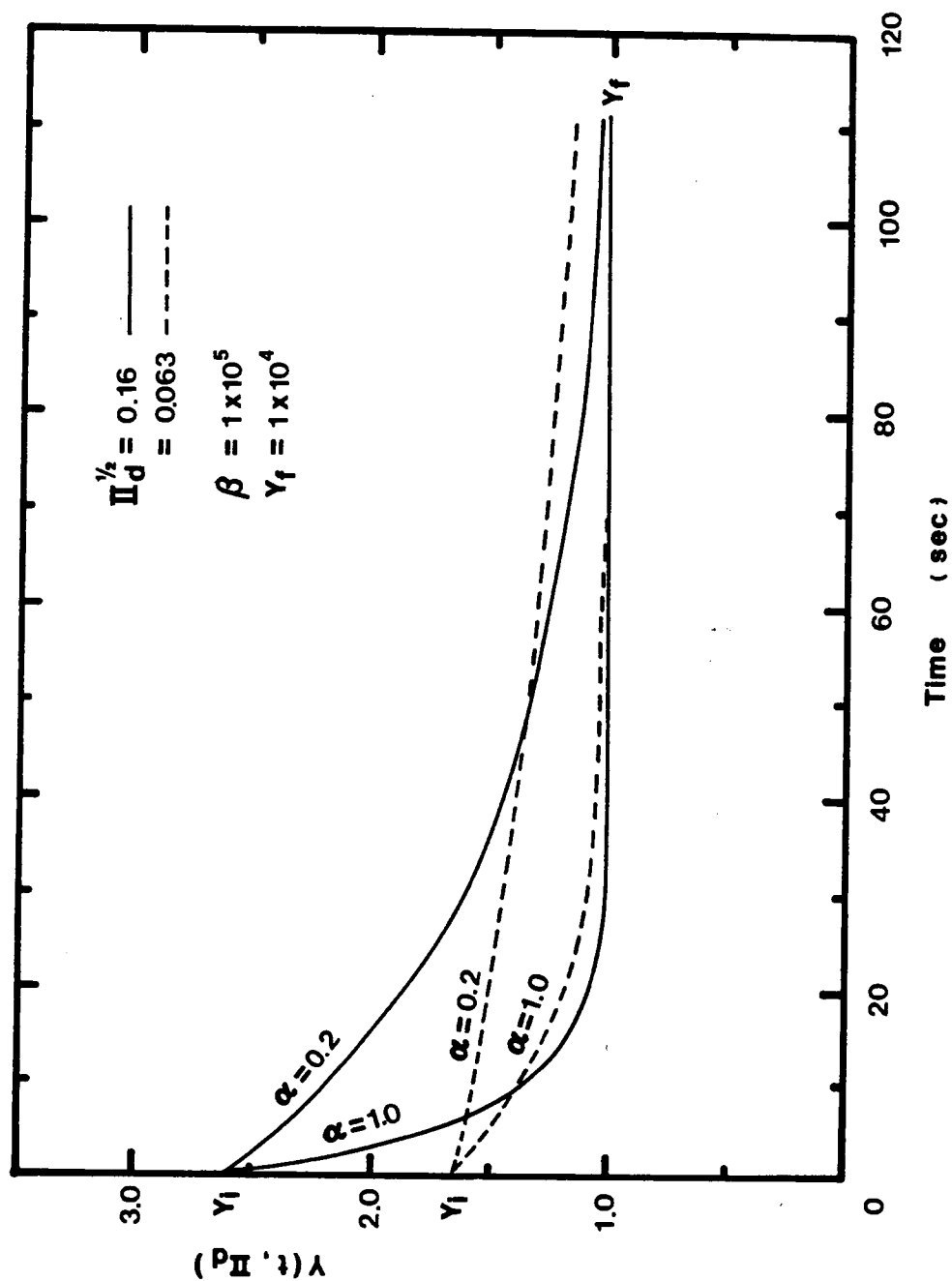


Figure VI.14. Characteristics of the newly proposed time-deformation rate dependent yield function.

$$Y(t, II_d) = Y_0 - \frac{\int_0^\infty II_d^{1/2} e^{-\alpha z} dz}{\beta + \int_0^\infty II_d^{1/2} e^{-\alpha z} dz} (Y_0 - Y_1) \quad [VI.49]$$

where α , β , Y_0 and Y_1 are the material constants. Figure VI.16 shows the characteristics of their formulation. The α and $II_d^{1/2}$ values were taken as variable parameters. The yield stress decays exponentially from Y_0 which is not dependent upon $II_d^{1/2}$ but is always constant, and reaches a steady state value. The steady state value of yield stress is a function of α , β and $II_d^{1/2}$.

$$\lim_{t \rightarrow 0} Y(t, II_d) = Y_0 \quad [VI.50.a]$$

$$\lim_{t \rightarrow \infty} Y(t, II_d) = Y_0 - \frac{II_d^{1/2}}{\alpha\beta + II_d^{1/2}} \cdot (Y_0 - Y_1) \quad [VI.50.b]$$

These characteristics for the initial and steady state values are different from those of the newly proposed yield stress function (Figure VI.15).

In addition, the rapidness of decay is largely dependent upon the α value, but the $II_d^{1/2}$ value is not influential in decay. This is also in contrast to the newly proposed yield stress function.

These characteristics are summarized in Table VI.3 for both yield stress formulations.

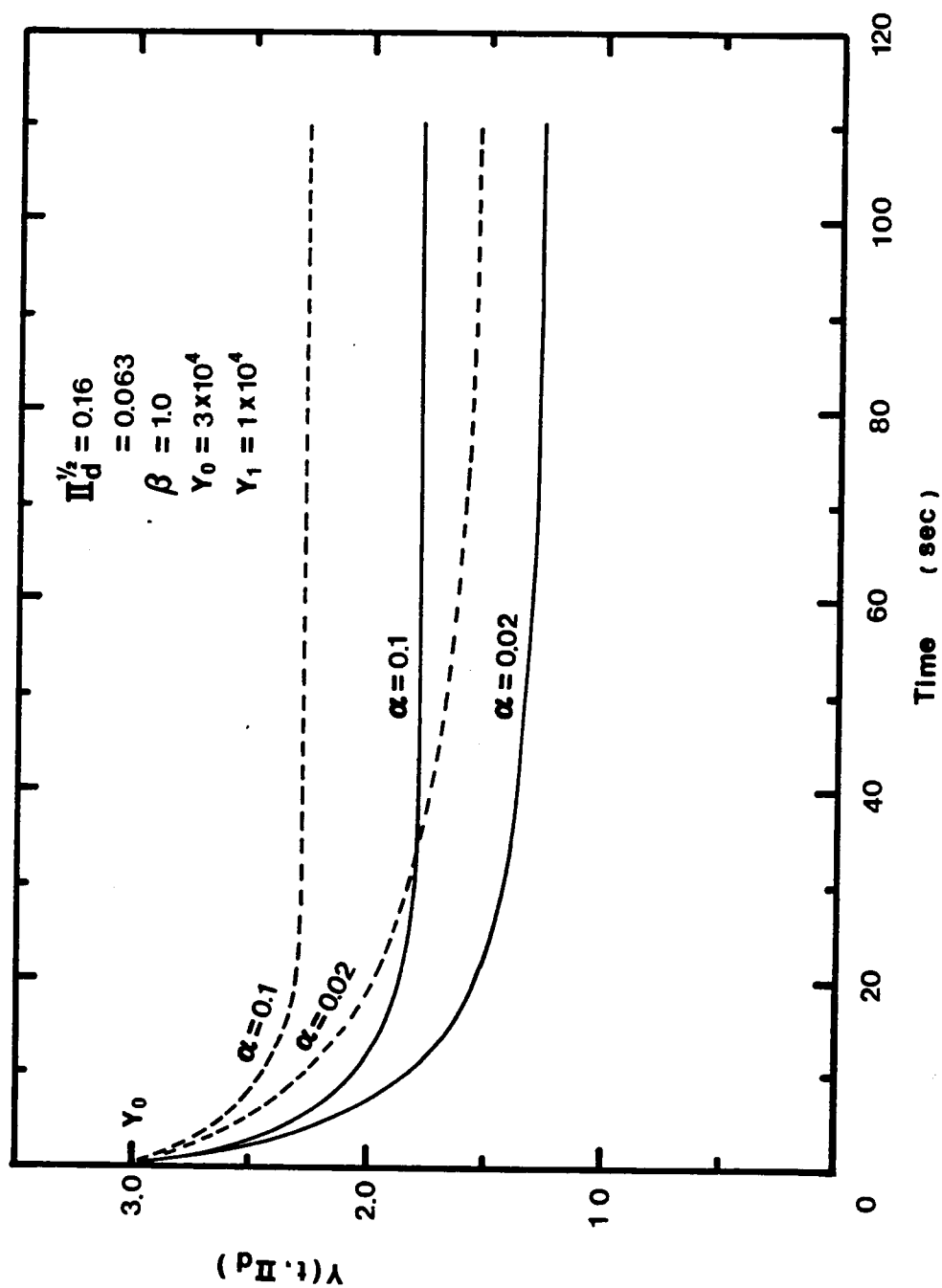


Figure VI.15. Characteristics of Slibar-Pasley time-deformation rate dependent yield function.

Table VI.3

Characteristics of Time-Deformation Rate
Dependent Yield Functions

	Initial Value of $Y(t_1 II_d)$ (at $t = 0$)	Final Value of $Y(t_1 II_d)$ (at $t = 0$)	Decay Tendency of $Y(t_1 II_d)$	
Newly Proposed $Y(t_1 II_d)$ Equations VI.45 and VI.46	increasing function of $II_d^{1/2}$	always constant: Y_f	$\alpha = \text{constant}$ $II_d^{1/2} = \text{variable}$	$\alpha = \text{variable}$ $II_d^{1/2} = \text{constant}$ decays more rapidly with increasing α
Slibar-Paslay's $Y(t_1 II_d)$ Equation VI.49	always constant: Y_i	function of α , β and $II_d^{1/2}$	$II_d^{1/2}$ does not influence decay	reaches a steady state in shorter period with increasing α

D.1 Application to Steady Shear Flow

We apply the viscoelastic plastic thixotropic theory to steady shear flow. The modified Bogue-White model (Equations VI.6 and VI.7) having the best agreement between theory and experiment was obtained in the previous section and will be used as a basis of the theory for filled systems.

We rewrite Equation VI.31

$$\text{tr} \underline{P}^2 \leq 2Y_i^2, \quad \sigma_{12} = G_{12}^{el} \gamma_{12} \quad [\text{VI.51}]$$

for the small stress-strain region. Here G_{12}^{el} denotes shear modulus in elastic deformation. The expression of time-deformation rate yield stress for steady shear flow is obtained by substituting Equations VI.13 and VI.46 into Equation VI.45, that is,

$$\text{tr} \underline{P}^2 > 2Y_i^2, \quad Y(t, II_d) = \beta \dot{\gamma} e^{-\alpha \dot{\gamma} t} + Y_f \quad [\text{VI.52}]$$

The deviatoric stress tensor, Equation VI.32 for shear flow is

$$P_{12}(t) = \left(1 + \frac{\beta \dot{\gamma} e^{-\alpha \dot{\gamma} t} + Y_f}{\left[\frac{1}{2} \text{tr} \underline{H}^2(t) \right]^{1/2}} \right) \cdot H_{12}(t) \quad [\text{VI.53}]$$

where

$$H_{12}(t) = G \dot{\gamma} \left[\tau_{eff} - e^{-\frac{t}{\tau_{eff}}} (t + \tau_{eff}) + t e^{-\frac{t}{\tau_0}} \right] \quad [\text{VI.54}]$$

$$\begin{aligned}
 \text{tr} \underline{\underline{H}}^2(t) = & \frac{2}{3} G^2 \dot{\gamma}^4 [2\tau_{\text{eff}}^2 - e^{-\frac{t}{\tau_{\text{eff}}}} (t^2 + 2\tau_{\text{eff}} t + 2\tau_{\text{eff}}^2) \\
 & + t^2 e^{-\frac{t}{\tau_0}}]^2 + 2G^2 \dot{\gamma}^2 [\tau_{\text{eff}} - e^{-\frac{t}{\tau_{\text{eff}}}} (t + \tau_{\text{eff}}) \\
 & + t e^{-\frac{t}{\tau_0}}]^2
 \end{aligned} \tag{VI.55}$$

A deviatric Finger deformation tensor (Equation VI.12) was used. The shear viscosity is, then, given by

$$\eta_{12}(t) = \frac{P_{12}(t)}{\dot{\gamma}} = \frac{1}{\dot{\gamma}} \left(1 + \frac{\beta \dot{\gamma} e^{-\alpha \dot{\gamma} t} + Y_f}{\left[\frac{1}{2} \text{tr} \underline{\underline{H}}^2(t) \right]^{1/2}} \right) \cdot H_{12}(t) \tag{VI.56}$$

for the transient state, and

$$\eta_{12} = \lim_{t \rightarrow \infty} \eta_{12}(t) = G\tau_{\text{eff}} + \frac{Y_f}{\dot{\gamma} \left(1 + \frac{4}{3} \tau_{\text{eff}}^2 \dot{\gamma}^2 \right)^{1/2}} \tag{VI.57}$$

for the steady state.

The first normal stress difference is given by

$$\begin{aligned}
 N_1 &= P_{11} - P_{22} \\
 &= 2G\tau_{\text{eff}}^2 \dot{\gamma}^2 + \frac{2Y_f \tau_{\text{eff}} \dot{\gamma}}{\left(1 + \frac{4}{3} \tau_{\text{eff}}^2 \dot{\gamma}^2 \right)^{1/2}}
 \end{aligned} \tag{VI.58}$$

As a comparison, we consider Slibar-Paslay's time-deformation rate dependent yield stress (Equation VI.49). Modifying Equation VI.49 for steady shear flow, we get

$$Y(t, II_d) = Y_0 - \frac{\frac{\dot{\gamma}}{\alpha\beta} (1 - e^{-\alpha t})}{1 + \frac{\dot{\gamma}}{\alpha\beta} (1 - e^{-\alpha t})} \cdot (Y_0 - Y_1) \quad [VI.59]$$

The transient shear viscosity is given by

$$\eta_{12}(t) = \frac{P_{12}(t)}{\dot{\gamma}} = \frac{1}{\dot{\gamma}} \left(1 + \frac{Y(t, II_d)}{[\frac{1}{2} \text{tr } \underline{H}^2(t)]^{1/2}} \right) \cdot H_{12}(t) \quad [VI.60]$$

where $Y(t, II_d)$, $H_{12}(t)$ and $\text{tr } \underline{H}^2(t)$ are equal to Equations VI.59, VI.54 and VI.55 respectively. The steady state viscosity is given by

$$\eta_{12} = \lim_{t \rightarrow \infty} \eta_{12}(t) = G\tau_{\text{eff}} + \frac{Y_0 - \frac{\dot{\gamma}}{\alpha\beta + \dot{\gamma}} (Y_0 - Y_1)}{\dot{\gamma} (1 + \frac{4}{3} \tau_{\text{eff}}^2 \dot{\gamma}^2)^{1/2}} \quad [VI.61]$$

The first normal stress difference is given by

$$\begin{aligned} N_1 &= P_{11} - P_{22} \\ &= 2G \tau_{\text{eff}}^2 \dot{\gamma}^2 + \frac{2 \tau_{\text{eff}} \dot{\gamma}^2}{\frac{\alpha\beta + \dot{\gamma}}{(1 + \frac{4}{3} \tau_{\text{eff}}^2 \dot{\gamma}^2)^{1/2}}} \end{aligned} \quad [VI.62]$$

D.2 Application to Elongational Flow

The modified Bogue-White model is used as a basis of the theory for filled systems here also. The expression for the time-deformation rate yield stress for elongational flow is obtained by substituting Equations VI.23 and VI.46 into Equation VI.45.

$$Y(t, II_d) = \sqrt{3} \beta E e^{-\sqrt{3} \alpha E t} + Y_f \quad [VI.63]$$

The deviatric stress tensor, Equation VI.32, for elongational flow is

$$P_{11}(t) = \left(1 + \frac{\sqrt{3} \beta E e^{-\sqrt{3} \alpha E t} + Y_f}{\left[\frac{1}{2} \text{tr} \underline{H}^2(t)\right]^{1/2}}\right) \cdot H_{11}(t) \quad [VI.64]$$

and

$$P_{22}(t) = \left(1 + \frac{\sqrt{3} \beta E e^{-\alpha E t} + Y_f}{\left[\frac{1}{2} \text{tr} \underline{H}^2(t)\right]^{1/2}}\right) \cdot H_{22}(t) \quad [VI.65]$$

where

$$\begin{aligned} H_{11}(t) = \frac{2}{3} G \left[\frac{1}{2E \tau_{eff} - 1} \left(e^{\frac{2E \tau_{eff} - 1}{\tau_{eff}} t} - 1 \right) \right. \\ \left. + \frac{1}{E \tau_{eff} + 1} \left(e^{-\frac{E \tau_{eff} + 1}{\tau_{eff}} t} - 1 \right) \right. \\ \left. + e^{-\frac{t}{\tau_0}} (e^{2Et} - e^{-Et}) \right] \end{aligned} \quad [VI.66]$$

and

$$H_{22}(t) = -\frac{1}{2} H_{11}(t) \quad [VI.67]$$

$$\text{tr} \underline{H}^2(t) = \frac{3}{2} H_{11}^2(t) \quad [VI.68]$$

Again, we note the deviatric Finger deformation rate tensor was used for these deviations.

The tensile stress acting on the filament during deformation is then given by

$$\begin{aligned} \frac{F(t)}{A(t)} &= P_{11}(t) - P_{22}(t) \\ &= \frac{3}{2} \left(1 + \frac{\sqrt{3} \beta E e^{-\sqrt{3} \alpha E t} + Y_f}{\left[\frac{1}{2} \operatorname{tr} \underline{H}^2(t) \right]^{1/2}} \right) \cdot H_{11}(t) \end{aligned} \quad [\text{VI.69}]$$

The transient elongational viscosity is given by

$$\chi(t) = \frac{3}{2E} \left(1 + \frac{\sqrt{3} \beta E e^{-\sqrt{3} \alpha E t} + Y_f}{\left[\frac{1}{2} \operatorname{tr} \underline{H}^2(t) \right]^{1/2}} \right) \cdot H_{11}(t) \quad [\text{VI.70}]$$

where $H_{11}(t)$ and $\operatorname{tr} \underline{H}^2(t)$ are equal to Equations VI.66 and VI.68.

The steady state form is

$$\begin{aligned} \chi &= \lim_{t \rightarrow \infty} \chi(t) = \left(1 + \frac{\sqrt{3} Y_f}{\frac{3\tau_{\text{eff}} E G}{(1 + \tau_{\text{eff}} E)(1 - 2\tau_{\text{eff}} E)}} \right) \\ &\quad \cdot \left(\frac{3\tau_{\text{eff}} G}{(1 + \tau_{\text{eff}} E)(1 - 2\tau_{\text{eff}} E)} \right) \end{aligned} \quad [\text{VI.71}]$$

when $E < 1/2 \tau_{\text{eff}}$ is satisfied.

As a comparison, again we consider Slibar-Paslay's time-deformation rate dependent yield function (Equation VI.41). Modifying Equation VI.49 for elongational flow, we get

$$Y(t, II_d) = Y_0 - \frac{\frac{\sqrt{3}E}{\alpha\beta} (1 - e^{-\alpha t})}{1 + \frac{\sqrt{3}E}{\alpha\beta} (1 - e^{-\alpha t})} \cdot (Y_0 - Y_1) \quad [VI.72]$$

The transient elongational viscosity is given by

$$\chi(t) = \frac{3}{2E} \left(1 + \frac{Y(t_1 II_d)}{\left[\frac{1}{2} \text{tr} \underline{H}^2(t) \right]^{1/2}} \right) \cdot H_{11}(t) \quad [VI.73]$$

where $Y(t_1 II_d)$, $H_{11}(t)$ and $\text{tr} \underline{H}^2(t)$ are equal to Equations VI.72, VI.66 and VI.68 respectively. The steady state form is given by

$$\begin{aligned} \chi = \lim_{t \rightarrow \infty} \chi(t) &= \left[1 + \frac{\sqrt{3} \left[Y_0 - \frac{\sqrt{3}E}{\alpha\beta + \sqrt{3}E} (Y_0 - Y_1) \right]}{\frac{3\tau_{\text{eff}} E G}{(1 + \tau_{\text{eff}} E)(1 - 2\tau_{\text{eff}} E)}} \right] \\ &\cdot \left(\frac{3\tau_{\text{eff}} G}{(1 + \tau_{\text{eff}} E)(1 - 2\tau_{\text{eff}} E)} \right) \quad [VI.74] \end{aligned}$$

where $E < 1/2 \tau_{\text{eff}}$ is satisfied.

E. Comparison of Theory and Experimental Data for Filled Systems

E.1 Evaluation of Material Constants for Filled Systems

E.1.a For newly proposed yield function. The material constants we ought to obtain are G^{el} , β , Y_f , $f(\phi)$ and α for

the theory of unfilled systems with the newly proposed yield function.

We are able to determine " G^{el} " and " β " values from the stress-strain relation at the small strain region. Figures VI.16 to VI.21 represent stress versus strain curves for various compounds at the very beginning of shear flow. Experimental results suggest that these compounds behave such as elastic materials at the small strain region. The initial slope of stress-strain curves is independent of the deformation rate. This slope is taken as the shear modulus in elastic deformation, G_{12}^{el} . The maximum stress for elastic deformation may be called the initial yield stress, Y_i . In all compounds, Y_i is found to be a function of the deformation rate. Figure VI.22 summarizes Y_i as a function of shear rate. We note that Y_i roughly increases linearly with increasing shear rate, and the intercepts at zero shear rate are nearly equal to the final yield stress, Y_f . Therefore, we obtain an empirical relation Equation VI.46. The β value is equivalent to the slope of this plot. The β values for each compound are shown in Table VI.4. The G^{el} and β values were not determined for elongational deformation because of the experimental difficulties in the small strain region.

" Y_f ," the final yield stress, can be determined considering steady state shear stress or elongational stress at $II_d^{12} \rightarrow 0$, that is,

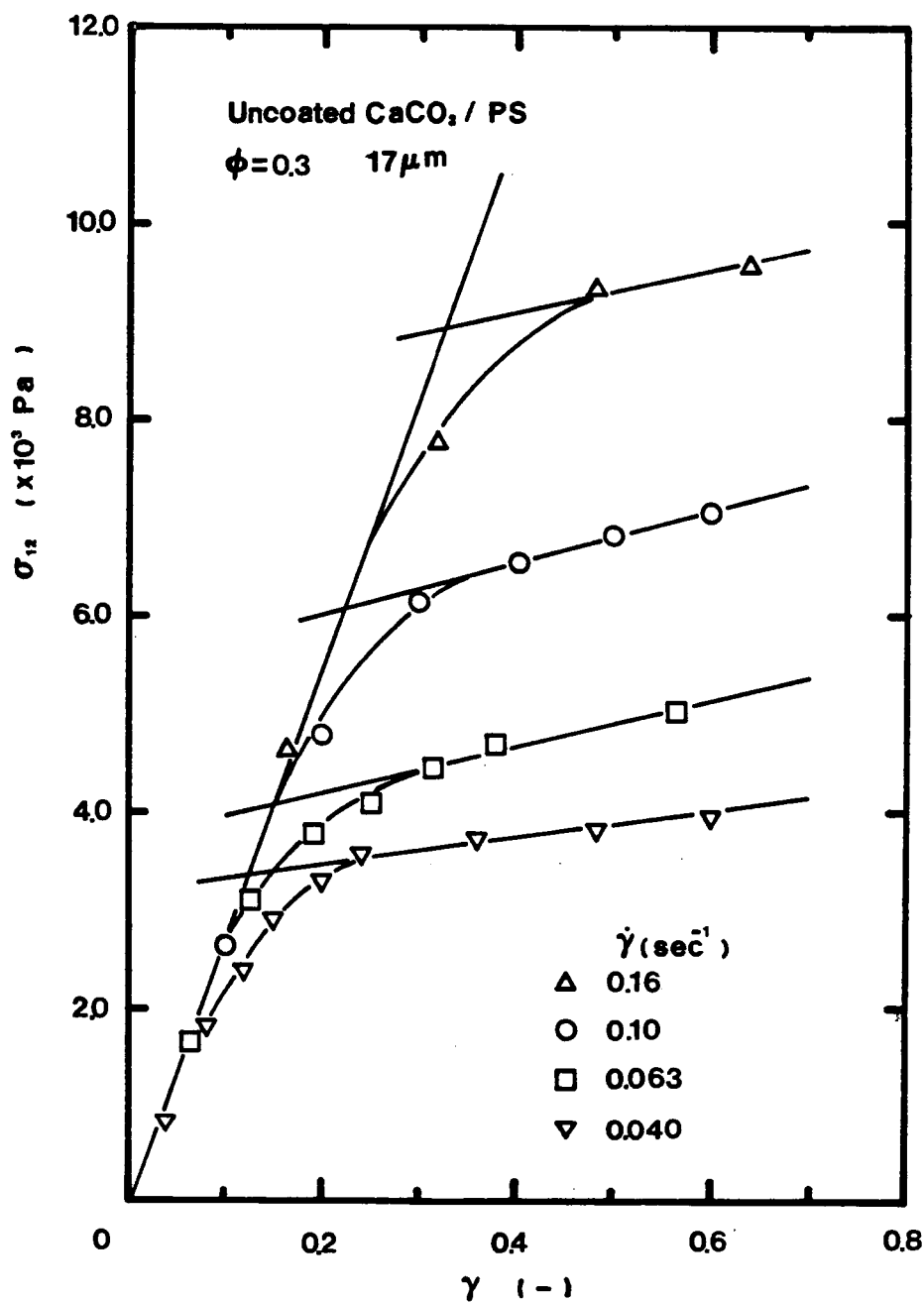


Figure VI.16. Stress-strain curves for uncoated CaCO_3 ($d_p = 17\mu\text{m}$) filled PS at various shear rates.

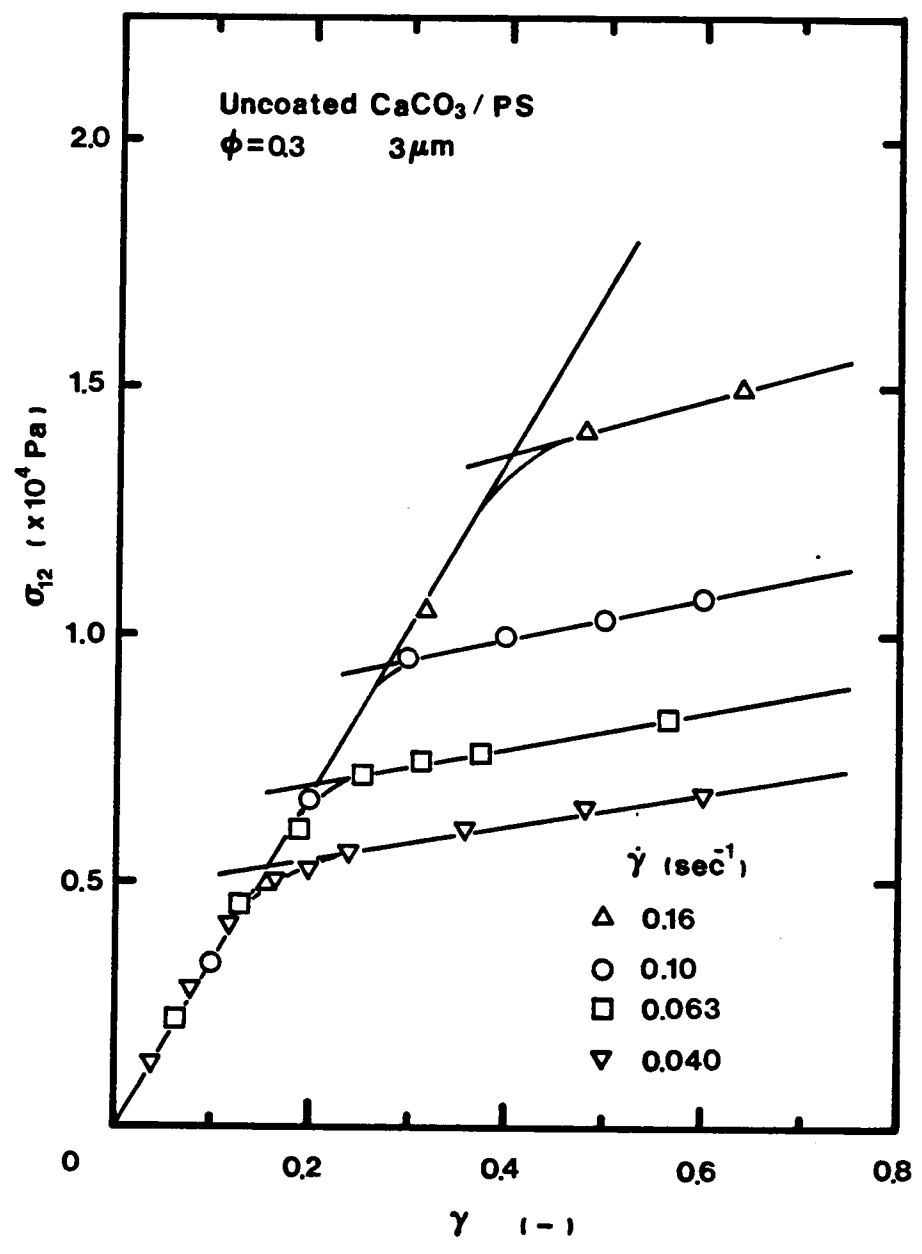


Figure VI.17. Stress-strain curves for uncoated CaCO_3 ($dp = 3\mu\text{m}$) filled PS at various shear rates.

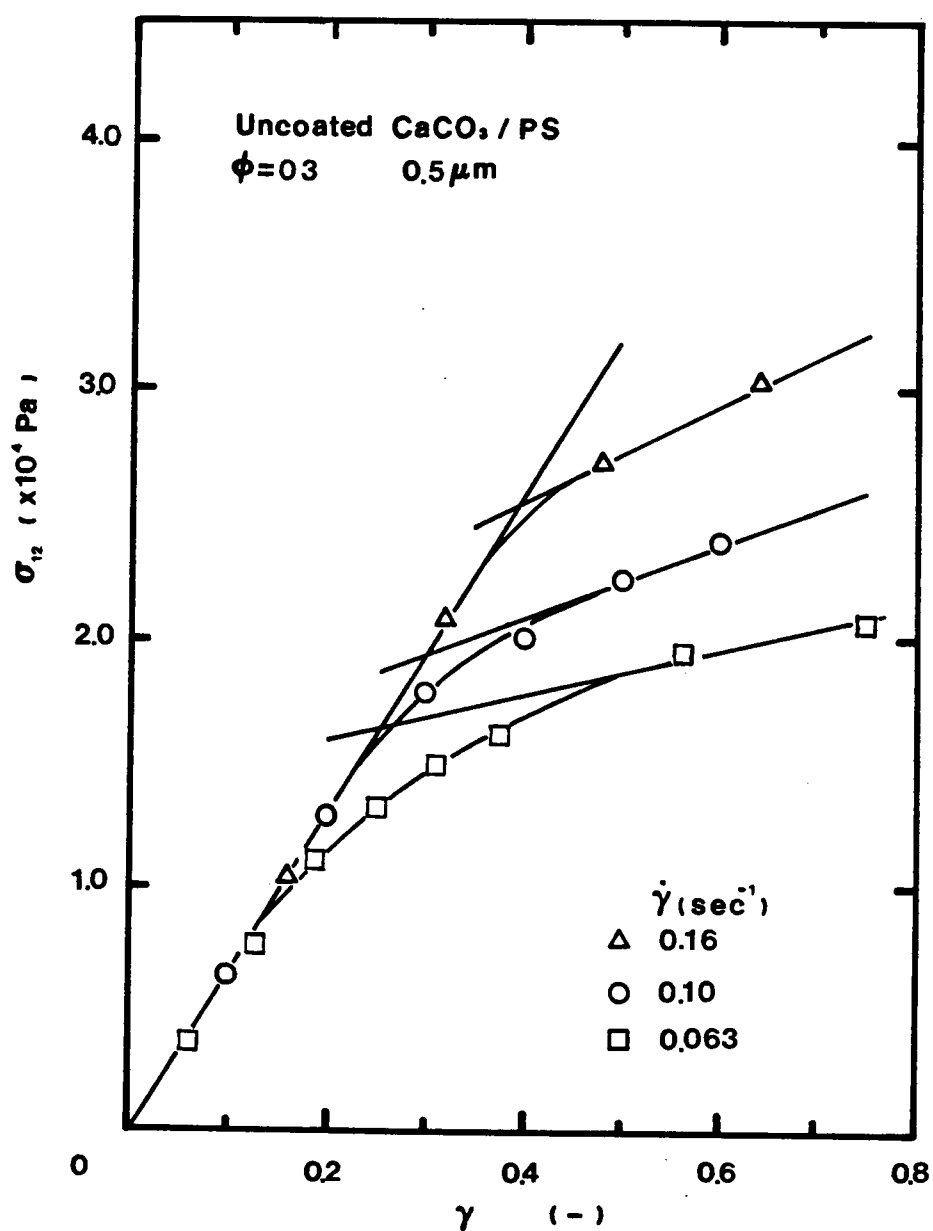


Figure VI.18. Stress-strain curves for uncoated CaCO_3 ($d_p = 0.5\mu\text{m}$) filled PS at various shear rates.

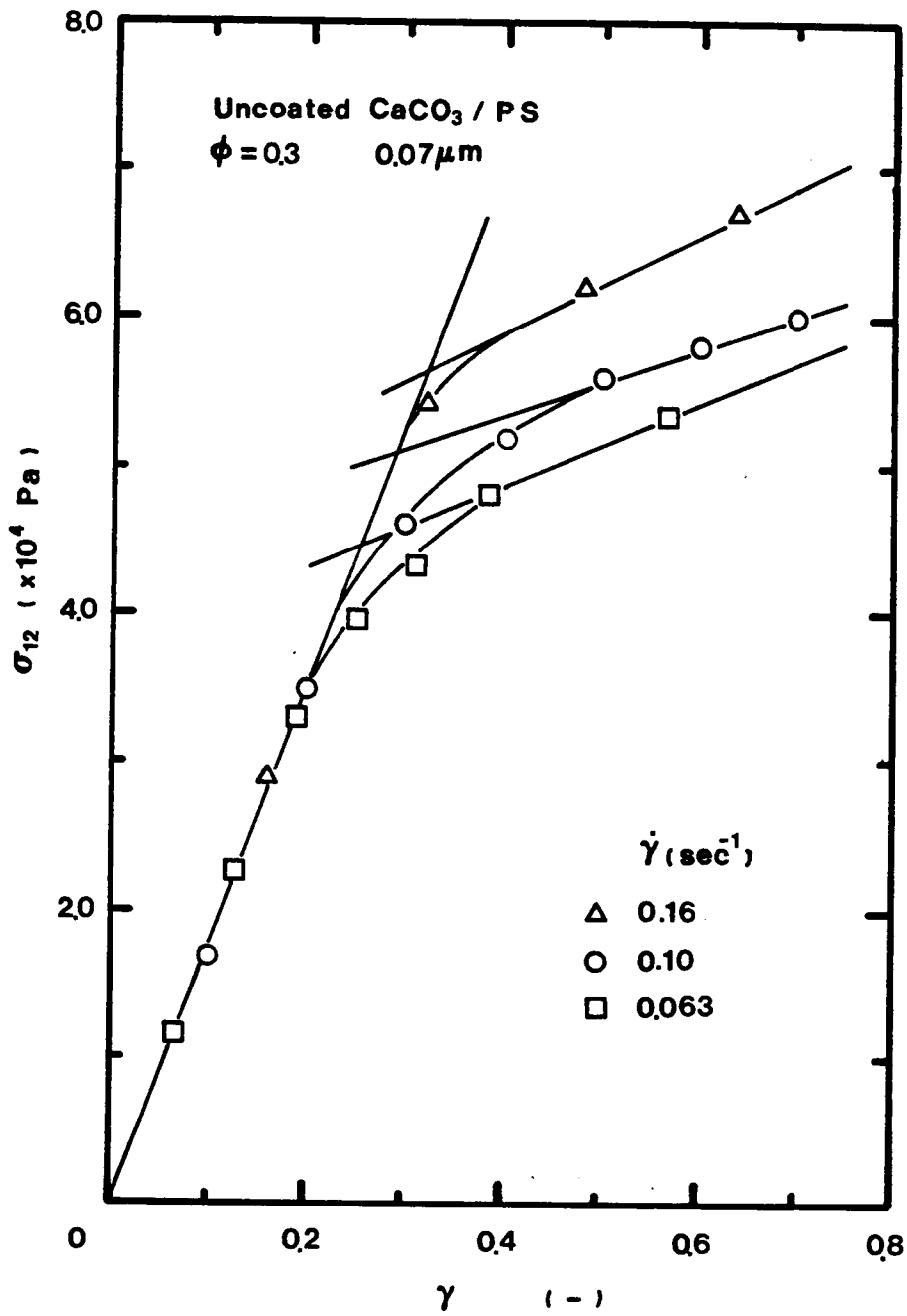


Figure VI.19. Stress-strain curves for uncoated CaCO_3 ($d_p = 0.07 \mu\text{m}$) filled PS at various shear rates.

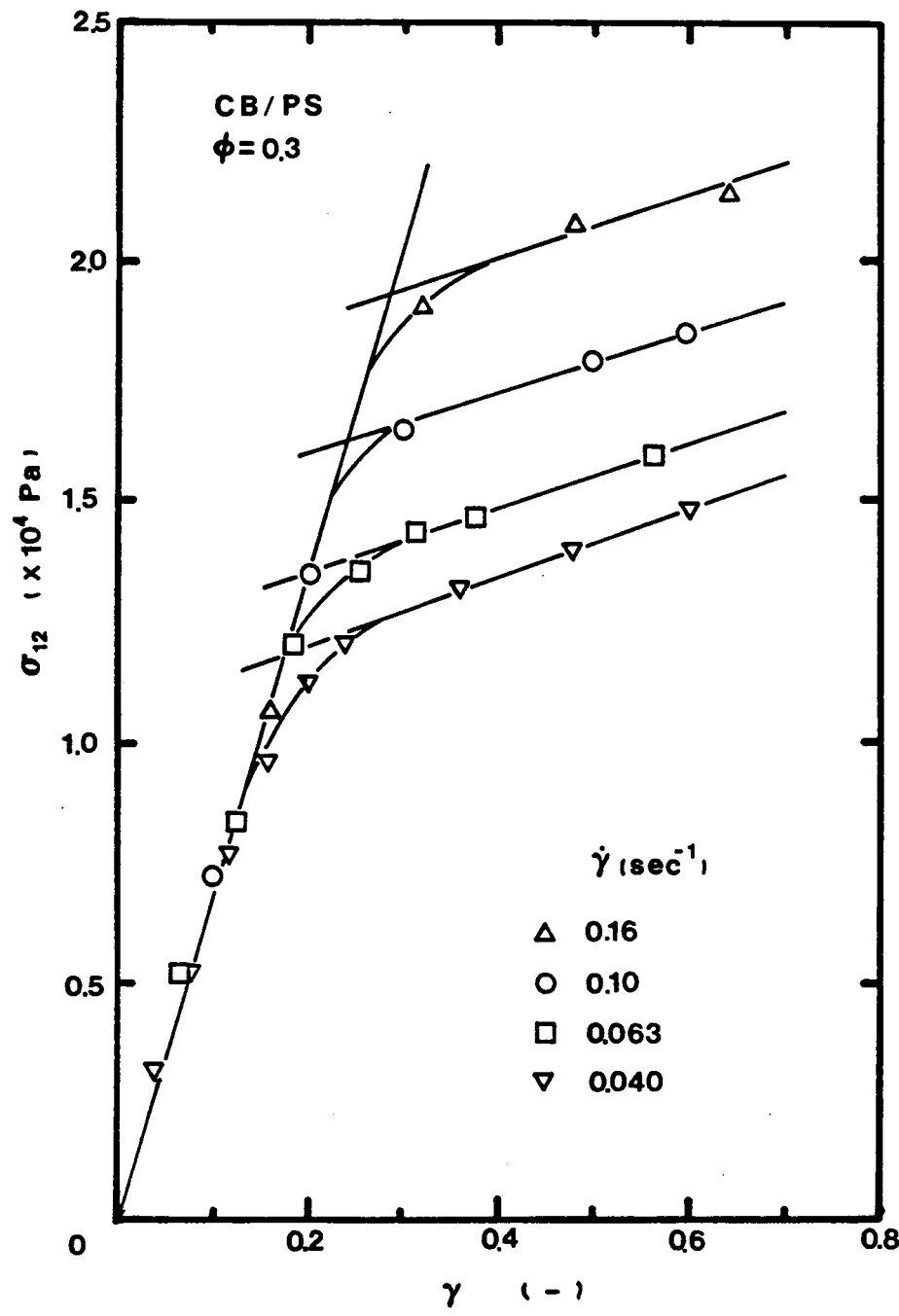


Figure VI.20. Stress-strain curves for CB filled PS ($\phi = 0.3$) at various shear rates.

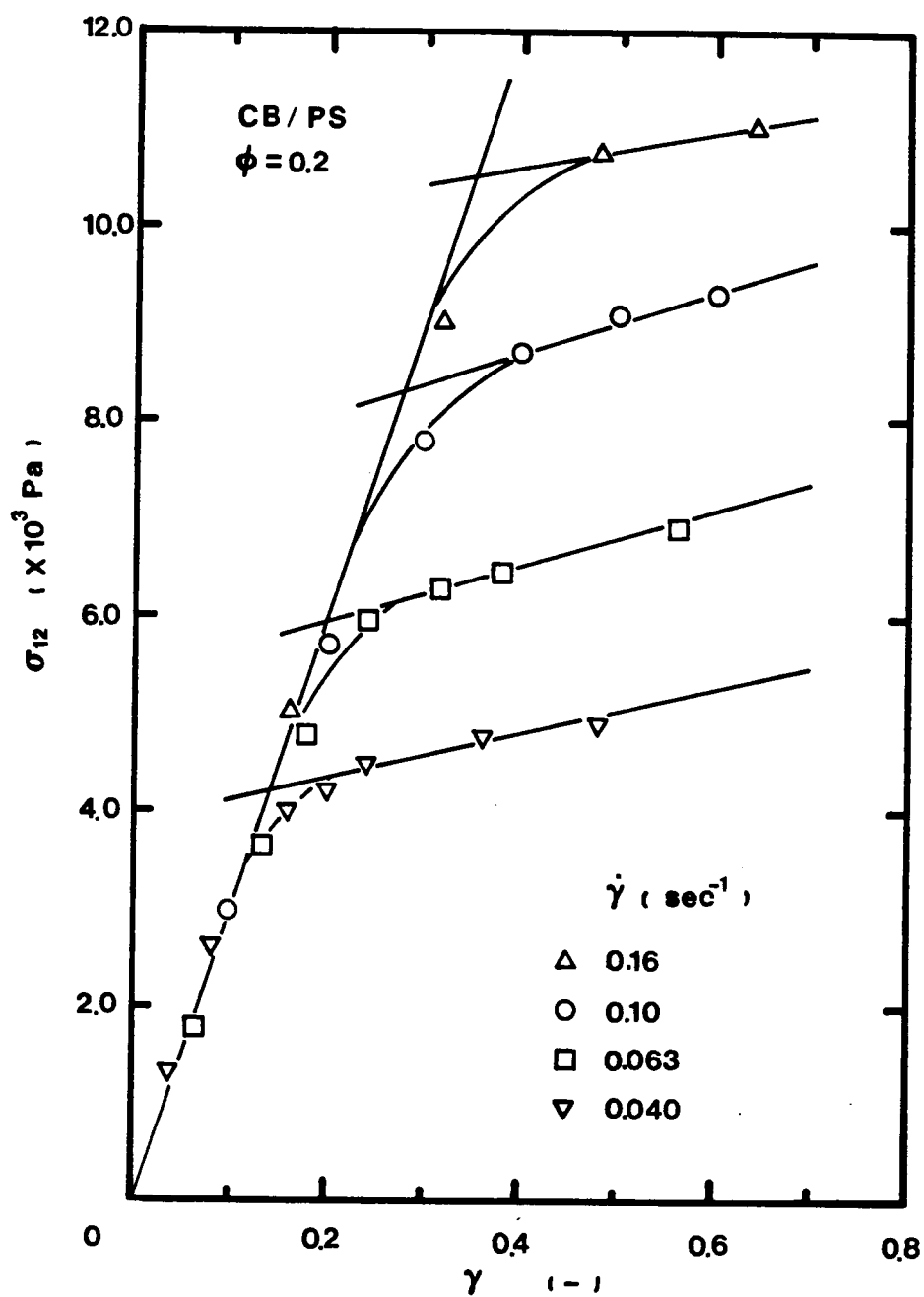


Figure VI.21. Stress-strain curves for CB filled PS ($\phi = 0.2$) at various shear rates.

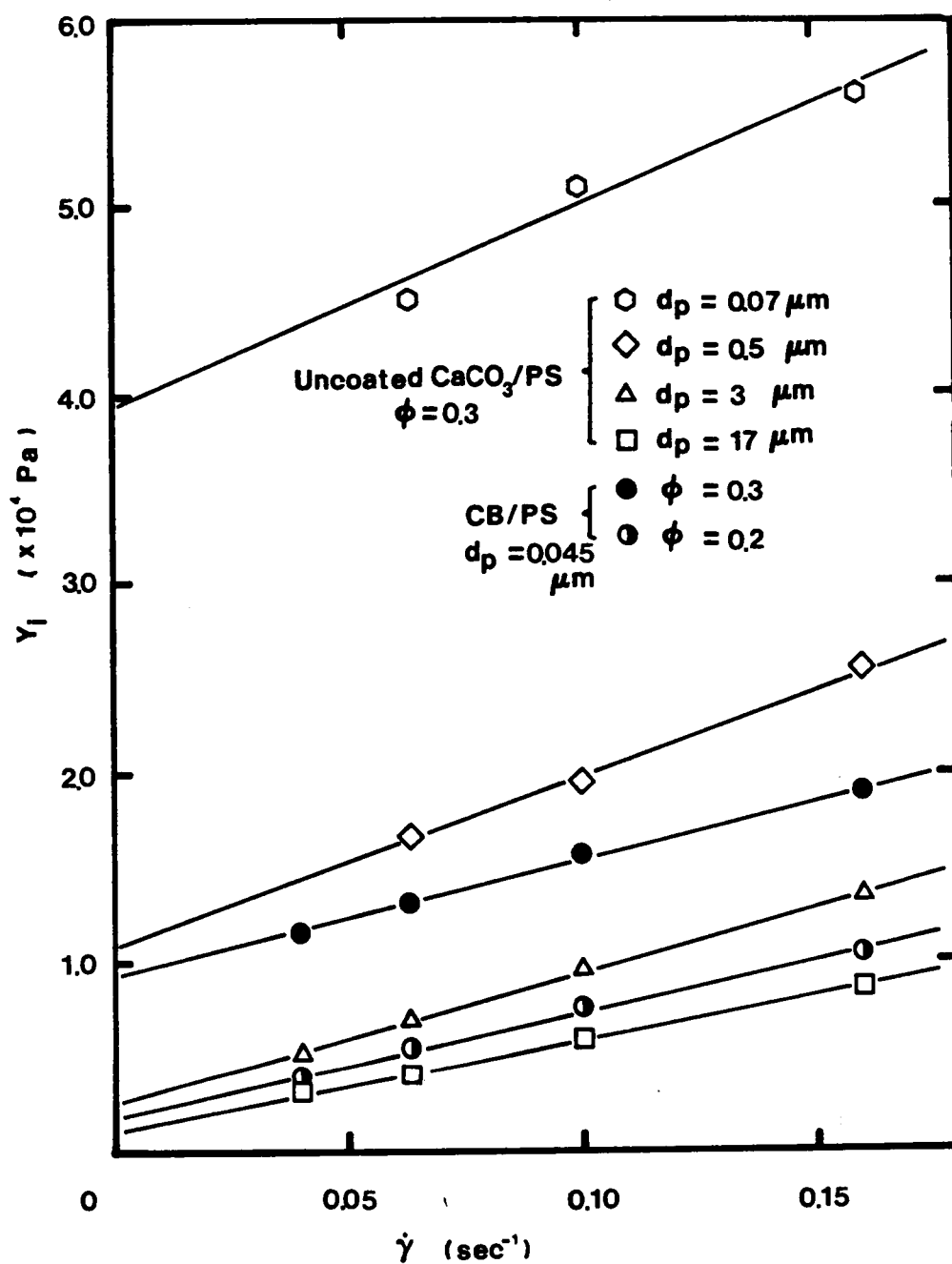


Figure VI.22. Initial yield stress as a function of shear rate.

Table VI.4

Material Constants for Theory for Filled Systems with Newly Proposed Yield Function, Equations VI.45, VI.46

Filler	Volume Content ϕ (-)	Average Particle Size d_p (μm)	el G12 Equation VI.51 ($Pa \times 10^{-4}$)	β ($Pa \cdot sec \times 10^{-4}$)	Y_f^* ($Pa \cdot sec \times 10^{-3}$)	f(ϕ) Equation VI.34 (-)	α (-)
Uncoated		17	2.8	4.8	Unclear (0.1)	2.5~3.0	
		3	3.8	6.9	1.5 (1.6)	4.5	
CaCO ₃	0.3	0.5	6.5	9.5	10 (9)	4.6	Fitting
		0.07	18	15	40 (38)	4.0	
Coated		17	-	-	Unclear (<0.1)	2.5	parameter
		3	-	-	Unclear (<0.1)	2.5	for
CaCO ₃	0.3	0.5	-	-	Unclear (0.16)	2.5~2.9	transient
		0.07	-	-	Unclear (1.0)	3.9	
CB	0.3		6.7	6.0	9 (8.8)	4.4	state
	0.2	0.045	3.0	5.7	~2 (1.3)	2.4	

*Values without parentheses are estimated from η versus σ_{12} plot; values with parentheses are estimated from Casson's plot.

$$\lim_{\substack{t \rightarrow \infty \\ \dot{\gamma} \rightarrow 0}} \sigma_{12}(t) = \lim_{\substack{t \rightarrow \infty \\ \dot{\gamma} \rightarrow 0}} \eta_{12}(t) \dot{\gamma} = Y_f \quad [\text{VI.75}]$$

where $\eta_{12}(t)$ is equal to Equation VI.55.

$$\lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \sigma_{11}(t) = \lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \chi(t) \cdot E = \sqrt{3} Y_f \quad [\text{VI.76}]$$

where $\chi(t)$ is equal to Equation VI.70. These results imply that the yield stresses determined from $\eta - \sigma_{12}$ and $\chi - \sigma_{11}$ plot, that is, Y_{shear} and Y_{elong} are equal to Y_f and $\sqrt{3} Y_f$ respectively. Therefore, the yield stresses obtained in Chapters IV and V can be adopted as material constant Y_f . Y_f values obtained in shear flow measurements are summarized for each compound in Table VI.4.

A material constant, " $f(\phi)$," viscosity or modulus increase due to volume content of filler, which appears in Equation VI.34 was already obtained in Chapter IV. The $f(\phi)$ values for each compound are summarized in Table VI.4.

There remains only one material constant, " α ," which implies rapidness of yield stress decay during deformation. This value is used as a fitting parameter in transient shear stress data.

E.1.b For Slibar-Paslay yield function. The material constants we need to determine are G^{el} , Y_0 , Y_1 , α , β and $f(\phi)$ for theory for filled systems with Slibar-Paslay yield function.

The material constant " G^{el} " was already determined in Section E.1.a. The relation between experimentally obtained yield stresses, Y_{shear} and Y_{elong} , from $\eta - \sigma_{12}$ and $\chi - \sigma_{11}$ plot, and material constants is determined by considering steady state shear and elongational stress at $II_d^{1/2} \rightarrow 0$.

$$\lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \sigma_{12}(t) = \lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \eta_{12}(t) \cdot \dot{\gamma} = Y_0 \quad [VI.77]$$

where $\eta_{12}(t)$ is equal to Equation VI.59.

$$\lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \sigma_{11}(t) = \lim_{\substack{t \rightarrow \infty \\ E \rightarrow 0}} \chi(t) \cdot E = \sqrt{3} Y_0 \quad [VI.78]$$

where $\chi(t)$ is equal to Equation VI.74. These results imply Y_0 and $\sqrt{3} Y_0$ are identical to the yield stresses experimentally obtained from η_{12} versus σ_{12} and χ versus σ_{11} plot.

The expression of initial yield stress in their formulation is

$$\lim_{t \rightarrow 0} Y(t, II_d^{1/2}) = Y_0 \neq Y_0(II_d^{1/2}) \quad [VI.79]$$

This disagrees with the experimental result shown in Figure VI.21. This value, Y_0 , cannot be determined.

The value of " $f(\phi)$ " for Slibar-Paslay form is not identical to that for the newly proposed yield function, because the steady state or final value of $Y(t, II_d)$ is a function of α , β and $II_d^{1/2}$ in Slibar-Paslay form (see Figure VI.14, p. 199). Substituting the final yield stress

of Slibar-Paslay form (Equation VI.50) into Equation VI.37, we obtain

$$f(\phi) = \frac{\eta(\dot{\gamma}) - [Y_0 - \frac{\dot{\gamma}}{\alpha\beta + \dot{\gamma}} (Y_0 - Y_1)]}{\eta^0(\dot{\gamma})} \quad [\text{VI.80}]$$

This implies $f(\phi)$ cannot be determined without knowing Y_0 , Y_1 , α and β .

The other material constants, α , β and Y_1 , remain as fitting parameters which must be evaluated by fitting η versus $\dot{\gamma}$, $\eta(t)$ versus time, χ versus E , etc., with experimental data. However, we cannot calculate η , χ , etc., for fitting because we do not know the $f(\phi)$ value which also contains fitting parameters α , β and Y_1 . All material constants are summarized in Table IV.5.

Slibar-Paslay's time-deformation rate dependent yield stress function contains too many constants which cannot be determined. Also, the physical meaning of these constants are not clear. Their formulation is not suitable and is not usable practically.

E.1.c Comparison of theory and experimental data for filled systems using newly proposed yield function. In this section, we compare the theoretical predictions and experimental data for each experiment. In Section C.1.c, it was found that material constants $(\tau_0^0; a; G^0) = (5.4; 0.4; 4.8 \times 10^3)$ with the modified Bogue-White model give

Table VI.5

Material Constants for Theory for Filled Systems with
Slibar-Paslay Yield Function, Equation VI.49

Filler	Volume Content ϕ (-)	Average Particle Size d_p (μm)	Gel G_{12} Equation VI.51 ($\text{Pax}10^{-4}$)	Y_0^* Equation VI.77 ($\text{Pax}10^{-5}$)	Y_0 Equation VI.79 (Pa)	$f(\phi)$ Equation VI.80 (-)	Y_1 (Pa)	α (-)	β (sec^{-1})
Uncoated CaCO_3	0.3	17	2.8	Unclear (0.1)	Cannot be determined (inconsistent with experimental results)	Cannot be determined	Fitting Parameter	Fitting Parameter	
		3	3.4	~ 1.5 (1.6)					
		0.5	6.5	10 (9)					
		0.07	18	40 (38)					
Coated CaCO_3	0.3	17	-	Unclear (<0.1)					
		3	-	Unclear (<0.1)					
		0.5	-	Unclear (0.16)					
		0.07	-	Unclear (1.0)					
CB	0.3		6.7	9 (8.8)					
	0.2		3.0	~ 2 (1.3)					

*Values without parentheses are estimated from η versus σ_{12} plot; values with parentheses are estimated from Casson's plot.

the best agreement with experimental data for most experiments including transient shear viscosity experiments. We use the above-mentioned values of τ_0^0 , a and G^0 for filled theory, too. The material constants which are used for theoretical predictions are shown in Table IV.6.

E.1.c.1 Transient shear viscosity. The transient shear viscosity was calculated using Equations VI.51, VI.45 and VI.56. We note that the present time t which appears in Equation IV.56 is not identical to the time in Figures VI.23 to VI.29. The present time zero is the time when elastic deformation ends and viscoelastic thixotropic deformation starts. In the figures, time zero denotes the initiation of deformation. This is summarized in Figure VI.23.

Figures VI.24 to VI.29 show comparisons between theory and experimental data. All material constants used are summarized in Table VI.6.

Figure VI.24 shows the transient viscosity of uncoated CaCO_3 ($d_p = 17 \mu\text{m}$) filled PS compounds. The " α " value was used for calculation. Reasonable agreement was obtained for $\alpha = 1.5$ at low shear rates ($0.04 < \dot{\gamma} < 0.10$). However, there were discrepancies at $\dot{\gamma} = 0.16 \text{ sec}^{-1}$. The theory predicts a slower viscosity decrease after an overshoot, and does not predict viscosity undershoot phenomenon which is observed in experiments.

Table VI.6
Material Constants Used for Theoretical Predictions
with Newly Proposed Yield Function

Filler	Volume Content ϕ (-)	Average Particle Size d_p (μm)	τ_o^o (sec)	a (-)	G^o ($\text{Pa} \times 10^{-3}$)	G_{12} ($\text{Pa} \times 10^{-4}$)	β ($\text{Pa} \cdot \text{sec} \times 10^{-3}$)	γ_f ($\text{Pa} \times 10^{-3}$)	$f(\phi)$ (-)	α (-)
Uncoated CaCO_3	0.3	17	5.4	0.4	4.8	2.8	4.8	0.7	2.5	1.0; 1.5
		3				3.4	6.9	1.6	4.5	1.0; 1.5
		0.5				6.5	9.5	10	4.6	0.2; 0.5
		0.07				18	15	40	4.0	0.2; 0.5
Coated CaCO_3	0.3	17	5.4	0.4	4.8	-	-	0.0	2.5	-
		3				-	-	0.0	2.5	-
		0.5				-	-	0.16	2.7	-
		0.07				-	-	1.0	3.9	-
CB	0.3	0.045	5.4	0.4	4.8	6.7	6.0	9.0	4.4	0.5; 1.0
	0.2					3.0	5.7	1.6	2.4	0.7; 1.0

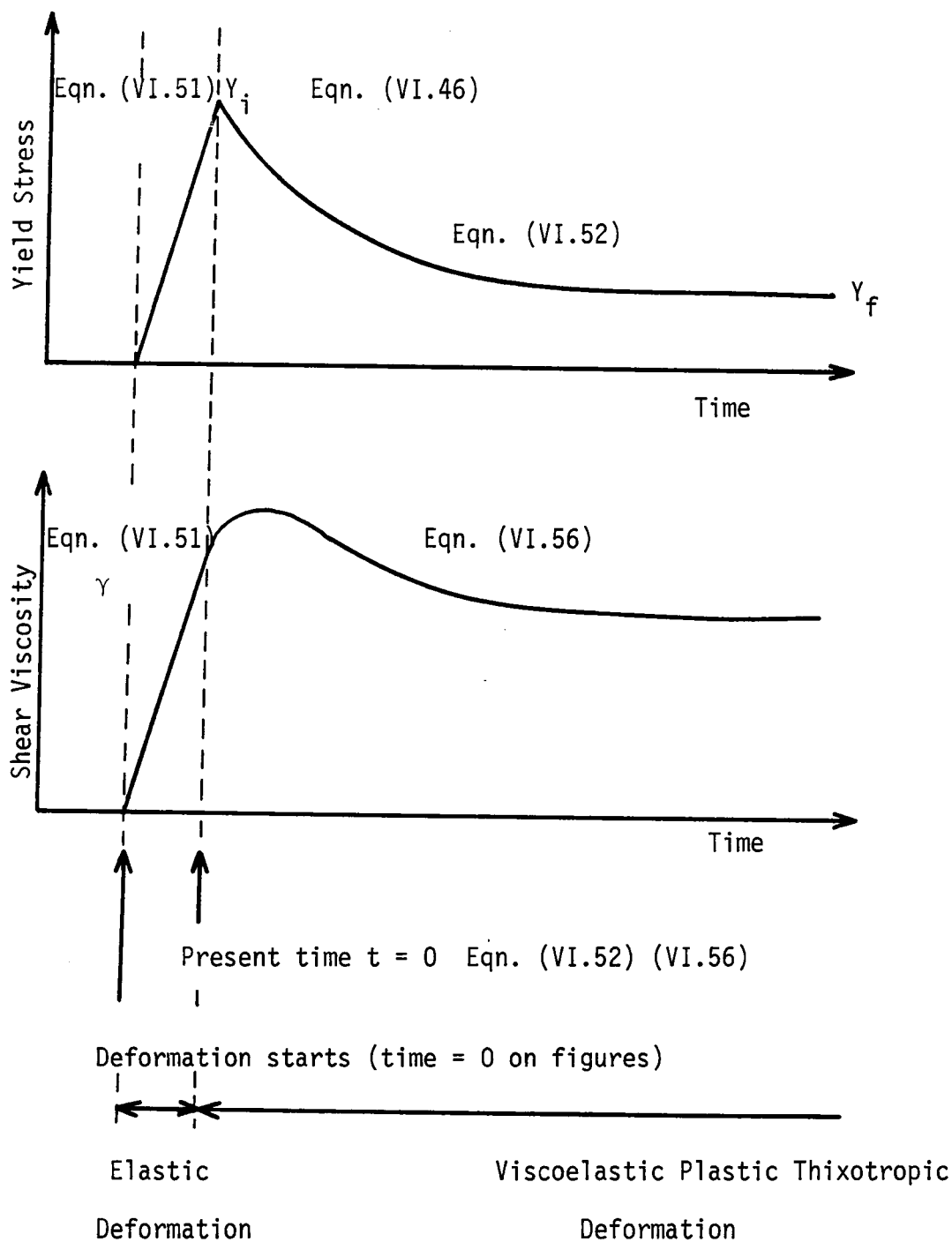


Figure VI.23. Time scales and equations used for theoretical predictions for transient shear viscosity of filled systems.

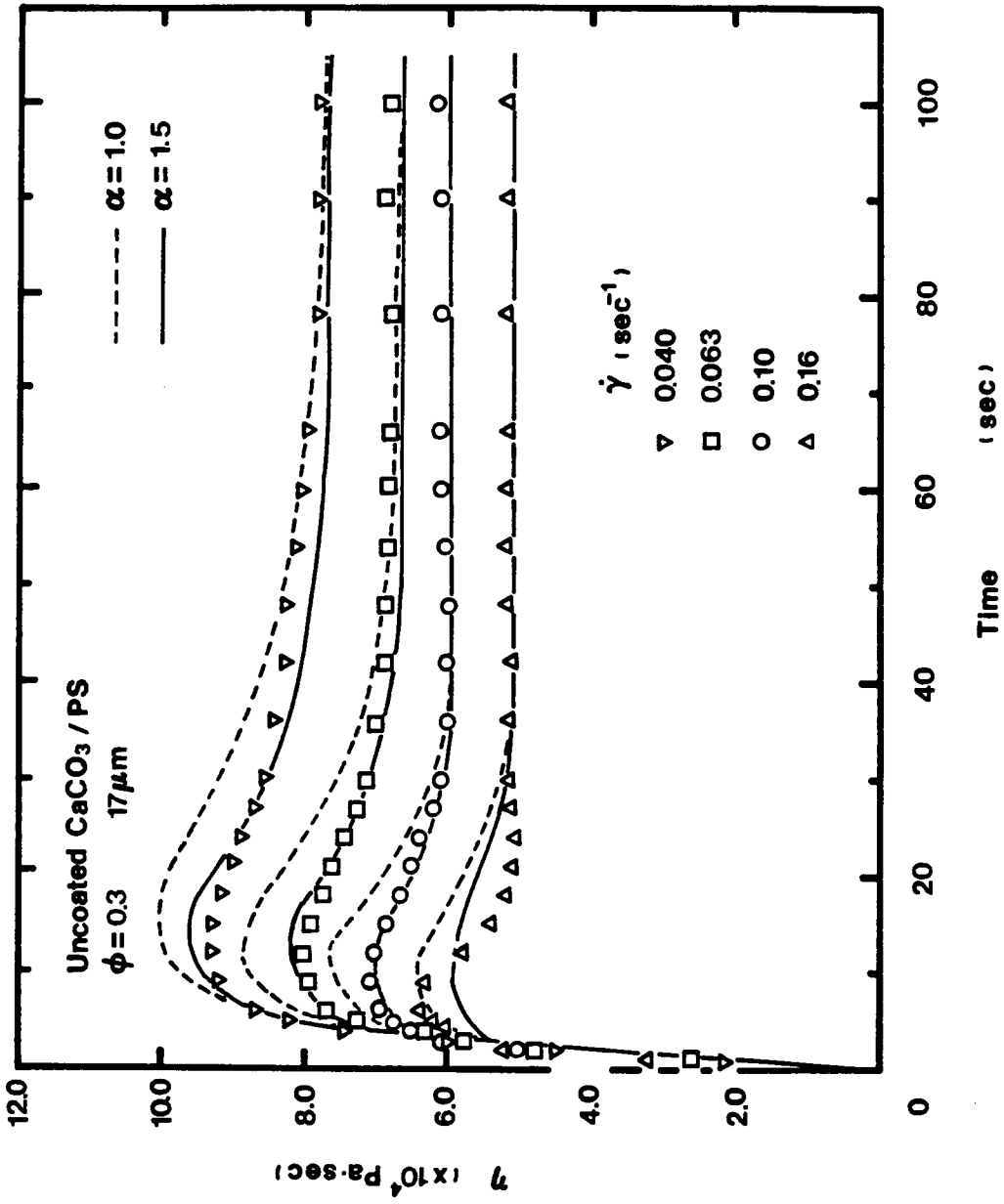


Figure VI.24. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of uncoated CaCO_3 ($d_p = 17 \mu\text{m}$) filled PS.

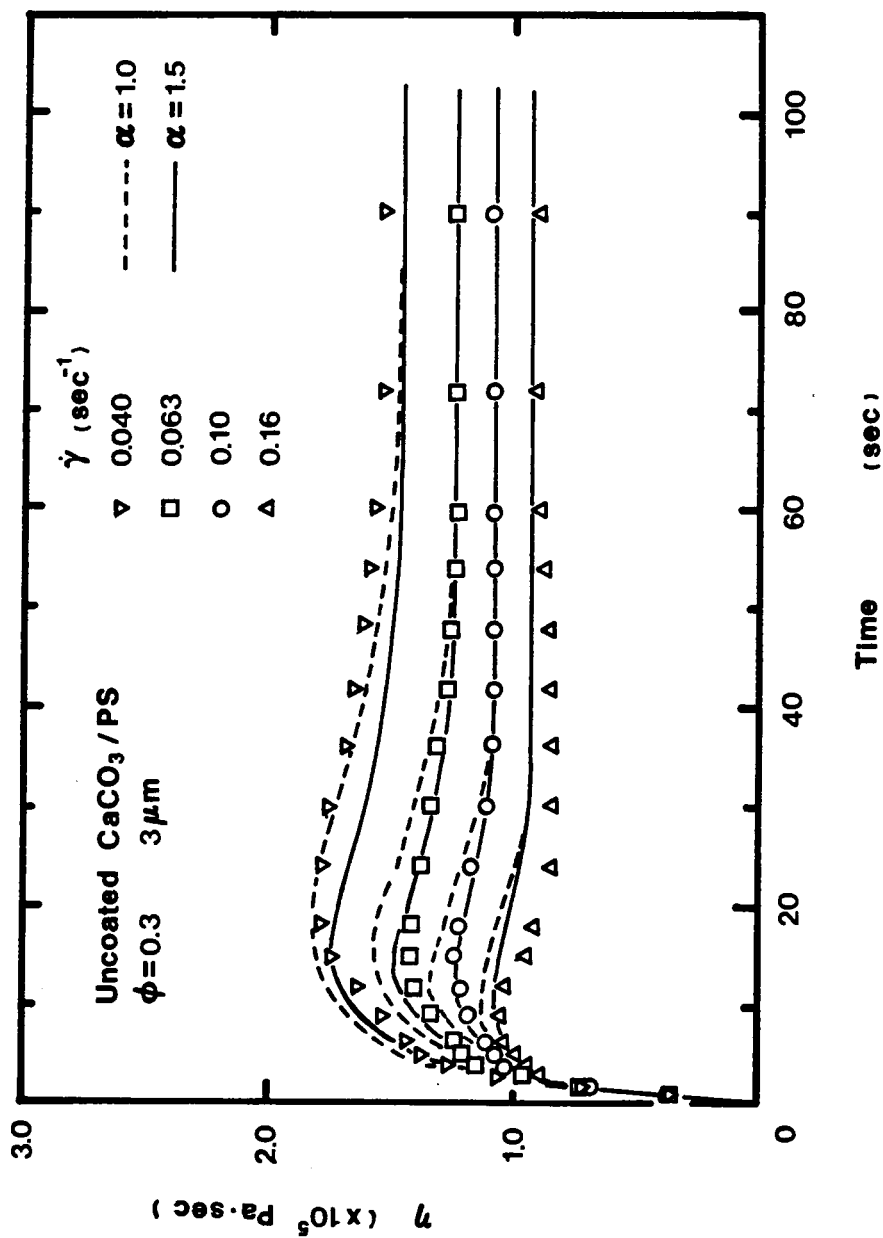


Figure VI.25. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of uncoated CaCO_3 ($d_p = 3\mu\text{m}$) filled PS.

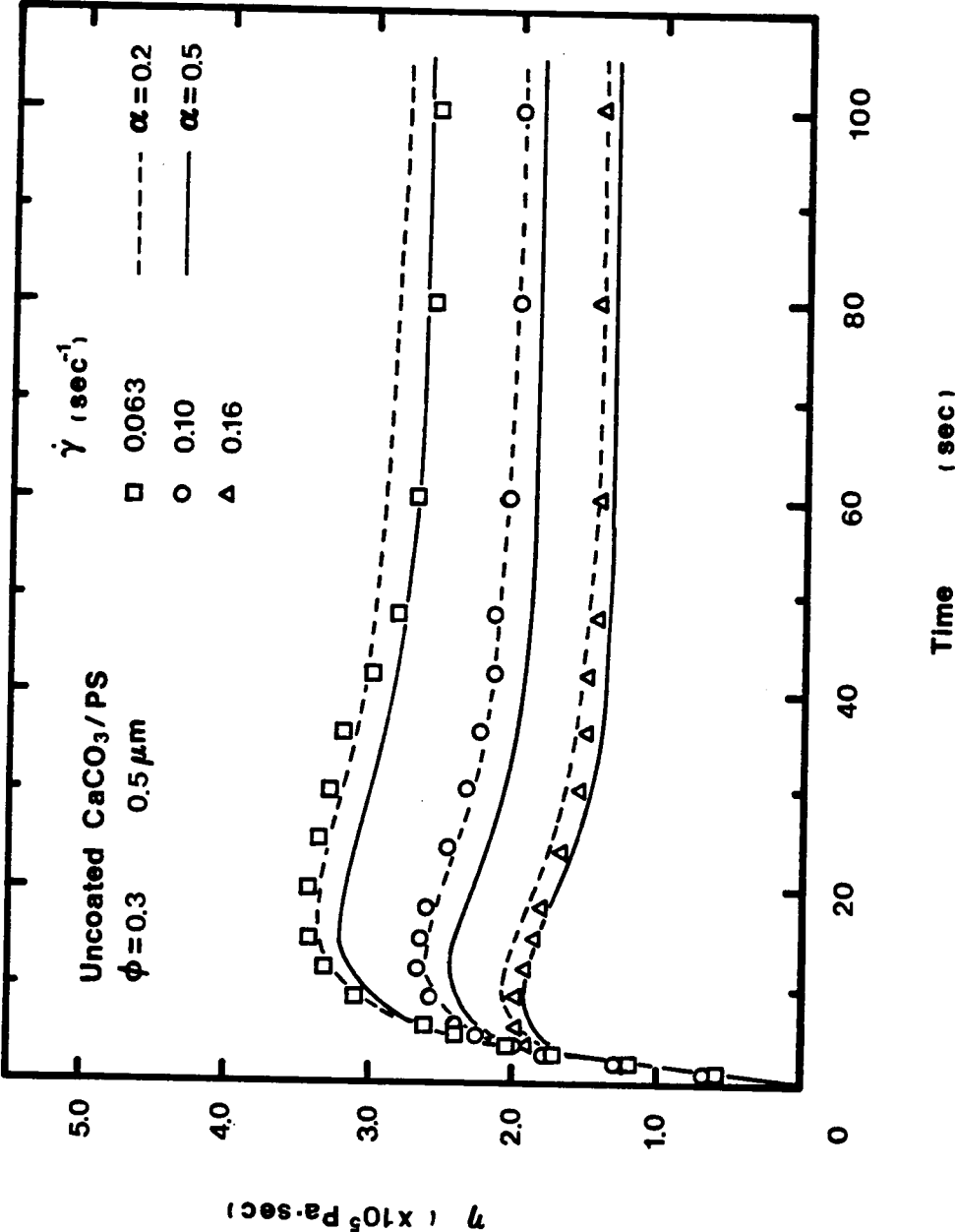


Figure VI.26. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of uncoated CaCO_3 ($d_p = 0.05 \mu\text{m}$) filled PS.

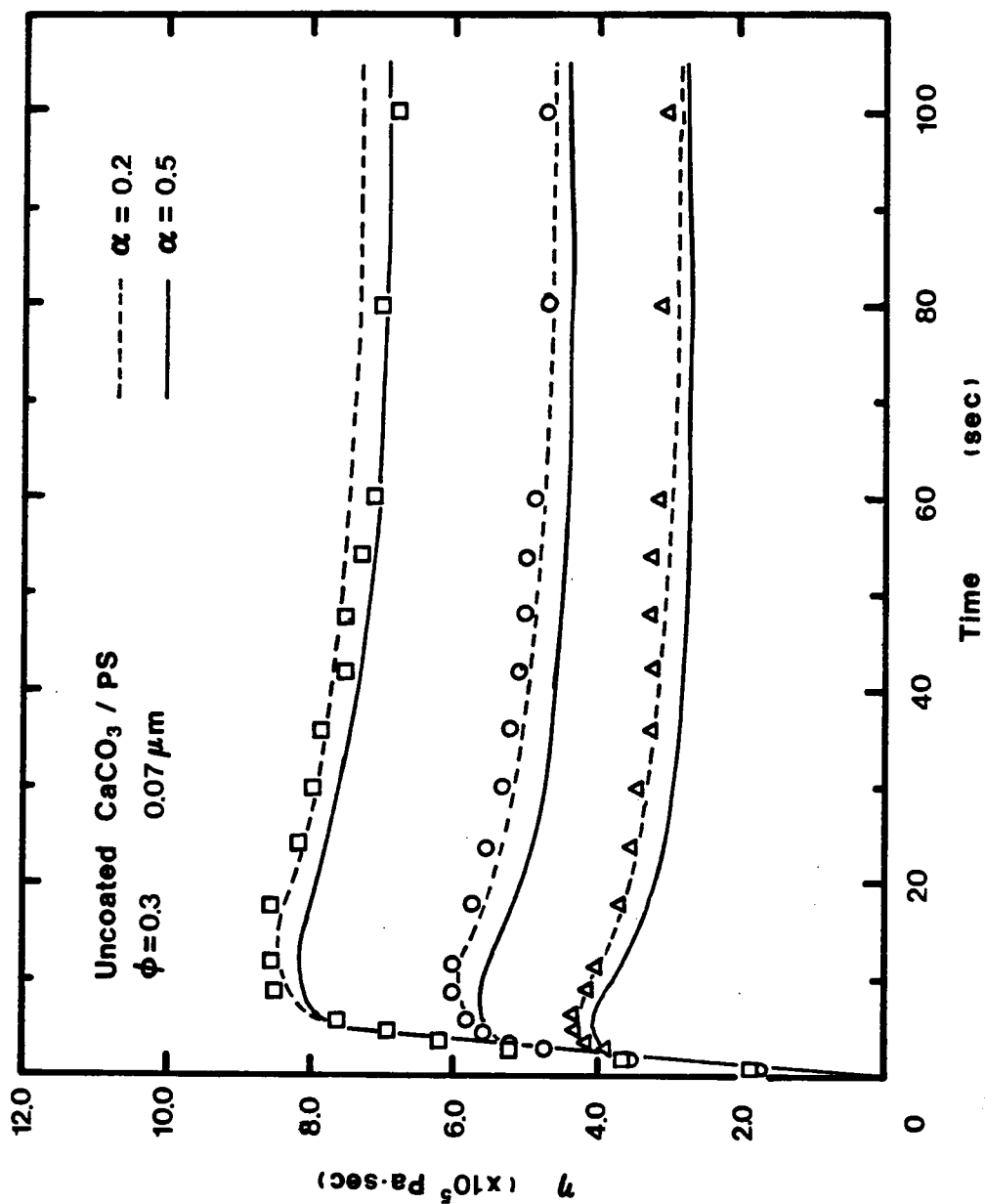


Figure VI.27. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of uncoated CaCO_3 ($d_p = 0.07 \mu\text{m}$) filled PS.

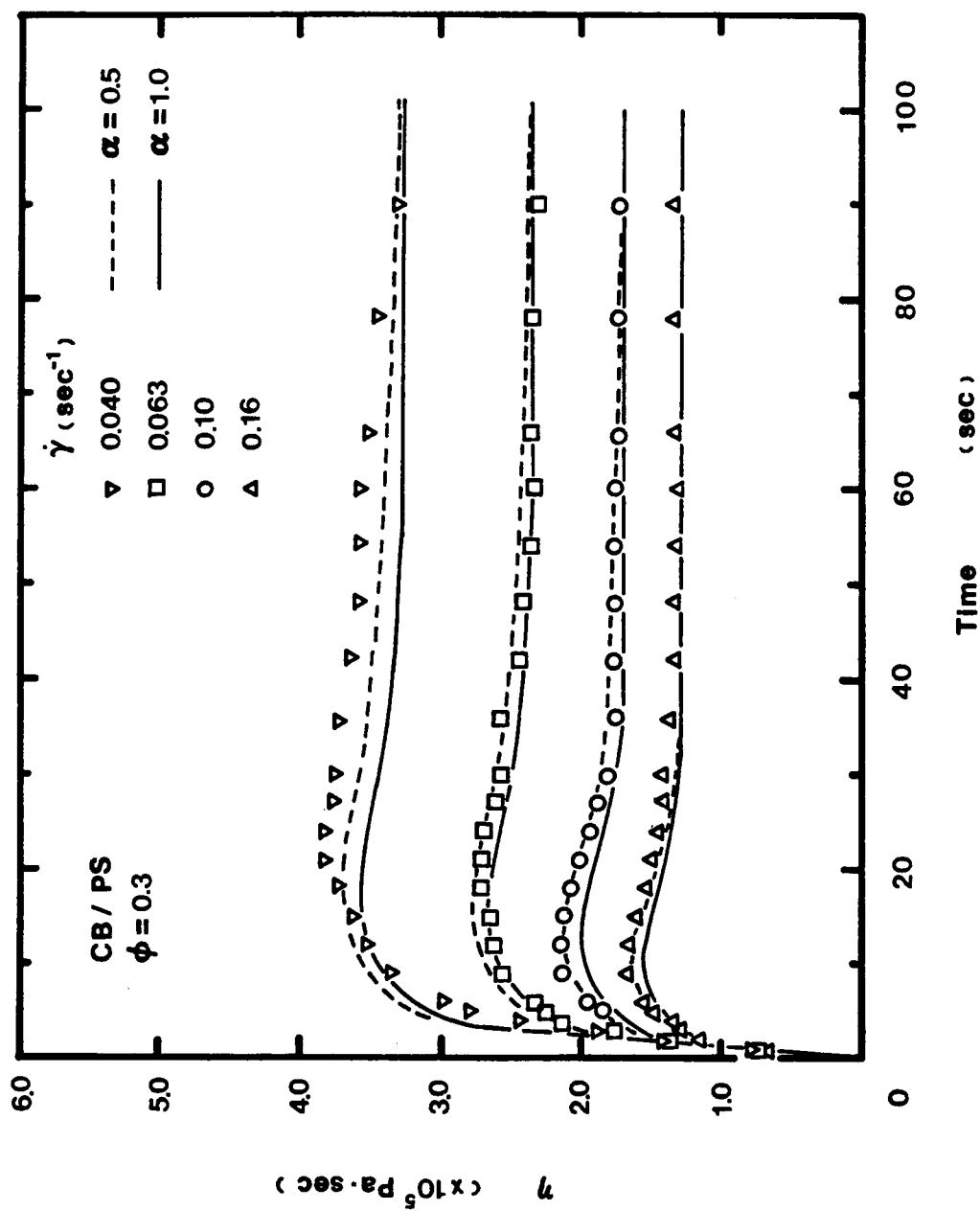


Figure VI.28. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of CB filled PS ($\phi = 0.3$).

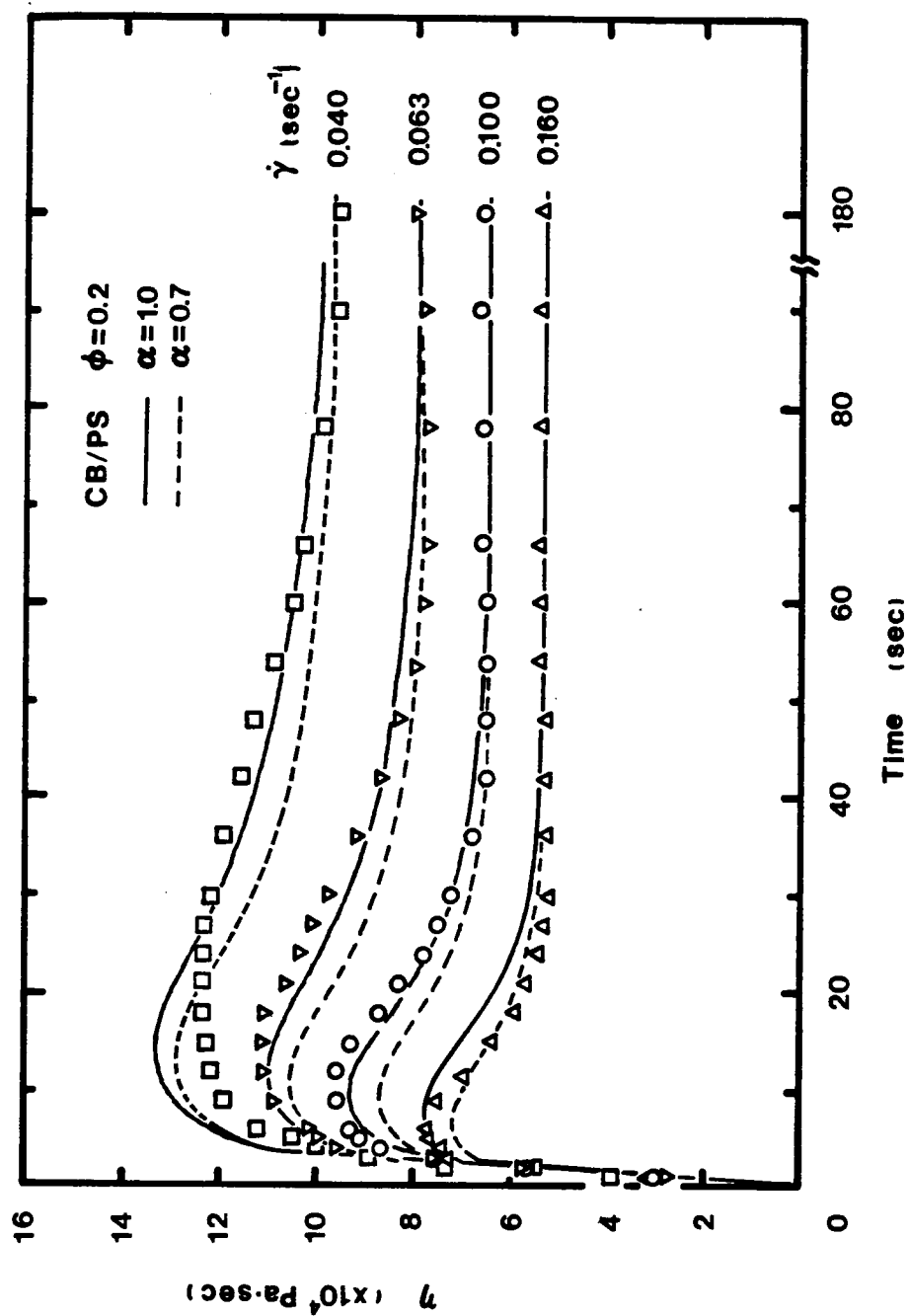


Figure VI.29. Comparison of experimental data with phenomenological theory for plot of transient shear viscosity of CB filled PS ($\phi = 0.2$).

Figure VI.25 shows the case of uncoated CaCO_3 ($d_p = 3 \mu\text{m}$) filled PS compound. The values $\alpha = 1.0$ and 1.5 were tried. At $\dot{\gamma} = 0.04 \text{ sec}^{-1}$, $\alpha = 1.0$ indicates better agreement. $\alpha = 1.5$ is a proper value at $\dot{\gamma} = 0.063$ and 0.10 . The discrepancy was again found at $\dot{\gamma} = 0.16 \text{ sec}^{-1}$ where the viscosity undershoot occurs.

Figure VI.26 represents the case of uncoated CaCO_3 ($d_p = 0.5 \mu\text{m}$) filled PS melt. The smaller α values indicate better fit with experimental data. $\alpha = 0.2$ and 0.5 were used. This compound does not show remarkable viscosity undershoot, and good agreement was obtained at $\dot{\gamma} = 0.16 \text{ sec}^{-1}$. The optimum value of α seems to be between 0.2 and 0.5 .

The comparison for uncoated CaCO_3 ($d_p = 0.07 \mu\text{m}$) filled PS melt was represented in Figure VI.27. $\alpha = 0.2$ or 0.5 again seems the optimum value. the optimum α value may decrease with decreasing average particle size of filler. This suggests the thixotropic yield stress decays more slowly when the particle size is smaller.

Figure VI.28 shows the case of CB filled PS compound ($\phi = 0.3$). $\alpha = 0.5$ and 1.0 were used for predictions. $\alpha = 0.5$ seems an optimum value.

Figure VI.29 represents the comparison for CB filled PS compound ($\phi = 0.2$). α values of 1.0 and 0.7 were used and $\alpha = 1.0$ gives the better agreement with experiments.

Summarizing the above discussion, the optimum value of α may decrease with decreasing particle size of filler, and with increasing volume content of filler. A discrepancy between predicted and experimental data was found when experimental data showed viscosity undershoot.

E.1.c.2 Steady state shear viscosity. The steady state shear viscosity was calculated from Equation VI.61 with the material constants in Table VI.6 which were obtained previously.

Figures VI.30 to VI.32 show a comparison of theory and experimental data in steady state viscosity versus shear rate plot for various compounds. Theoretical predictions show good agreement with experimental data for most cases. Small inconsistencies were found at the very low shear rate region in uncoated CaCO_3 ($d_p = 17, 3 \mu\text{m}$) filled PS compounds. This is probably due to the limited performance of the instrument in the very small shear rate region.

Figures VI.33 and VI.35 show a comparison in steady state viscosity versus steady shear stress plot. Theory predicts the experimental data reasonably well. The discrepancy at the low shear rate region is due to experimental error.

E.1.c.3 First normal stress difference. The first normal stress difference was calculated from Equation VI.58. In Figures VI.36 to VI.38, the solid lines represent the

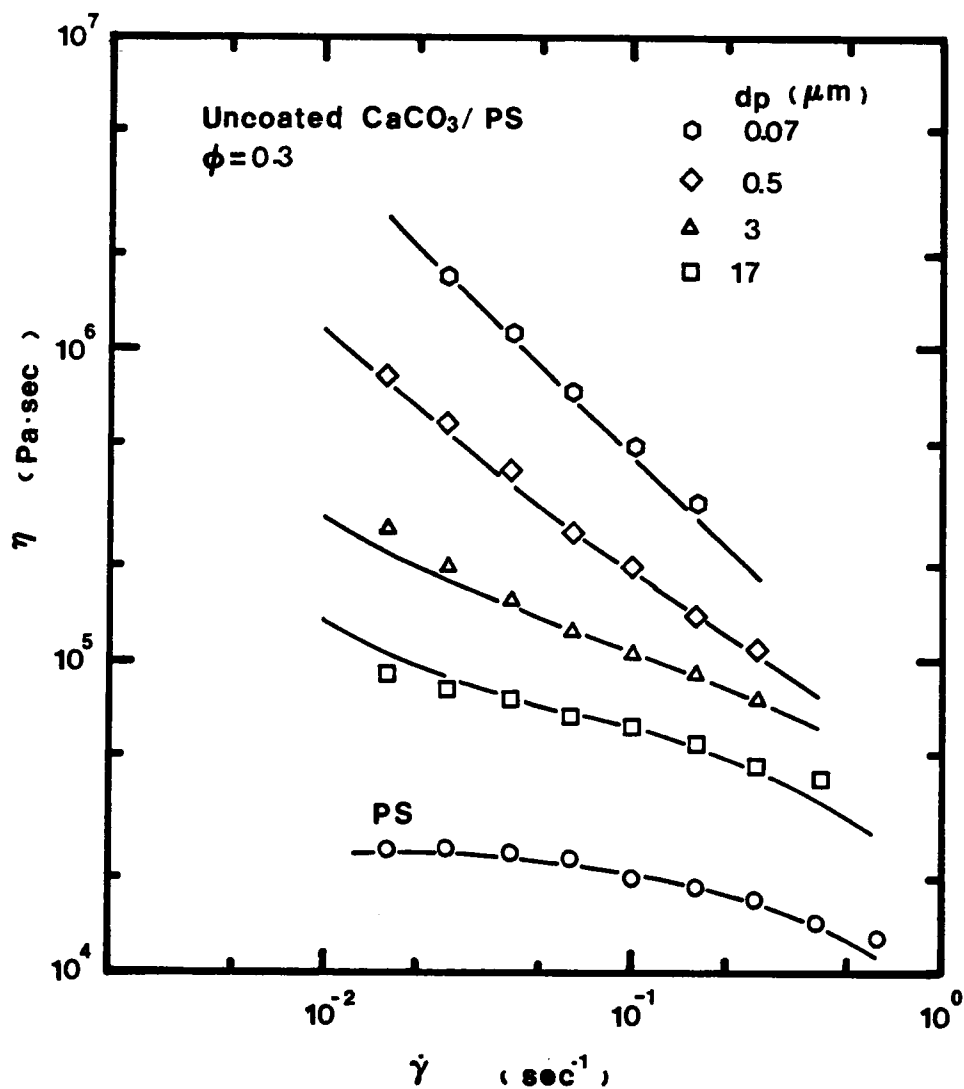


Figure VI.30. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear rate for uncoated CaCO_3 filled PS.

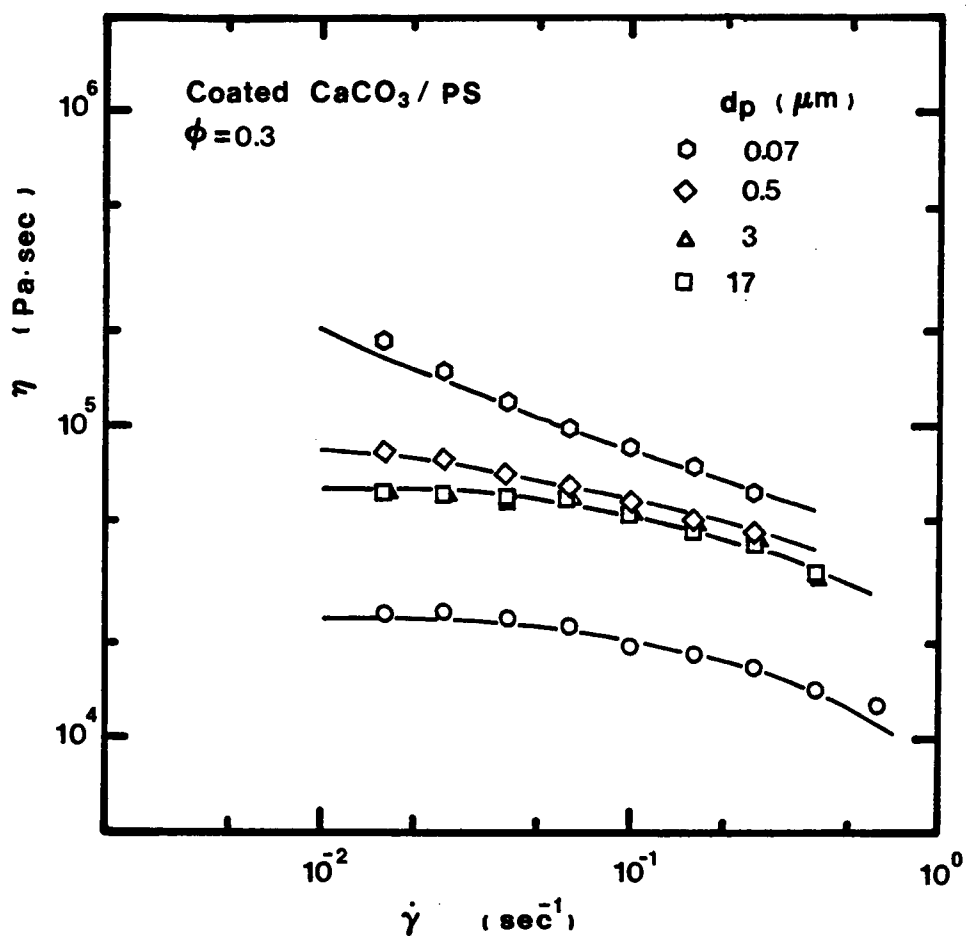


Figure VI.31. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear rate for coated CaCO_3 filled PS.

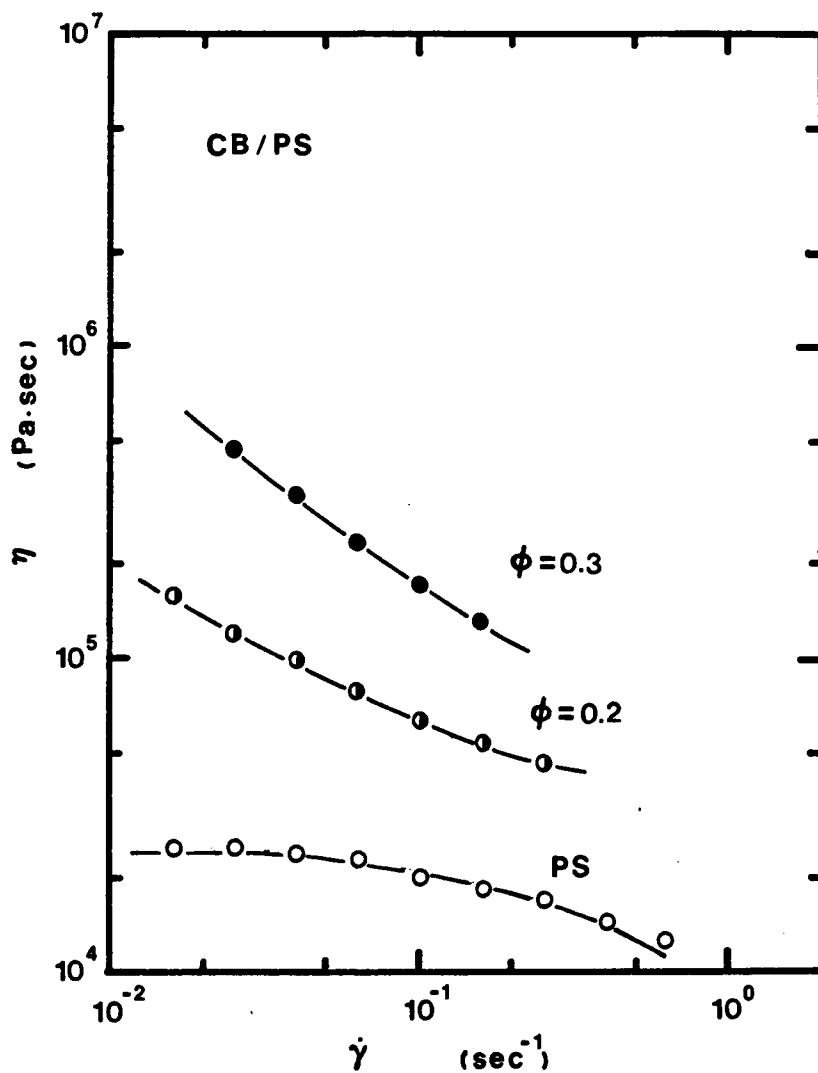


Figure VI.32. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear rate for CB filled PS.

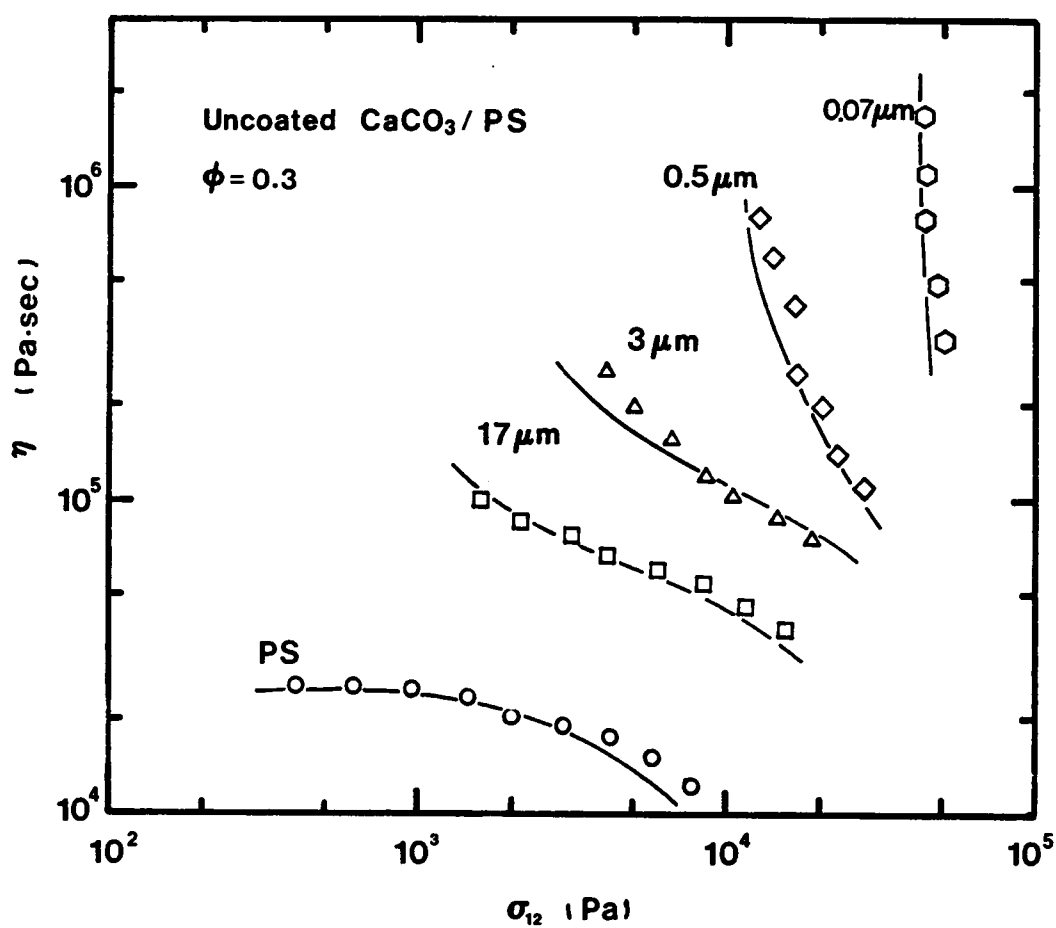


Figure VI.33. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear stress for uncoated CaCO_3 filled PS.

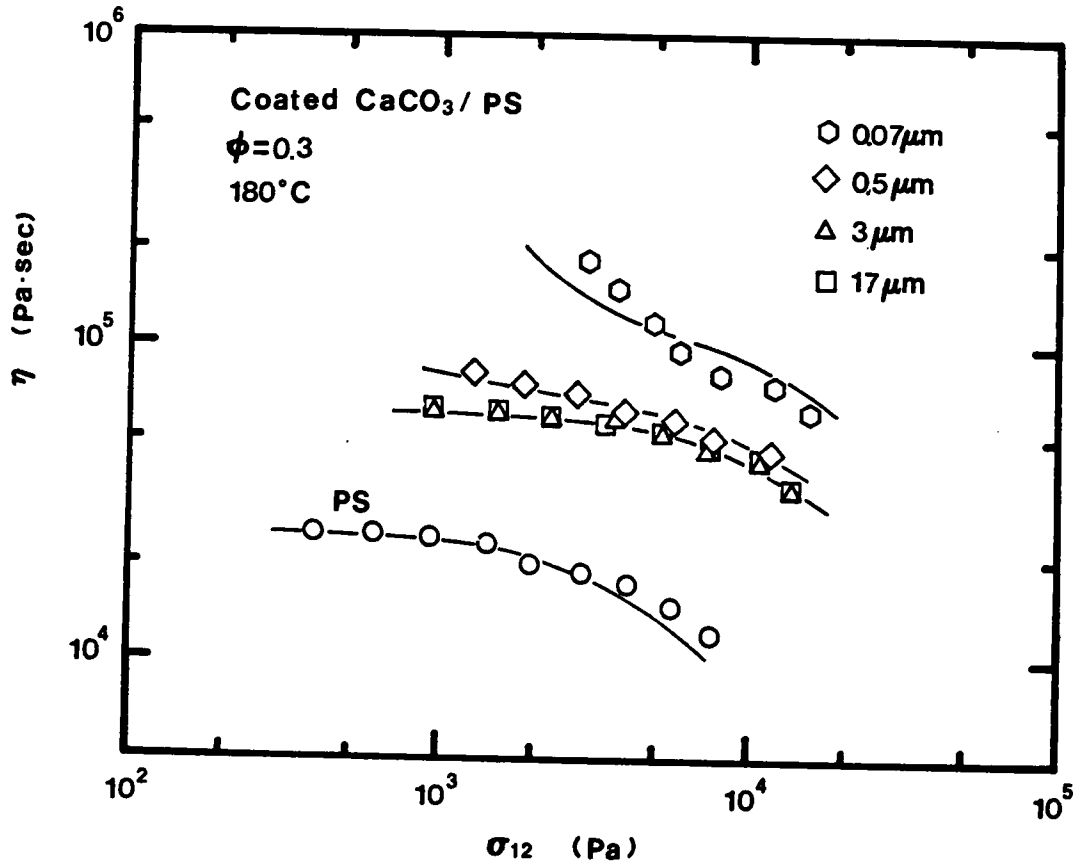


Figure VI.34. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear stress for coated CaCO_3 filled PS.

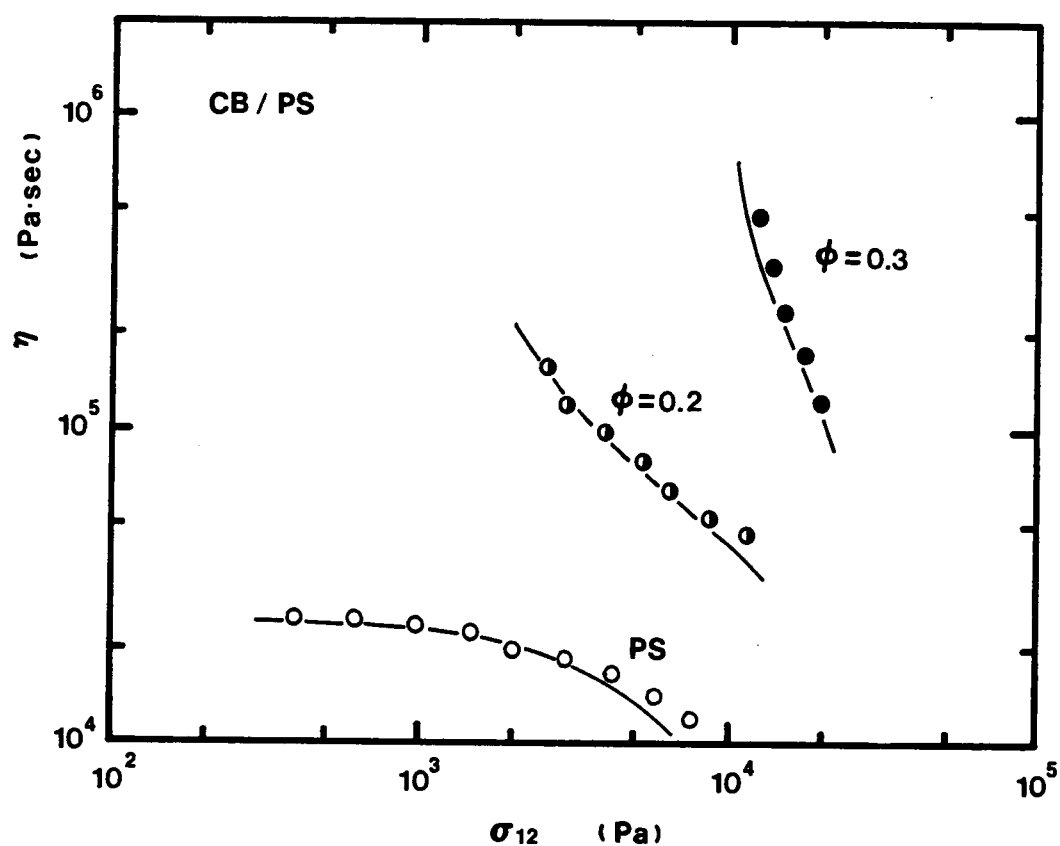


Figure VI.35. Comparison of experimental data with phenomenological theory for plot of steady state shear viscosity versus shear stress for CB filled PS.

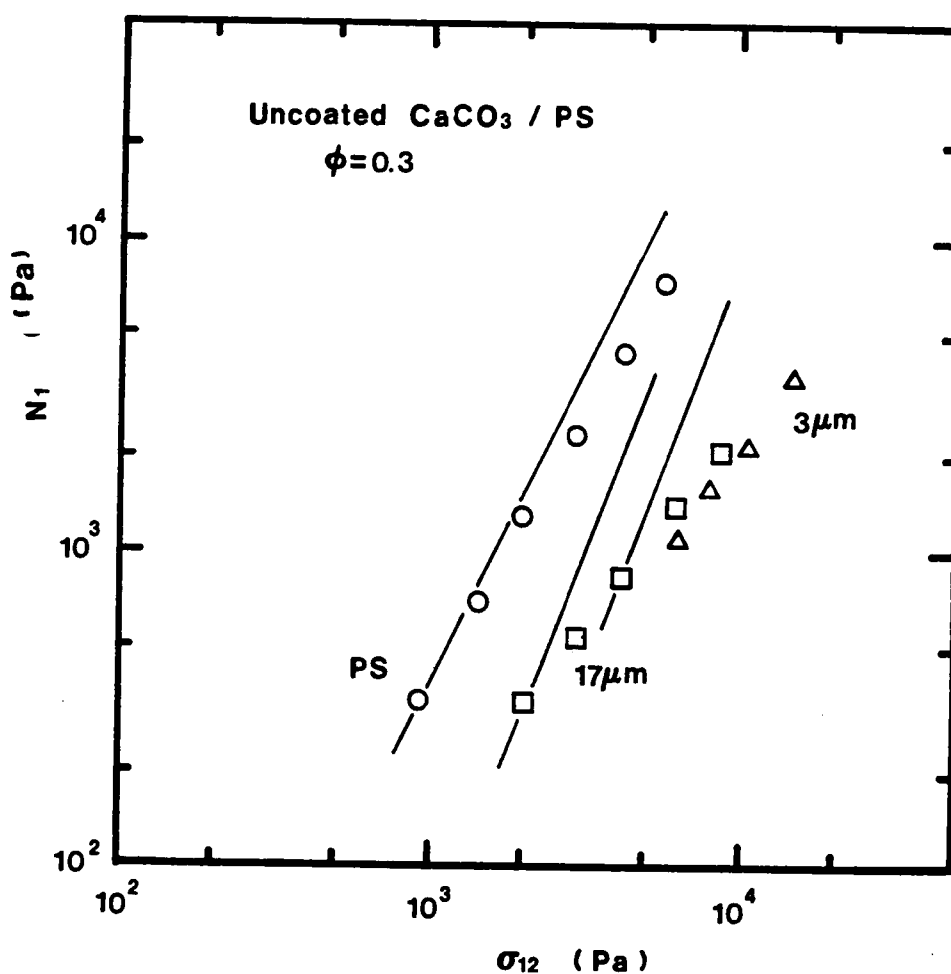


Figure VI.36. Comparison of experimental data with phenomenological theory for plot of first normal stress difference versus shear stress for uncoated CaCO_3 filled PS.

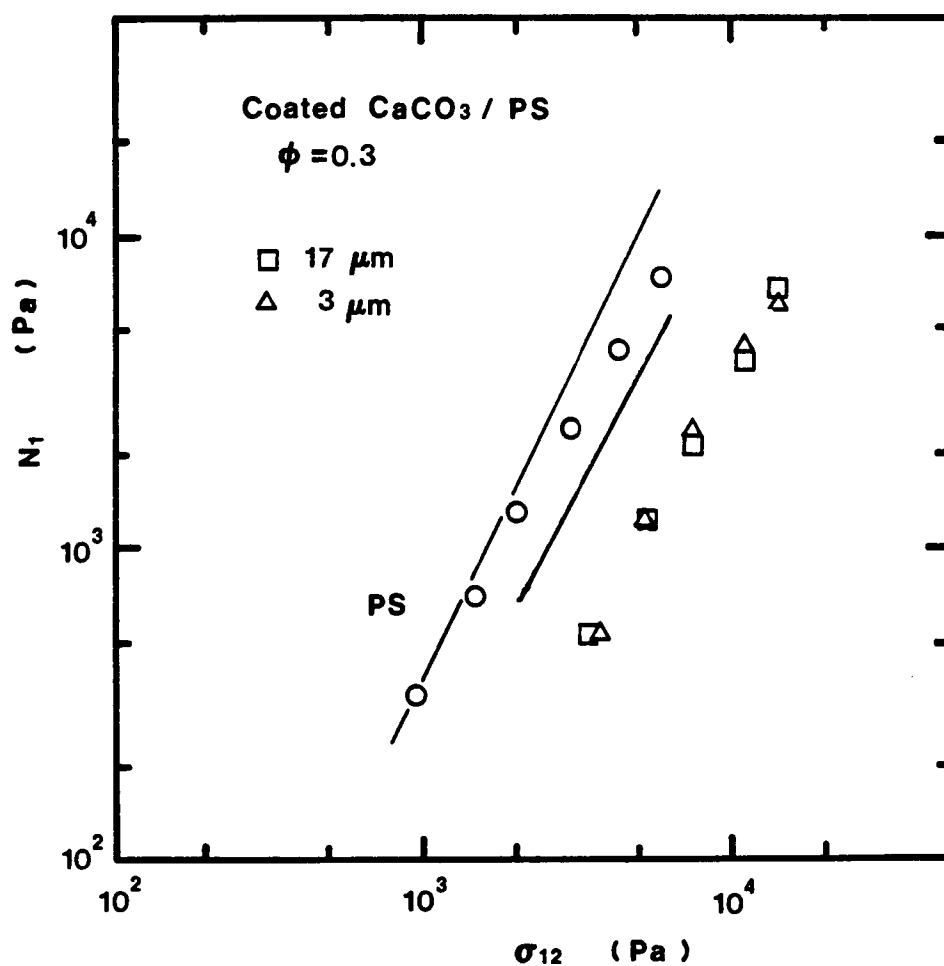


Figure VI.37. Comparison of experimental data with phenomenological theory for plot of first normal stress difference versus shear stress for coated CaCO_3 filled PS.

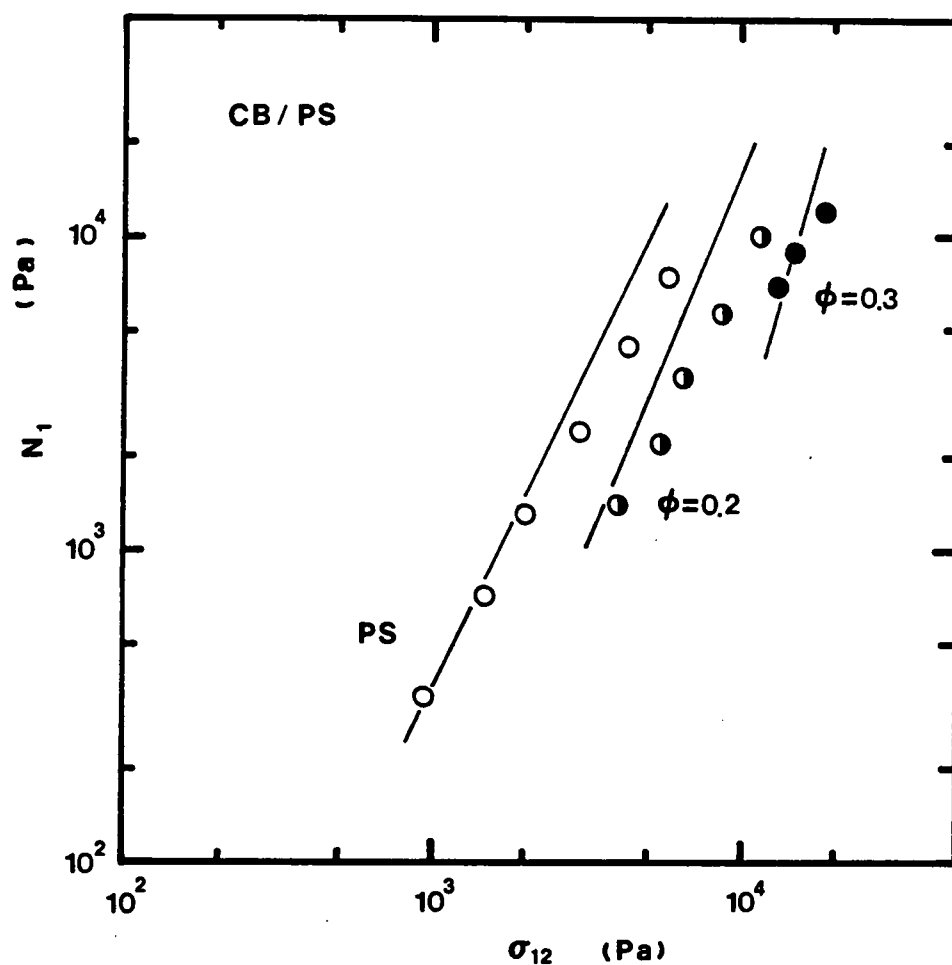


Figure VI.38. Comparison of experimental data with phenomenological theory for plot of first normal stress difference versus shear stress for CB filled PS.

predictions with previously obtained material constants in Table VI.6, and the broken lines are the predictions with a second "a" value, $a = 1.0$.

Figure VI.36 shows the case of uncoated CaCO_3 filled PS compounds. Theoretical predictions with both $a = 0.4$ (solid lines) and $a = 1.0$ (broken lines) agree reasonably well at the low shear stress region. Disagreement is, however, found at the high shear stress region for both $a = 0.4$ and $a = 1.0$. The plot of N_1 versus σ_{12} seems not sensitive to α value.

Figure VI.38 shows the case of CB filled PS melts. Reasonable agreement was obtained at the low shear stress region, but some discrepancy was found at the high shear stress region for both $a = 0.4$ and 1.0 .

E.1.c.4 Steady state elongational viscosity. The steady state elongational viscosity was calculated with Equation VI.71. The previously obtained material constants shown in Table VI.6 were used.

Figures VI.39 to VI.41 represent χ versus E plots for various compounds. Good agreement is obtained for most compounds except in the large elongational rate region. Some inconsistency was found in the coated CaCO_3 filled PS compounds. This is probably due to the experimental difficulty in systems which have low elongational viscosities.

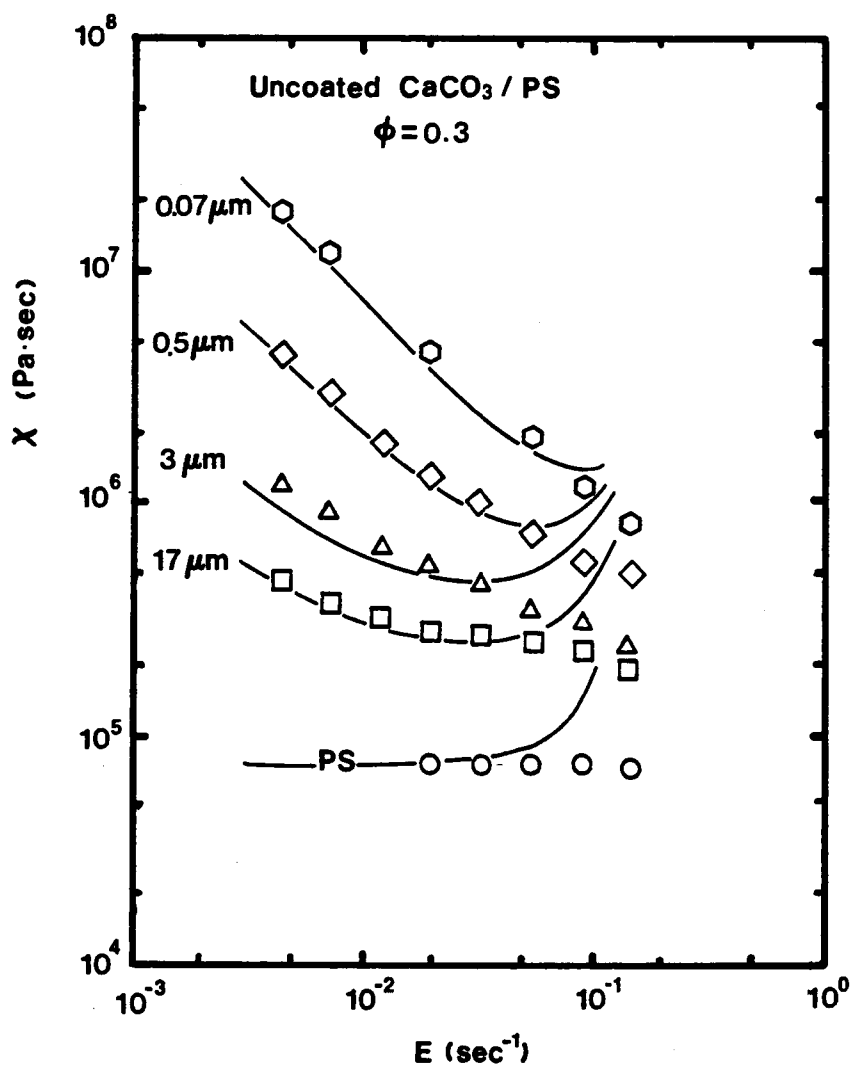


Figure VI.39. Comparison of experimental data with phenomenological theory for plot of elongational viscosity versus elongational rate for uncoated CaCO_3 filled PS.

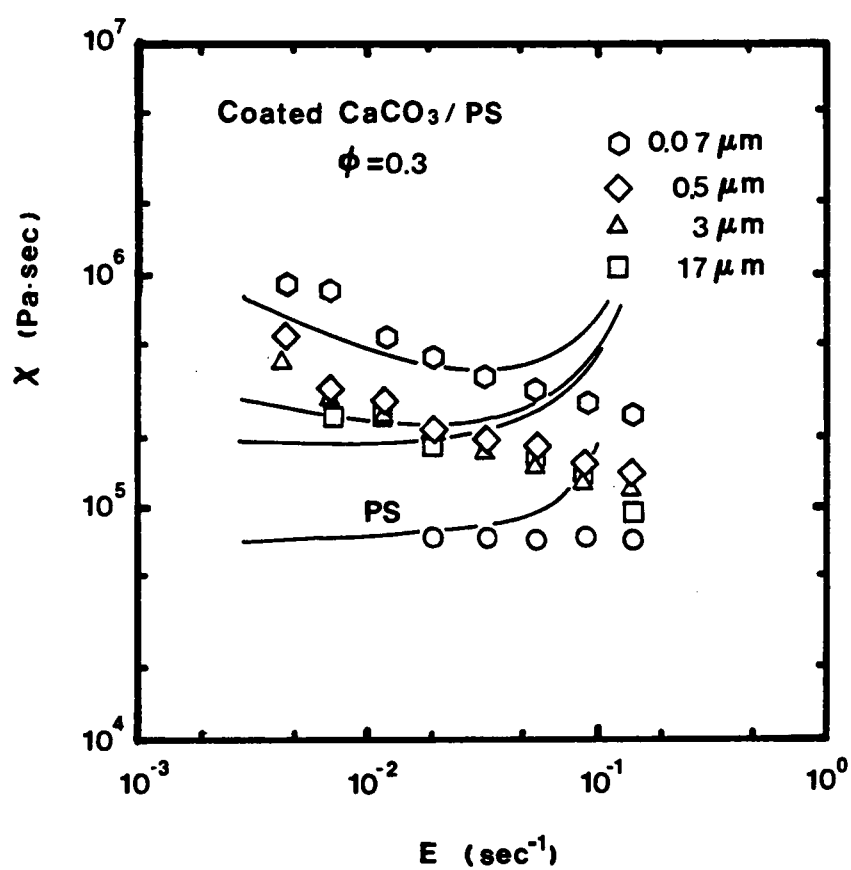


Figure VI.40. Comparison experimental data with phenomenological theory for plot of elongational viscosity versus elongational rate for coated CaCO_3 filled PS.

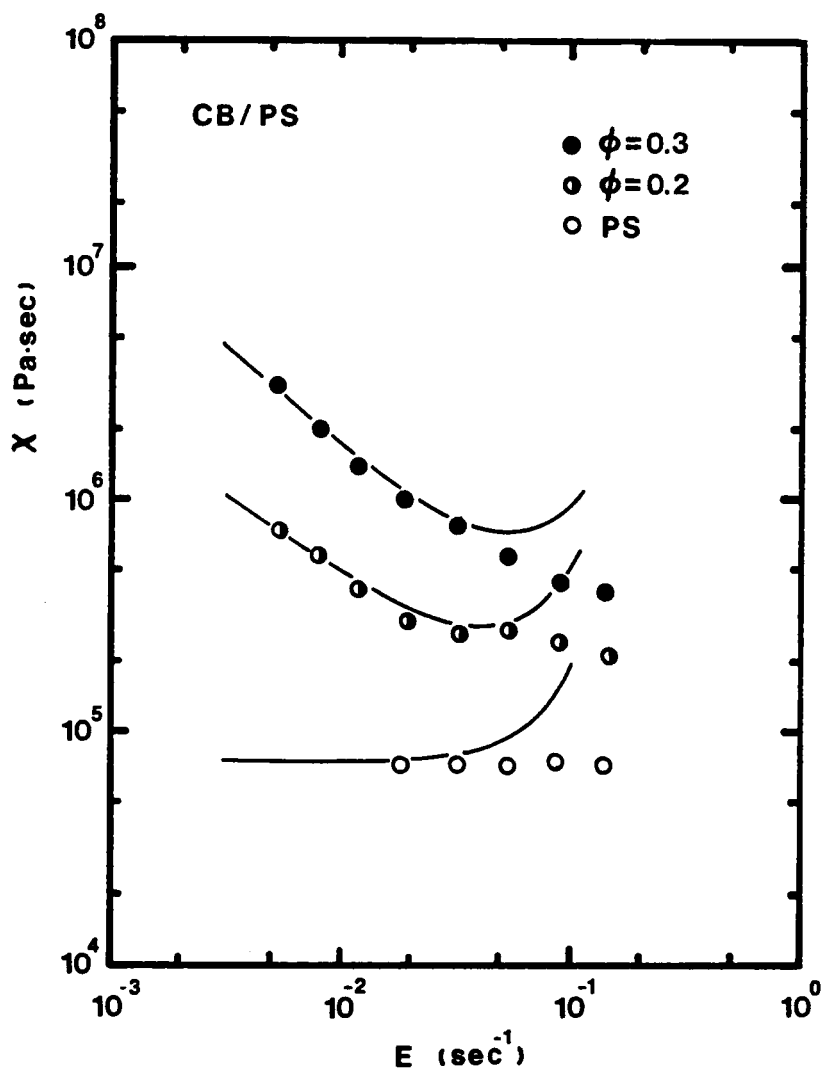


Figure VI.41. Comparison of experimental data with phenomenological theory for plot of elongational viscosity versus elongational rate for CB filled PS.

Figures VI.42 to VI.44 represent χ versus σ_{11} plot for various compounds. Reasonable agreement was obtained for most compounds except coated CaCO_3/PS systems again.

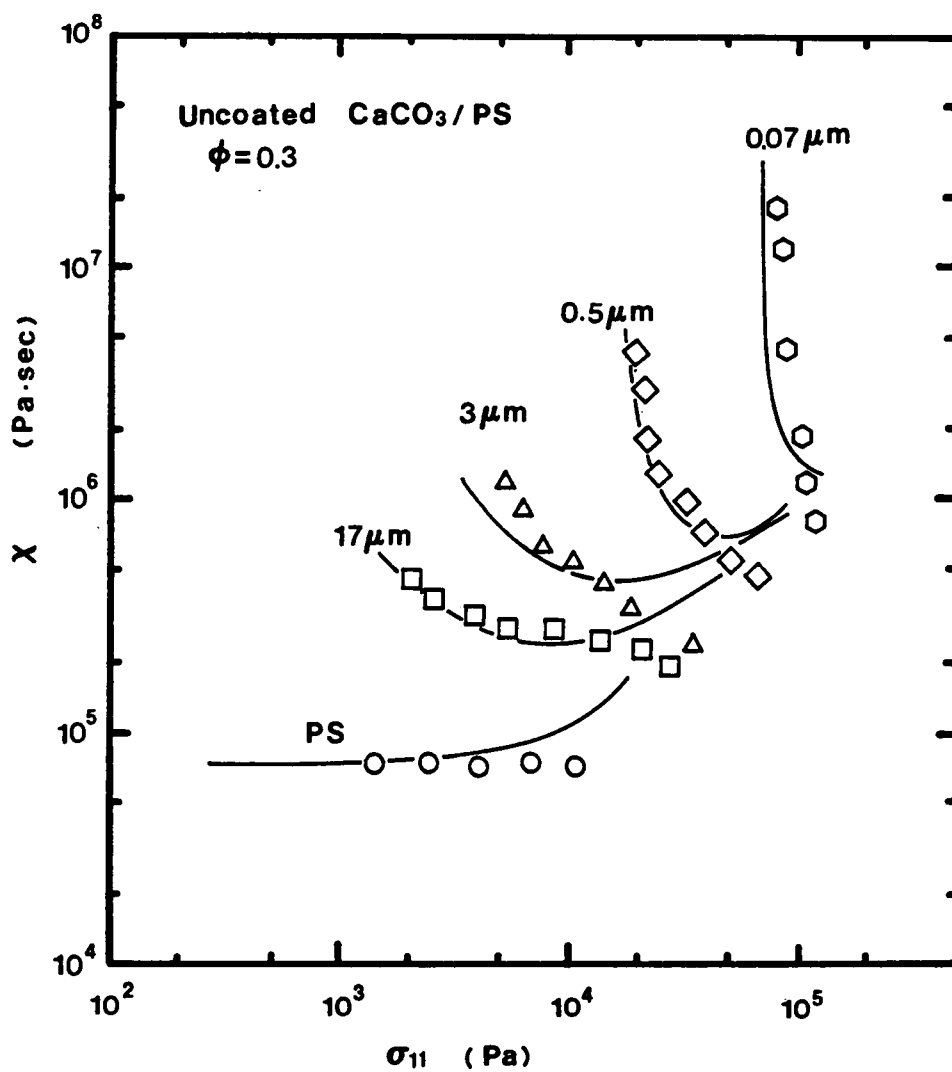


Figure VI.42. Comparison of experimental data with phenomenological theory for plot of elongational viscosity versus tensile stress for uncoated CaCO_3 filled PS.

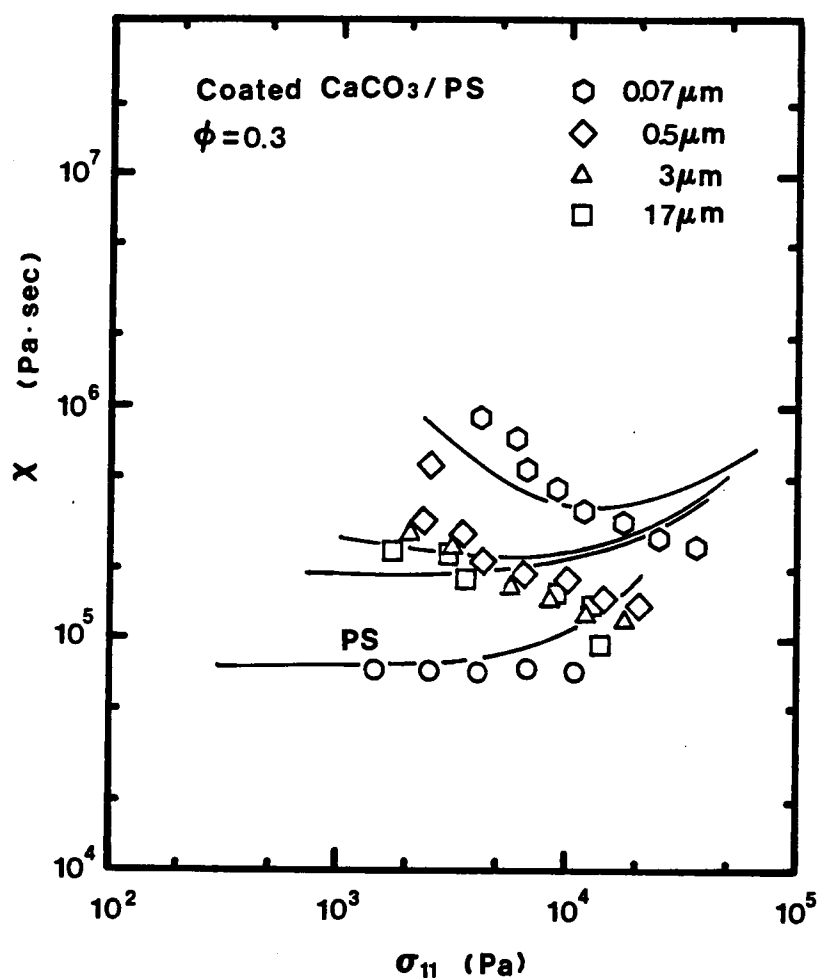


Figure VI.43. Comparison of experimental data with phenomenological theory for plot of elongational viscosity versus tensile stress for coated CaCO_3 filled PS.

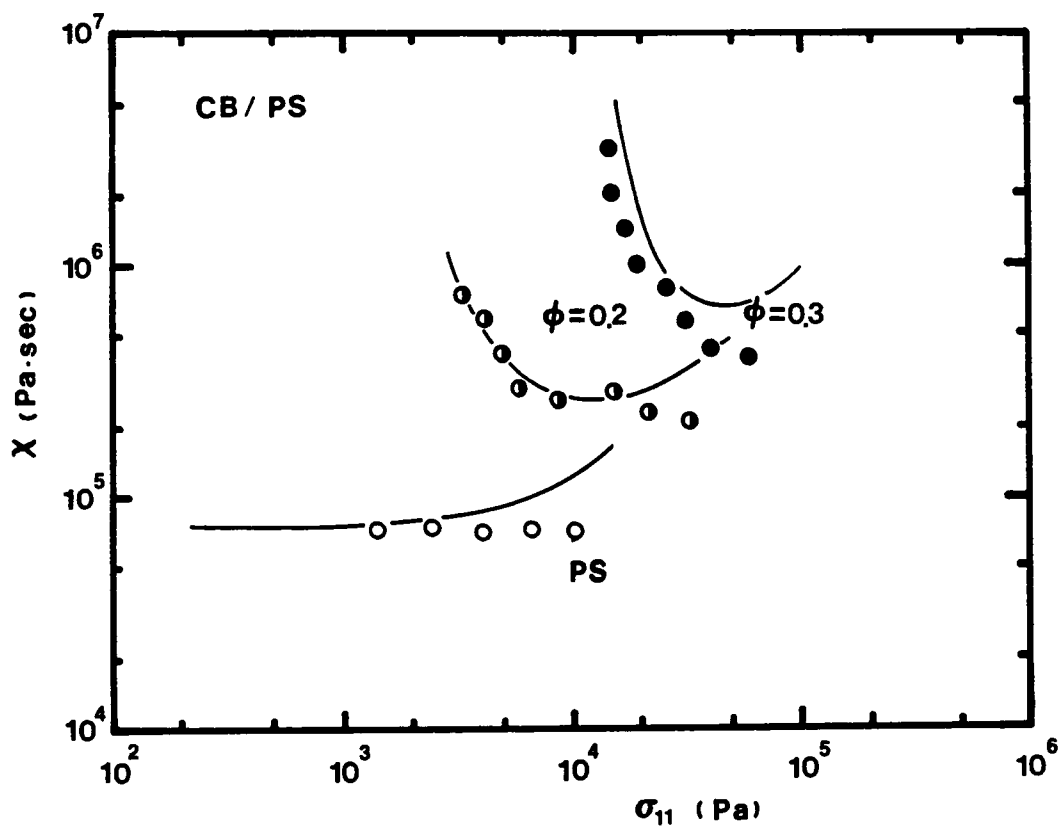


Figure VI.44. Comparison of experimental data with phenomenological theory for plot of elongational viscosity versus tensile stress for CB filled PS.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The rheological behavior of small rigid particle filled polystyrene melts were studied in both steady shear and elongational flow. In these experiments, the shear viscosity, the first normal stress difference, and the elongational viscosity in both transient and steady states, and elongation to break were measured.

The main conclusions obtained in the experimental studies of filled systems were as follows:

- (1) The addition of filler shows an increased stress or viscosity overshoot phenomenon in a transient state. Stearic acid surface treatment is observed to reduce the overshoot phenomenon.
- (2) In complex shear history experiments, the viscosity overshoot grows during the intervening period. The longer the intervening period, the more the recovery of the overshoot.
- (3) The shear viscosity increases with decreasing average particle size of filler and increasing loading level. The surface treatment of the CaCO_3 decreases the shear viscosity.

- (4) Highly filled systems do not possess a Newtonian region in shear flow, and exhibit yield stresses. The yield stress increases with decreasing average particle size and increasing loading level. Surface coating of calcium carbonate particles decreases the yield stress drastically for any particle size.
- (5) The steady state elongational viscosity increases with decreasing particle size and increasing loading level. Surface treatment of calcium carbonate particles decreases the elongational viscosity.
- (6) The yield stress in elongational flow increases with decreasing particle size and increasing loading level of filler. The surface treatment of calcium carbonate particles decreases the yield stress.
- (7) The first normal stress difference at constant shear stress decreases with decreasing particle size and increasing loading level. Surface treatment was found to slightly increase the first normal stress difference.
- (8) The elongation to break in elongational flow decreases with decreasing particle size and increasing loading level of filler. Surface treatment increases elongation to break especially when the particle size is relatively small.
- (9) A phenomenological theory of plastic viscoelastic fluids with a time-deformation rate dependent von Mises yield function agrees reasonably with experimental data.

B. Recommendations

The following studies on rheological properties are recommended for future investigators:

- (1) It is desirable to determine the suspension micro-mechanism of shear stress or viscosity overshoot in transient states including the start-up of flow and during sequential steps in complex shear history experiments.
- (2) An understanding of the basis of normal stress measurement in particle filled systems is needed. A theory including sample insertion is needed.
- (3) Better phenomenological theories are required which can describe the rheological characteristics appearing in complex shear history experiments. Such a theory should be useful to understand the phenomena of (2) above.

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VITA

Yoshiyuki Suetsugu (末次義幸) was born in Ube-city, Japan on September 19, 1956, as the oldest son of Mr. and Mrs. Yoshinori Suetsugu. After completing his basic education, he was admitted to Kyushu University in April 1975. He studied Nuclear Engineering and received a Bachelor of Science degree in March 1979. Then, he entered The University of Tennessee, Knoxville, in September 1979. After getting a degree of Master of Science, he will continue his studies for a Ph.D. at The University of Tennessee. Good luck!