

Modeling Linear Viscoelastic Behavior with a Truncated Relaxation Time Spectrum

J. K. JACKSON, G. GARCIA-FRANCO, AND H. H. WINTER

University of Massachusetts at Amherst
Department of Chemical Engineering
Amherst, MA 01002, U.S.A.

1. INTRODUCTION AND BACKGROUND

It is desirable to relate the molecular weight distribution and branching characteristics of commercial high density polyethylene (HDPE) to viscoelasticity and processing behavior. A barrier to this goal is the limited rheological experimental window, which frequently lacks terminal zone or glass transition information. To compound the problem, many of these materials are characterized by time-temperature shift factors of approximately unity. This incomplete linear viscoelastic picture prevents accurate calculation of zero shear viscosity, which is of interest for parison stability, or the viscosities at high shear rates seen in processing.

To propose a reasonable extrapolation it is necessary to be familiar with the methods used to obtain discrete and continuous relaxation time spectra. It is well known that the relaxation behavior of a polymer can be expressed as a summation of discrete Maxwell modes such that

$$G(t) = \sum_{i=1}^N g_i e^{-t/\lambda_i} \quad [t_{\min} < t < t_{\max}] \quad (1)$$

Several methods for obtaining the set of g_i and λ_i have been discussed by Orbey and Dealy [1]. The parsimonious model, developed by Baumgaertel and Winter, will be used in this study [2]. This method calculates the discrete relaxation spectrum from the dynamic moduli. The moduli are defined in terms of the discrete spectrum where

$$G' = \sum_{i=1}^N g_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \quad [\omega_{\min} < \omega < \omega_{\max}] \quad (2)$$

and

$$G'' = \sum_{i=1}^N g_i \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2} \quad [\omega_{\min} < \omega < \omega_{\max}] \quad (3)$$

The continuous relaxation spectrum, $H(\lambda)$, is normally defined in relation to $G(t)$ such that

$$G(t) = \int_0^{\infty} \frac{H(\lambda)}{\lambda} e^{-t/\lambda} d\lambda \quad (4)$$

Equations 2-4 and several numerical approximations of $H(\lambda)$ are presented in detail by Ferry [3]. Studies on the effectiveness of these approximations, which rely on viscoelastic data as input, have shown them to be quite sensitive to

small fluctuations in the input data [4-5]. Recently, it was shown [6] that this problem is avoided when the continuous spectrum, $H(\lambda)$, is calculated from the discrete relaxation spectrum using the relation

$$H(\lambda_i) = \frac{g_i}{\ln a_i} \quad (5)$$

where a_i is a local spacing that can be approximated by

$$a_i = \sqrt{\frac{\lambda_{i+1}}{\lambda_{i-1}}} \quad (6)$$

The discrete relaxation spectrum obtained fully describes the data in the experimental window, but the continuous spectrum is an approximation subject to error at large spacing values, a_i . The end values of the continuous spectrum also cannot be calculated accurately because Equation 6 cannot be evaluated.

We begin our analysis of this problem by quantifying the effects of modeling flow behavior with a truncated data set. This allows us to define the scope of the problem and provides valuable information regarding a reasonable extrapolation. We then combine information from the rheology (truncated dynamic data) and molecular weight information (GPC) to propose an extrapolation.

2. EXPERIMENTAL

The truncation analysis and extrapolation technique were applied to three commercial polyethylenes obtained from Exxon Chemical Corporation and a polycarbonate acquired from General Electric. The material characteristics for each of these samples are listed in Table 1. The molecular weight information was obtained via GPC analysis. The latter two columns in Table 1 represent parameters used in calculating $H(\lambda)$ and will be described later in this work.

Dynamic mechanical testing of the HDPE samples was performed on a Rheometrics RDS-7700 spectrometer. Parallel plate geometry with plate diameter of 25 millimeters was used. Strain levels were maintained below 20%, the linear viscoelastic limit. The reference temperature for all HDPE measurements and calculations is 150° C. Tangent delta for PE-1, PE-2, and PE-3 are shown in Figure 1.

The commercial polycarbonate (PC-0) obtained from General Electric was used for the truncation study and initial extrapolation attempt. It was chosen for its polydispersity and wide experimental window. The dynamic data for PC-0 has been previously reported [6]. Tangent delta for PC-0 is displayed in Figure 2. All polycarbonate data and calculations correspond to a reference temperature of 190° C. The vertical lines labeled 1-5 in Figure 2 represent

successive truncation points corresponding to PC-1, PC-2, PC-3, PC-4, and PC-5 respectively.

3. ANALYSIS

The results are presented in three categories: the effect of truncating the polycarbonate on subsequent modeling, the extrapolation of truncated polycarbonates, and the extrapolation of the commercial polyethylenes.

3.1 TRUNCATION EFFECTS ON MODELING

While progress has been made in determining discrete relaxation spectra from experimental data, the limitations to the use of such spectra in modeling are not well understood. To study this problem, we chose a dynamic data set for which ten decades of frequency were experimentally accessible. This dynamic data set (PC-0) was systematically truncated and discrete spectra were calculated for each truncated set. Both the glass regime and the flow regime were truncated.

Linear viscoelastic modeling of creep, start-up, step shear recovery, step strain recovery, and viscosity was performed with the complete data set and the truncated sets. The following shear flow relations were chosen because they represent a broad class of linear viscoelastic experiments. A modified creep equation was used for simplicity

$$\text{Modified Creep} \quad \frac{Y(t)}{Y_0} = \sum_{i=1}^N j_i (1 - e^{-t/\lambda_i}) \quad (7)$$

The expression in Equation 7 does not include the $(J_g + t/\eta_0)$ term. Similarly, the equation for start-up is modified such that

$$\text{Modified Start-Up} \quad \frac{t(t)}{Y_0} = \sum_{i=1}^N g_i \lambda_i (1 - e^{-t/\lambda_i}) \quad (8)$$

For a liquid the $(G_0 t)$ term is neglected. The step strain recovery expression refers to the case where the strain has been stepped up to Y_0 and then back down to zero. It takes the form

$$\text{Step Strain Recovery} \quad \frac{Y_t}{Y_0} = \frac{\sum_{i=1}^N g_i \lambda_i e^{-t/\lambda_i}}{\sum_{i=1}^N g_i \lambda_i} \quad (9)$$

For step shear recovery we use the relation

$$\text{Step Rate Recovery} \quad \frac{Y_t}{Y_0} = \frac{\sum_{i=1}^N g_i \lambda_i^2 (1 - e^{-t^*/\lambda_i})}{\sum_{i=1}^N g_i \lambda_i} \quad (10)$$

In Equation 10, the quantity t^* refers to the duration of the steady shear experiment. The dynamic viscosity is given in terms of the previously defined storage modulus and loss modulus

$$\text{Viscosity} \quad \eta^*(\omega) = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad (11)$$

Equation 11 was used in conjunction with the well known Cox-Merz rule to predict viscosity curves. An explanation of Equations 7, 8 and 11 can be found in Ferry [3] while Equations 9-10 are developed by several authors [7-9]. To allow comparison of these models, the error was plotted as a percentage such that

$$\text{Error} - E = \frac{Y_c - Y_t}{Y_c} \quad (12)$$

The Y refers generically to the value (modulus, stress, or strain) being calculated and the subscripts c and t refer to complete data set and truncated data set respectively. It was also necessary to define some measure of truncation. The simplest definition is

$$\text{Truncation} - T = \frac{\log \omega_f - \log \omega_0}{\log \omega_{cf} - \log \omega_{co}} \quad (13)$$

where the subscripts o and f refer to the smallest and largest frequencies measured. Truncation frequencies for each data set are listed in Table 2. The far right column gives the degree of truncation.

Tangent delta of the complete data set is shown in Figure 2. The viscosities plotted in Figure 3 correspond to a complete data set (PC-0 in Table 2), a data set with glass truncation (PC-6) and a data set with flow truncation. (PC-5) Each spectra is consistent within the time window corresponding to its inverse frequency window.

To show this correlation explicitly, we plot error versus time for PC-5 and PC-6. The error predicted from Equations 7-11 in conjunction with 12 is shown in Figures 4-5. The abrupt transition to 100% error occurs consistently at the inverse of the truncation frequency (indicated by a vertical line) for all models.

3.2 EXTRAPOLATION OF SYSTEMATICALLY TRUNCATED POLYCARBONATE

The information obtained from the truncated data set is combined with GPC data to predict an extrapolation of the continuous relaxation time spectrum. The specific form of the continuous spectrum for a polydisperse material is arrived at through fitting a curve to the truncated spectrum of the entanglement regime and predicting the glass transition behavior from the monodisperse behavior.

It has been shown [10] that the continuous relaxation spectrum for a monodisperse linear flexible polymer takes the form

$$H(\lambda) = \begin{cases} H_1 \lambda^{\alpha_1} + H_2 \lambda^{\alpha_2} & \lambda \leq \lambda_{\max} \\ 0 & \lambda > \lambda_{\max} \end{cases} \quad (14)$$

The first term ($H_1 \lambda^{\alpha_1}$) represents the entanglement regime and the second term, ($H_2 \lambda^{\alpha_2}$) represents the glass transition regime. The glass transition behavior is independent of the molecular weight distribution and should be valid for materials of any polydispersity. Values of the constants have been reported for several polymers [11].

For a polydisperse linear polymer one can use a polynomial form for the behavior in the flow regime. Analysis of several polydisperse materials suggests that many broadly distributed materials can be represented by

$$H(\lambda) = \begin{cases} 10[A + B \log \lambda + C(\log \lambda)^2] + H_2 \lambda^{\alpha_2} & \lambda \leq \lambda_{\max} \\ 0 & \lambda > \lambda_{\max} \end{cases} \quad (15)$$

The parameters A , B , and C can be evaluated by means of a least squares fit to the available data.

In addition to proposing a form for $H(\lambda)$ in the entanglement regime it is necessary to specify a cut-off longest relaxation time that determines the terminal zone. For a monodisperse polymer we know [12-13]

$$\lambda_{\max} = \lambda_c \left(\frac{M}{M_c} \right)^{3.4} \quad (16)$$

Values of λ_c and M_c have been recorded in the literature [11]. We propose for a polydisperse system that M_{\max} approximately equals PM_w such that

$$\lambda_{\max} = \lambda_c \left(\frac{PM_w}{M_c} \right)^{3.4} \quad (17)$$

where P is the polydispersity of the material M_w is the weight average molecular weight. This approximation should be reasonable for gaussian type molecular weight distributions.

It is assumed that the continuous spectrum of a polydisperse material takes the form proposed in Equation 15. A discrete relaxation spectrum is calculated for the data set one wishes to extend and a continuous relaxation spectrum is obtained using Equation 5. Then a least squares fit is performed to obtain the parameters A , B , and C . These parameters are then used to predict an extended spectrum which is cut off at λ_{\max} according to Equation 17.

We utilize the polycarbonate data set shown in Figure 2 to test the validity of Equations 15 and 17. In Figure 6, we plot $\log H(\lambda)$ vs. $\log \lambda$ of PC-0. The glass is fit with a line and the entanglement region is fit with a quadratic equation according to Equation 15 using the values of H_2 , n_2 , P , and M_w shown in Table 1. To test the ability of a truncated set to recover the same parameters as the complete data set, we fit a quadratic equation to the truncated sets PC-1 through PC-5. Table 3 lists the values of A, B, and C recovered for each truncated set.

The parameters obtained from the truncated data set PC-5 are used in conjunction with Equations 5-6 to predict the complete curve for tangent delta shown in Figure 7. The extrapolation of PC-5 is shown as a line while the symbols indicate the original data points of PC-0.

The viscosity of the same extrapolated spectrum is plotted in Figure 8 and compared to the predicted viscosity of the complete data set. Agreement between the two is easily within the realm of experimental error.

3.3 APPLICATION OF EXTRAPOLATION TO POLYDISPERSE HDPE RESINS

To extend this treatment to broadly distributed HDPE resins, we use values of H_2 and n_2 reported in the literature and values of P and M_w from GPC (Table 1). The dynamic data obtained for these resins is converted to a continuous relaxation spectrum and fit to Equation 15. The parameters obtained are listed in Table 4. The resulting predictions for tangent delta are shown in Figure 9 along with the original data sets.

The predictions for viscosity of the HDPE resins are shown in Figure 10. The flow regime extrapolation allows an estimate of zero shear viscosity while the glass transition extrapolation extends the viscosity curve to rates comparable to processing rates.

The available experimental data for HDPE cannot confirm the accuracy of the value for λ_{max} predicted from Equation 17. Instead, a comparison is made between the values of λ_{max} predicted from Equation 17 and the values predicted from Equation 16 with $M=M_{max}$ where M_{max} is estimated from GPC distributions. The results of this analysis are given in Table 5.

4. DISCUSSION

Analysis of the truncation effects for the polycarbonate gives us a tool to evaluate the proposed extrapolation. In turn, the verified procedure for polycarbonate can be applied to the HDPE materials.

4.1 TRUNCATION

We have demonstrated (via the viscosities plotted in Figure 3) the reliability of the spectra calculation within the time window corresponding to the inverse frequency window. The viscosity curves also illustrate the large error in the zero shear viscosity when there is truncation in the flow regime. Truncation in the glass regime has a similar effect on estimates of high shear rate viscosity. In both cases, the truncation results in an underestimate of the viscosity.

The effect of truncation is quite similar for a variety of linear viscoelastic calculations as demonstrated in Figure 4. In the case of flow regime truncation an abrupt transition to large error values occurs at approximately $1/\omega_1$ for all of the calculated models.

The results for glass truncation (Figure 5) are not quite so consistent. It can be seen that the error in prediction at $1/\omega_1$ is quite large for creep and grows quickly for start-up while each of the other models shows very little effect. Thus one could predict step strain or step shear recovery outside the inverse frequency window. While there is an appreciable percentage error at inverse glass truncation frequency for creep modeling, the absolute values and hence the absolute error is quite small.

4.2 POLYCARBONATE EXTRAPOLATION

When performing the fit of the continuous relaxation spectrum as shown in Figure 6, it is important to remember that the end points should not be included in the fitting. As was mentioned in section 1, conversion of the discrete spectra to the continuous spectra is not possible at the end points according to Equation 6.

We see from Figures 7 and 8 that the extrapolation predicted from PC-5 is quite good, but not exact. We also note that the parameters listed in Table 3

show some change with truncation. There are several sources of error to create these minor discrepancies. It is probable that the quadratic form assumed for the flow regime does not capture completely the experimental behavior. In addition, the prediction for the glassy behavior relies on monodisperse material parameters. Any error in evaluating the monodisperse parameters is reflected in the extrapolation.

The success of this model with the polycarbonate sample can be traced to the nature of the molecular weight distribution for this material. The distribution has a simple gaussian form, which when transformed into time domain behavior can be reasonably approximated with a three parameter model. A more complex distribution would result in a continuous relaxation spectrum that could not be approximated with such a simple equation. The reasonable fit of the terminal zone in Figure 7 implies the success of Equation 17 for approximating λ_{max} .

4.3 HDPE EXTRAPOLATION

The discrepancies between the extrapolation and the actual data for the HDPE samples PE-2 and PE-3 shown in Figure 9 can be attributed to the very limited experimental data. After eliminating the end points of the continuous spectrum from consideration, only 4 data points remain to fit the parameters A, B, and C. As expected in this extreme case of truncation, the fit is not very good.

We see from the fit of PE-1 in Figure 9, however, that one or two additional decades of experimental data alleviate the problem of fitting the curve. Thus only a little more experimental information is required to find success for these materials.

By comparing values of λ_{max} listed in Table 5, we see that Equation 17 becomes a poor approximation for distributions of a more strongly bimodal nature (PE-2). For such distributions one should use Equation 16 with $M=M_{max}$.

5. CONCLUSIONS

Dynamic moduli in a frequency window $[\omega_0, \omega_f]$ can be successfully used to model the linear viscoelastic behavior in the time window $[1/\omega_f, 1/\omega_0]$. In the case of glass truncation, it is evident that very little truncation error occurs for modeling of step strain and step shear even outside the expected window. Further work is necessary to generalize these results to a variety of materials ranging from monodisperse to polydisperse.

In addition, this study of truncation effects has led us to a reasonable extrapolation procedure for polydisperse materials with simple molecular weight distributions. While this method cannot be applied to materials with sharply bimodal distributions, it shows reasonable success for distributions of a simpler nature.

In the case of HDPE samples, it is apparent that a slight improvement in our ability to gather experimental results would be sufficient to allow use of the extrapolation for PE-2 and PE-3. It is encouraging that the fit of PE-1 is quite good despite the slightly bimodal nature of its molecular weight distribution. This emphasizes the point that the finer details of molecular weight distributions are not discernible in rheology and consequently a simple form of the flow regime relaxation spectrum will suffice.

6. REFERENCES

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TABLE 1. MATERIAL DATA

	M_w	$P=M_w/M_n$	PM_w	M_{max}	n_2	H_2
PC-0	150000	2.4	3.6E+5	-----	-.80	417
PE-1	159000	14.5	2.3E+6	2.9E+6	-.67	5.9
PE-2	225000	35.1	7.9E+6	3.6E+6	-.67	5.9
PE-3	153000	15.1	2.3E+6	2.9E+6	-.67	5.9

TABLE 2. FREQUENCIES OF TRUNCATION

	$\omega_0 = \omega_{min}$	$\omega_c = \omega_{max}$	$t_{min} = 1/\omega_c$	$t_{max} = 1/\omega_0$	T
PC-0	3.548E-5	2.691E6	3.716E-7	2.818E4	1.00
PC-1	1.288E-4	2.691E6	3.716E-7	7.764E3	0.95
PC-2	1.288E-3	2.691E6	3.716E-7	7.764E2	0.86
PC-3	1.230E-2	2.691E6	3.716E-7	8.130E1	0.77
PC-4	1.202E-1	2.691E6	3.716E-7	8.319	0.68
PC-5	1.202	2.691E6	3.716E-7	8.319E1	0.58
PC-6	3.548E-5	8.913E1	1.122E-2	2.818E4	0.59

TABLE 3. PARAMETERS OF QUADRATIC FIT OF POLYCARBONATE

	A	B	C
PC-0	5.250	-.488	-.106
PC-1	5.254	-.468	-.107
PC-2	5.260	-.462	-.111
PC-3	5.253	-.462	-.111
PC-4	5.244	-.456	-.106
PC-5	5.234	-.449	-.102

TABLE 4. PARAMETERS OF QUADRATIC FIT OF HDPE

	A	B	C
PE-1	3.769	-.669	-.075
PE-2	4.183	-.469	-.079
PE-3	3.651	-.660	-.052

TABLE 5. PREDICTIONS FOR LONGEST RELAXATION TIME

	λ_{max} (Eqn 17)	λ_{max} (Eqn 16)
PE-1	1.9E+3	4.2E+3
PE-2	1.3E+5	8.7E+3
PE-3	1.9E+3	4.2E+3

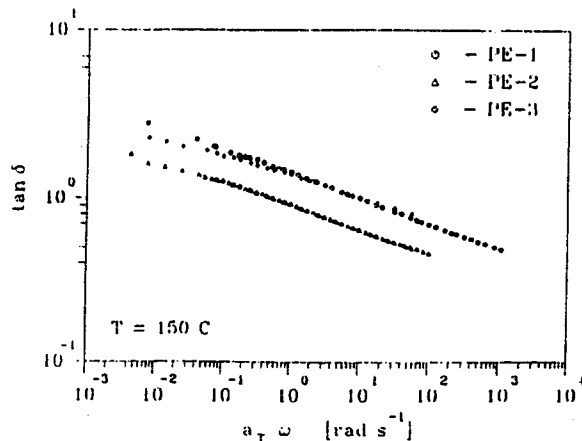


Figure 1. Tangent Delta for HDPE materials

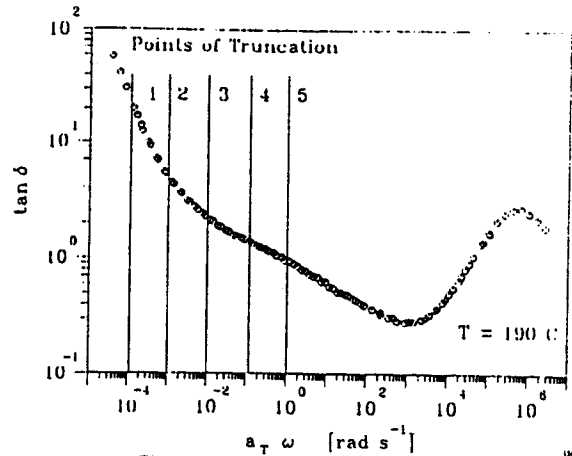


Figure 2. Tangent Delta for PC-0

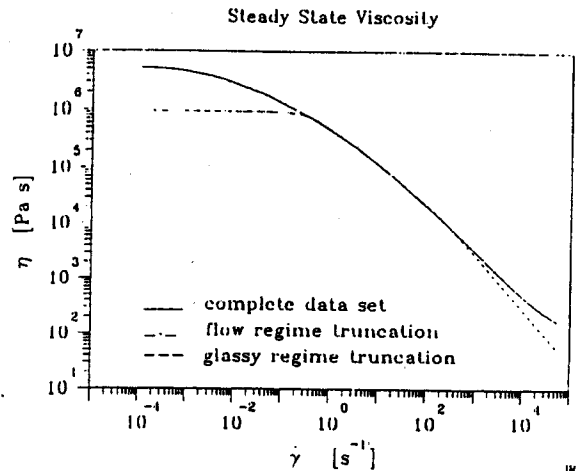


Figure 3. Viscosity for PC-0, PC-5, PC-6

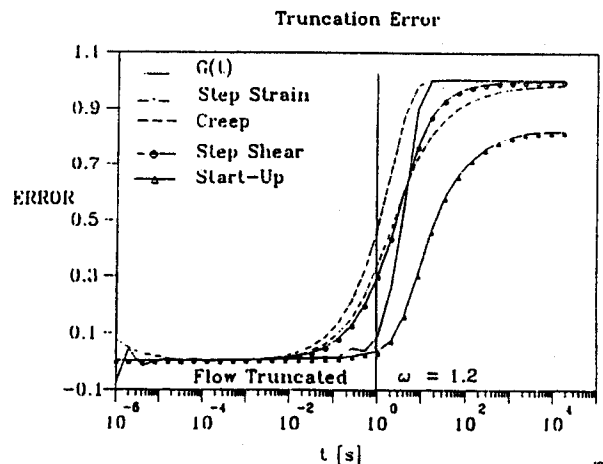


Figure 4. Flow Truncation Error for Several Viscoelastic Models

Truncation Error

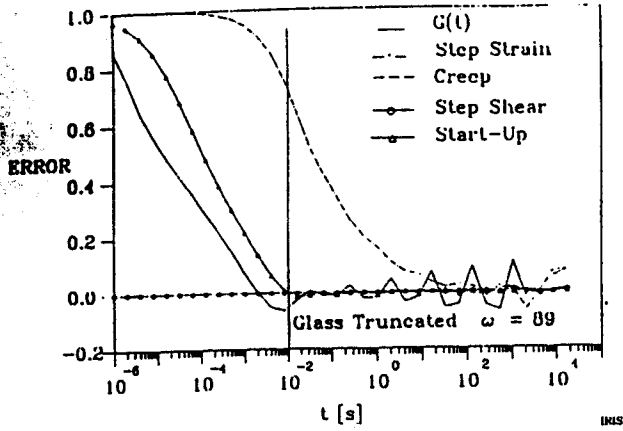


Figure 5. Glass Truncation Error for Several Viscoelastic Models

Steady State Viscosity

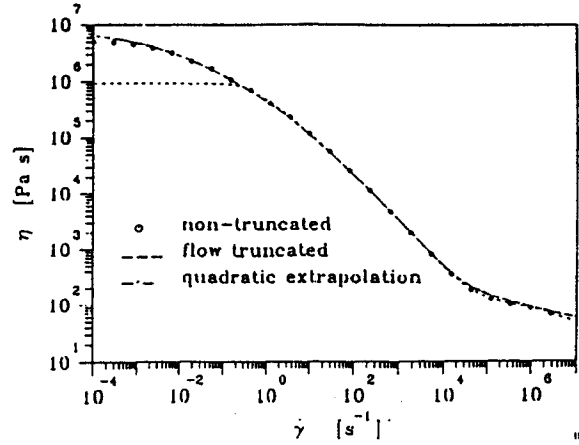


Figure 8. Viscosity Comparison of PC-0, PC-5 and Extrapolation

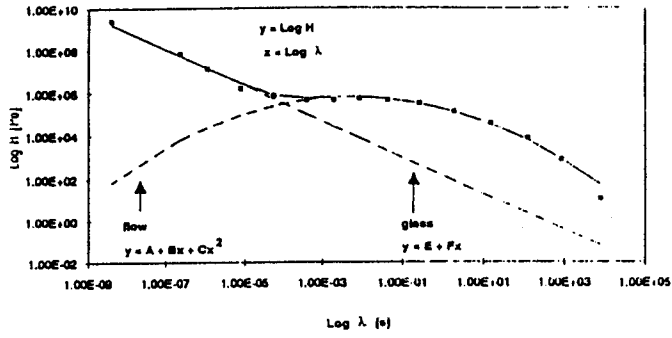


Figure 6. Continuous Relaxation Spectrum of PC-0 and Equation 15 Fit

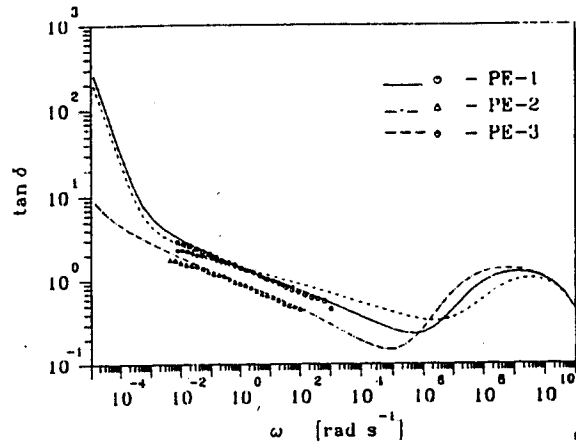


Figure 9. Comparison of IIDPE Data to Extrapolation

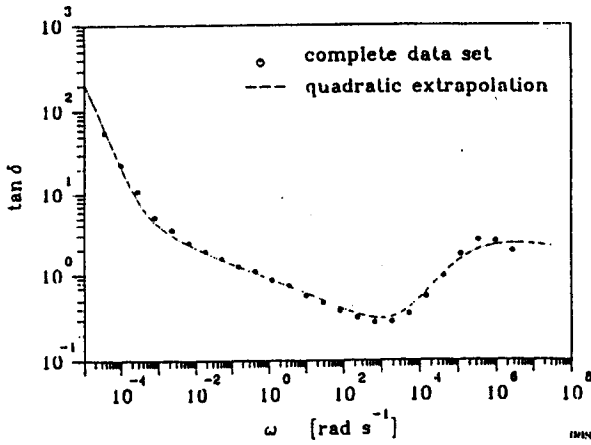


Figure 7. Comparison of PC-0 to Extrapolation

Steady State Viscosity

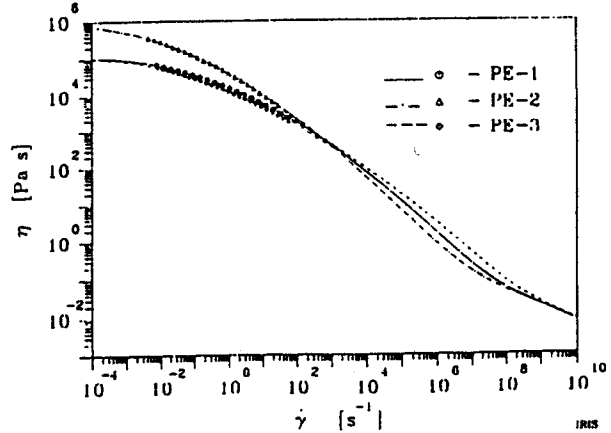


Figure 10. Comparison of IIDPE data to Extrapolation