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A COMPARISON OF FRACTIONAL ORDER TIME DERIVATIVE MODELS OF THE VISCOELASTIC STRESS RELATIONS IN THERMORHEOLOGICALLY COMPLEX MATERIALS

THESIS

Victor B. Chambers, Captain, USAF

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THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Aeronautical Engineering

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Preface

The purpose of this thesis was to examine the viscoelastic behavior of thermorheologically complex materials, a typical example of which is a soft, rubbery material. Materials such as these are very useful in damping vibrations in structures, but the relaxation moduli of these materials change significantly with temperature and frequency. In the case of space structures applications where temperatures vary greatly and a stable platform is necessary, a method to predict this changing modulus is needed.

I was interested in the subject for two reasons. First, this thesis allows me to apply some of my controls knowledge if the task is treated like a problem of finding the transfer function of a system. Secondly, this thesis gave me the opportunity to learn about the fractional derivative.

The original approach was to validate a previously developed viscoelastic model, but the task expanded to include extending the model to materials with two transitions from a low modulus value to a higher value and applying thermodynamic principles to validate the extended model. The results were very promising.

I could not have performed this analysis or have written this thesis without a great deal of help. I would like to give special thanks to my faculty advisor, Lt Col Ronald Bagley, for his continuing patience and strong guidance in times of

need. I would like to thank my sponsor, Dr David Jones of the Flight Dynamics Directorate for his assistance and support of this project and I would like to thank Mr Paul Macioce of the Anatrol Corp. for his assistance. Finally, I want to thank my wife, Earlean, for her understanding, concern and motivation through the long, frustrating days and nights devoted to this thesis.

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List of Symbols

$\alpha(T)$ - Temperature Dependent Shift Parameter

$\beta(T)$ - Temperature Dependent Derivative Order

$\Gamma(x)$ - Gamma Function

Δ - Activation Energy

ΔH - Activation Energy

δ - Rate of Energy Dissipation

ε - Strain

ε^* - Transform of the Strain

Θ - Barrier Distribution Parameter

ν - Barrier Shape Parameter

σ - Stress

τ - Stress Relaxation Time

$\Phi(t)$ - Energy Transition Probability

Ψ - Free Energy

ω - Frequency

A1 - Constant #1

A2 - Constant #2

ASCII - American Standard Code Information Interchange

$d(x)/dt$ - Time Derivative Operator

$D^\beta[x]$ - Fractional Order Derivative Operator

E - Modulus

E_∞ - "Rubbery" Modulus

E_0 - "Glassy" Modulus

E_{rel} - Relaxation Modulus

G - Shear Modulus

i - Imaginary Number

J - Shear Compliance Modulus

k - Boltzman's Constant

p - Mechanical Internal Work

R - Ideal Gas Constant

s - Laplace Domain Variable

T - Temperature

T_s - Reference Temperature

t - time

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Abstract

The research presented here was accomplished in three parts. In the first part, a fractional order time derivative model of viscoelastic behavior was validated using experimental data for viscoelastic materials. Descriptions of internal energy loss at the molecular level led to the fractional order time derivative model. The fractional calculus stress-strain constitutive laws used in the model are easily applied to the temperature and frequency dependent moduli of viscoelastic materials. The second portion describes the extension of the above fractional order time derivative model to predict the viscoelastic behavior of thermorheologically complex materials that exhibit two modulus transitions with respect to frequency. The final portion determines the necessary restrictions on the parameters of the double transition viscoelastic model to insure the model doesn't violate thermodynamic principles.

A COMPARISON OF FRACTIONAL ORDER TIME DERIVATIVE MODELS OF THE VISCOELASTIC STRESS RELATIONS IN THERMORHEOLOGICALLY COMPLEX MATERIALS.

I. Introduction

Approach. The approach taken is to validate a previously developed model by applying it to candidate materials. Once the model is validated, the approach is to extend the model to capture more complex viscoelastic behavior.

Problem Statement. This thesis presents the evaluation and development of mathematical models used to predict the viscoelastic behavior of amorphous polymers and similar materials. Knowing the viscoelastic behavior of these amorphous polymers is essential to employing these materials properly as damping materials in a wide range of structures and applications. The basis of the process of learning the viscoelastic behavior of these materials is through experimental measurement. Experimental measurement under all possible conditions over the entire operating envelope of an application would be extremely expensive. An accurate model that would be simple enough to be used as an engineering tool would eliminate the need for exhaustive experimental measurement. The model also should characterize viscoelastic behavior under conditions that cannot be duplicated in the laboratory [1:1]. One way to simplify the model necessary to capture the viscoelastic behavior of an amorphous polymer is to assume the material acts as a thermorheologically simple one.

In the past, the idea of the thermorheologically simple material was used as the basis for describing the viscoelastic behavior of the material. Using this approach, the frequency dependent complex modulus for additional temperatures could be constructed by shifting measured storage and loss moduli by some experimentally derived shift factor. The thermorheologically simple material is one in which the frequency dependent modulus retains the same shape over a large temperature range. By choosing a specific temperature as a reference temperature, a "master curve" for the entire temperature range can be created. Adjusting the "master curve" using the shift factor corresponding to a particular temperature will give the viscoelastic modulus of the material at that temperature [2:52]. The principle motivation for modeling a material as thermorheologically simple is that all of the mechanical modulus values lie on a single "master curve". Changes in the viscoelastic behavior of a material caused by temperature variations are nonlinear. Changes in the viscoelastic relationship due to mechanical stress or strain are linear processes if the stress or strain stays within the elastic range [2:14]. The assumption of thermorheologically simple behavior is acceptable for a large class of materials, but is not acceptable for all materials, as may be expected. The progression from the idea of a thermorheologically simple material to the idea of a thermorheologically complex material, in which the shape of the frequency dependent modulus is temperature dependent, is natural.

Summary of Approach. While developing a simple model that captures the viscoelastic relationship of a thermorheologically complex material, Bagley used a theory based on internal energies at the molecular level that lead to a fractional order time derivative model [3:2]. The model will be the starting point for the research presented in this thesis, which is divided into seven chapters and three appendices. The first chapter is the introduction. Chapter two provides the background information on the fractional order derivative and how molecular theory leads to a fractional order time derivative viscoelastic model. Chapter three discusses the Modplot.ex executable file developed for this thesis and the procedure used to curve-fit the measured viscoelastic data. Chapter four examines the ability of the model described in chapter two to predict the thermorheologically complex behavior of several materials correctly. These materials are polyisobutylene, polyvinyl chloride dimethyl thianthrene, atactic polystyrene, and a material designated C-1002 and manufactured by the EAR Corp. of Indianapolis, Indiana. The fifth chapter of the thesis develops and discusses the extension of the chapter two model to materials that exhibit two distinct moduli transitions with respect to frequency. The new double transition model also will be applied to atactic polystyrene data. The sixth chapter checks the double transition model to insure that it does not violate the First and Second Laws of Thermodynamics. The final chapter provides a summary of the results and discusses some recommendations for future research. The first appendix contains the listings of the programs written specifically for this research effort and the two remaining appendices list the data obtained from unpublished sources.

II. Background

To understand the particular approach taken in this research effort, one must understand what is the theory and development of the model that represents the starting point. This section will briefly discuss the fractional order time derivative. This section also will quickly detail the development and derivation of the fractional order time derivative viscoelastic model, which constitutes the starting point of this research.

Since the early 1950s, researchers have alluded to the idea of using fractional order time exponentials as phenomenological descriptors of linear viscoelasticity [3:3]. Examples can be found in the work of Debast and Gilard in 1965 [4]. Examples also can be found in the work of Leko and Meshcheryakova in 1976 and in both cases the researchers tried to describe the strain in silica glasses using an exponential time function with time taken to a fractional power [5]. There were several other researchers that developed similar equations, but none seemed to grasp the full application of the fractional order time derivative.

The Fractional Order Time Derivative The fractional order time derivative is defined as a linear convolution operator as seen in Equation 1 [3:10]:

Definition of the Fractional Derivative

$$D^{\beta}[\varepsilon(t)] = \frac{1}{\Gamma(1-\beta)} \frac{d}{dt} \int_0^t \frac{\varepsilon(t-\tau)}{\tau^{\beta}} d\tau \qquad (1)$$

$$0 < \beta < 1$$

$$(i\omega)^{\beta} \varepsilon^*(i\omega) \leftrightarrow s^{\beta} \varepsilon^*(s) \leftrightarrow D^{\beta}[\varepsilon(t)] \qquad (2)$$

Equation 2 shows the relationship of the fractional derivative in the Fourier, Laplace, and time domains. The Fourier domain is a very convenient domain in which to pose the viscoelastic model because it directly shows the frequency content of the function. Convolution in the time domain is performed by multiplication in the Fourier domain, so the transform of the β order derivative of a function is obtained by multiplying its Fourier transform by $(i\omega)^{\beta}$. This is similar to the way a transform of a first order integer derivative would be obtained in the Fourier domain, multiplying the Fourier transformation by $(i\omega)$. Using the one-sided Laplace transform was another way to simplify some calculus used in the derivation. The Laplace domain is easily associated with the Fourier domain.

<u>Fractional Order Time Derivative Viscoelastic Model</u> The

viscoelastic model is based on a theory of internal energy loss at the molecular level. The complete derivation of the model can be found in Reference 3. The theory hypothesizes that the mechanical stress relaxation in viscoelastic polymers is the result of a reduction in the elevated energy states of the polymer chains [3:5]. The polymer chains are stretched in their elevated energy state and relaxation occurs as the chains return to their random orientations.

The derivation begins from the development of a time dependent probability density function of the internal energy. With the probability density, the model predicts the probability that the material of interest has or has not transitioned from an elevated energy state to a more relaxed energy state. The probability function also accounts for barrier energies that must be overcome in order for the material to transition to a relaxed energy state. The result of this derivation is a fractional order derivative constitutive law, shown in Equation 3, that describes the fractional order viscoelastic relationship between stress and strain existing in these polymers. The shift parameter, α, and β, the derivative order of the equation, are both functions of temperature. Because the parameters, $\alpha(T)$ and $\beta(T)$, are functions of temperature, they describe frequency dependent moduli curves of different shapes for different temperatures which would correspond to behavior of a thermorheologically complex material.

Fractional Order Derivative Contitutive Law

$$\sigma(t) + \alpha^{\beta} D^{\beta}[\sigma(t)] = E_{\infty}\varepsilon(t) + E_{0}\alpha^{\beta} D^{\beta}[\varepsilon(t)] \qquad (3)$$

$$\alpha(T), \quad \beta(T)$$

The shift parameter is related to the temperature dependent energy barrier shape of the material. The concept of a barrier shape is a hypothesis about various types of particles migrating and impeding motion during the relaxation process. The shift parameter is a crude descriptor of these barriers' interference with the energy transition that determines the frequency dependent modulus [3:7-11]. As stated earlier, it is the transition to higher internal energy levels that are believed to be the cause of the modulus transition in the amorphous polymers. In the cases presented in this thesis, the stimulus to higher internal energy levels is an applied stress.

As it pertains to the model, the shift parameter, which accounts for the barrier shape, determines the frequency at which the modulus transition will occur. An increase in the shift parameter moves the model curve to the left and a decrease in the shift parameter moves the model curve to the right.

The fractional derivative order describes the fractal dimension of the Cantor set of the underlying energy decay process that causes the energy transitions [3:10-11]. In the model, the derivative order affects the slope of the model predictions in the regions in which the prediction curves resemble lines. For the regions of the model predictions that are curved, the derivative order affects the amount of curvature. An increase in the derivative order increases the slope or increases the amount of curvature. A decrease in the derivative order decreases the slope or decreases the amount of curvature.

Another equation that results from the derivation is the relaxation modulus shown in Equation 4. The "rubbery" modulus, E_∞, represents the material's normal steady state modulus and E_0, the "glassy" modulus represents the highest energy state modulus or stiffest modulus. The last term in the

Relaxation Modulus

$$E_{rel}(t) = E_\infty + (E_o - E_\infty) E_\beta(-(t/\alpha)^\beta) \qquad (4)$$

relaxation modulus equation is a β order Mittag-Leffler function, which is defined in Equation 5.

Mittag-Leffler Function

$$E_\beta(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(1+\beta n)} \qquad (5)$$

$$0 < \beta < 1$$

The Mittag-Leffler function is very similar in form to the exponential function [3:11-12].

The result of the derivation is the fraction order time derivative viscoelastic model. The model shown in Equation 6 is rewritten as a transfer function and posed in the Fourier domain. This eases the interpretation of the output with respect to frequency [3:13].

Fractional Order
Time Derivative Model

$$E(\omega) = \frac{E_\infty + E_0 \alpha^\beta (i\omega)^\beta}{1 + \alpha^\beta (i\omega)^\beta} \qquad (6)$$

The resulting four parameter transfer function is compact and easy to implement, making it suitable for engineering analysis. Two of the four parameters, E_∞ and E_0 can be determined directly from viscoelastic data and are constant for all temperatures for the materials analyzed in this thesis. The remaining two parameters can be determined through curve fits of viscoelastic data. Details of the process of determining the parameters will be discussed in Chapter Four which presents the effort to validate the model.

III. Curve Fit Procedure

The phenomena this model was developed to predict is a very complex process and an accurate model would be a significant advance for the rheological sciences. Past methods used to characterize the viscoelastic behavior of amorphous polymers involved empirical formulas and educated guessing. This chapter will examine how accurately the model characterizes the viscoelastic behavior of amorphous polymers by comparing the predicted behavior obtained from the viscoelastic model to actual viscoelastic data obtained from several sources. Through the comparison, the four parameters of the model can be determined. The four parameters that characterize the material are the combination of parameter values that gives the curves that best match the data curves. The model curves can then be analyzed for how well they match the data curves.

The first step in determining the model parameters involved finding the "glassy" and "rubbery" modulus. Both parameters can be read directly off the data curves if a wide enough frequency and temperature range was used for the data acquisition. If the data was taken over a wide enough frequency range, the modulus transitions from an asymptotes that can be found at very low frequencies or high temperatures to another asymptote that can be found at very high frequencies or low temperatures, respectively.

The "glassy" modulus represents the condition in the material where the bond energies are in an excited state and are not allowed enough time to relax because of the high frequencies or low temperatures and therefore the modulus is at its maximum [3:7]. The "rubbery" modulus represents the softer modulus measured at high temperatures or low frequencies, where the material has the time to continually relax.

Because the data used for this research was not taken with a sufficiently wide frequency range, the asymptote were estimated from the available data and adjusted using the data curves at several different temperatures. It should be noted that although each the viscoelastic response due to frequency was different at each temperature for the materials modelled in this thesis, the data used for this research suggests the "glassy" and "rubbery" moduli are constants throughout the process for each material. The lower temperature conditions were used to adjust the "glassy" modulus. At the lower temperatures, the modulus values tended to be the largest and were more heavily influenced by the "glassy" modulus. The higher temperature conditions were used to adjust the "rubbery" modulus. At the higher temperatures, the modulus values tended to be the smallest and more heavily influenced by the "rubbery" modulus.

The curve fits were performed using just a visual approach. Although it would have been desirable to have the degree to which the curve fits matched the data based on some objective norm and the process automated, the nonlinear behavior of the viscoelastic response of the materials made these tasks very difficult. By adjusting the temperature dependent shift parameter, $\alpha(T)$, and the fractional derivative order, $\beta(T)$, accurate curve fits of the measured data could be obtained. The shift parameter slips the model curve left or right over the frequency range while the derivative order changes the slope of the model curve.

The approach taken to perform the adjustments to the "glassy" and "rubbery" moduli was to start the curve fits with the first couple of high temperature data curves and adjust the "rubbery" modulus. Next, the first couple of low temperature data curves were fitted to adjust the "glassy" modulus. For the data curve at the highest temperature, one would attempt to curve fit with estimated values of the "glassy" and "rubbery" moduli. The values for the shift parameter and the derivative order were estimated also and were adjusted until the predicted curves for the real and imaginary portions matched the data curves for the real and imaginary portions as well as possible. The "glassy" and "rubbery" moduli would then be adjusted to try to improve the match. Next, one would attempt to curve fit data at the next lower temperature using all of the parameters from the previous curve fit attempt at the higher temperature. The shift parameter and the derivative order would be adjusted to give the best possible match between the predicted curves and the data curves. The "rubbery" modulus would then be adjusted to improve the match. The parameters for the previous curve fit with the new value for the "rubbery" modulus would be checked to insure they still produced a good match between the predicted curves and the data curves. If not, the change in the "rubbery" modulus would be reduced enough to give the best curve fit at both temperatures. This procedure of curve fitting the next lower temperature, adjusting the value of the "rubbery" modulus, checking how the change in the "rubbery' modulus affects the previous curve fits, and adjusting to give the best fit in all cases was repeated one or two more times.

Next, attention would be focused on determining the "glassy" modulus. The procedure was very similar. The difference was the procedure started with the lowest temperature and the value for the "rubbery" modulus was assumed to be known. Again, the procedure involved, curve fitting the three or four lowest temperatures in increasing order, adjusting the value of the "glassy" modulus, checking the previous curve fit, and adjusting the changes to the "glassy" modulus to give the best fit in all cases. After these tasks were completed, the "rubbery" and "glassy" moduli were assumed constants.

It is important to note that the four parameters of the model may simultaneously give accurate curve fits for both the real and the imaginary portions of the modulus. The parameters, αT) or β(T), may by determined more readily from the real or the imaginary portion of the modulus. The best portion of the modulus to use depends on the frequency range that is being modelled and learning the best portion to use is a judgement that comes with experience in curve fitting these materials.

IV. Validation of the Viscoelastic Model

Polyisobutylene The first material the Modplot.ex program was used to model was really a test case for the program. Polyisobutylene was modelled previously in Reference 3. The same experimentally measured viscoelastic data for Polyisobutylene was used to determine the model parameters[6:655]. Using Polyisobutylene made it possible to check the previous results as well as test the Modplot.ex program. The results matched the work previously done except for one minor adjustment in the shift parameter at the temperature of 232.8 K. The results of the curve fits are contained in Fig. 1 and Fig. 2. The figures show that the model accurately represents the viscoelastic behavior of polyisobutylene by closely matching approximately two decades of measured viscoelastic data. The data and the predictions are of the compliance modulus which is the inverse of the shear modulus. The results are equally good for both the real and imaginary portions of the modulus, which is important to note since only two parameters were varied over the temperature range modelled and only four parameters were used in the model overall. The parameters used to produce the curves displayed in Fig. 1 and Fig. 2 are listed in Table 1.

Also included in Table 1 are cutoff frequency values for

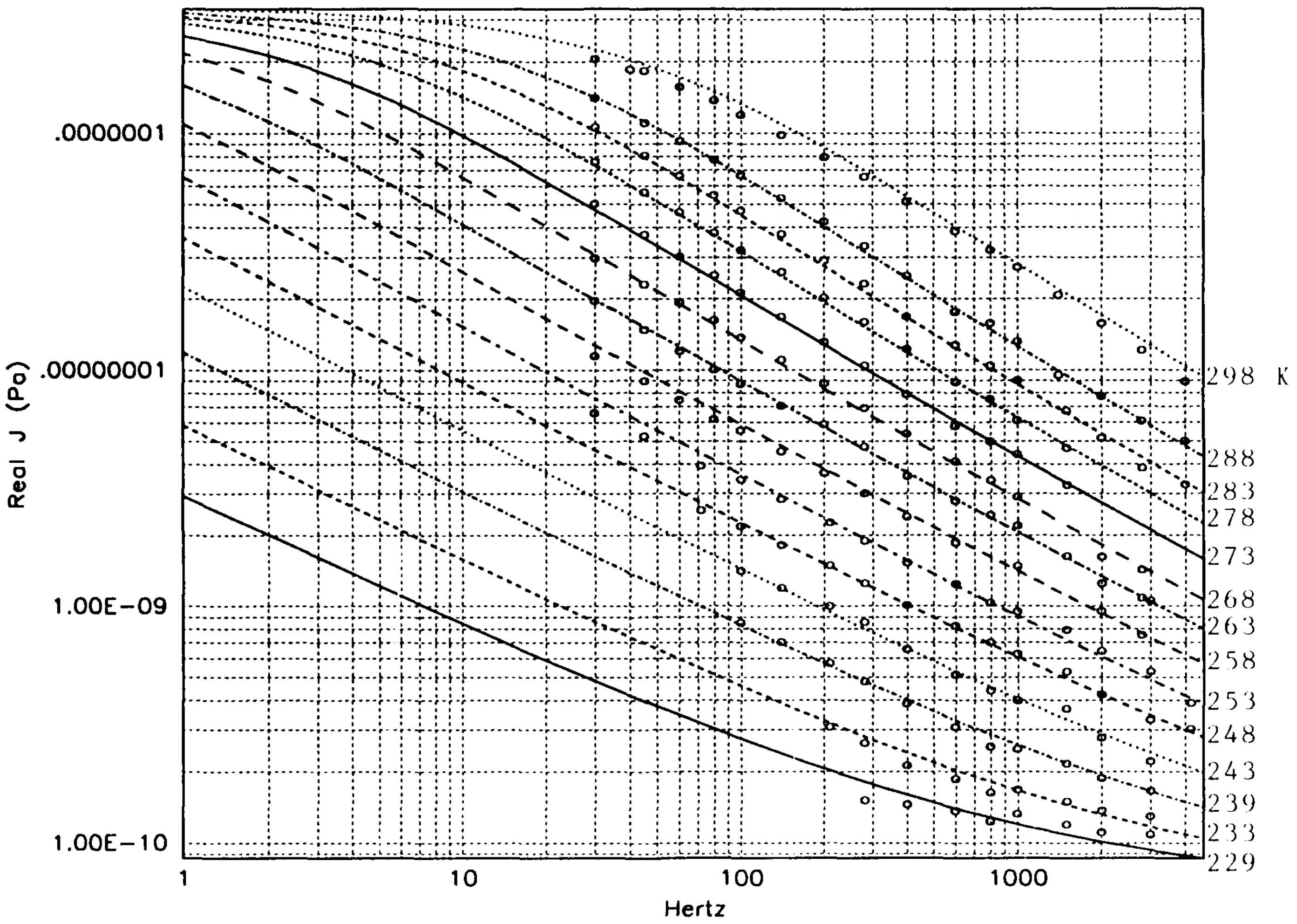

Fig 1. Compliance Modulus of Polyisobutylene (R)

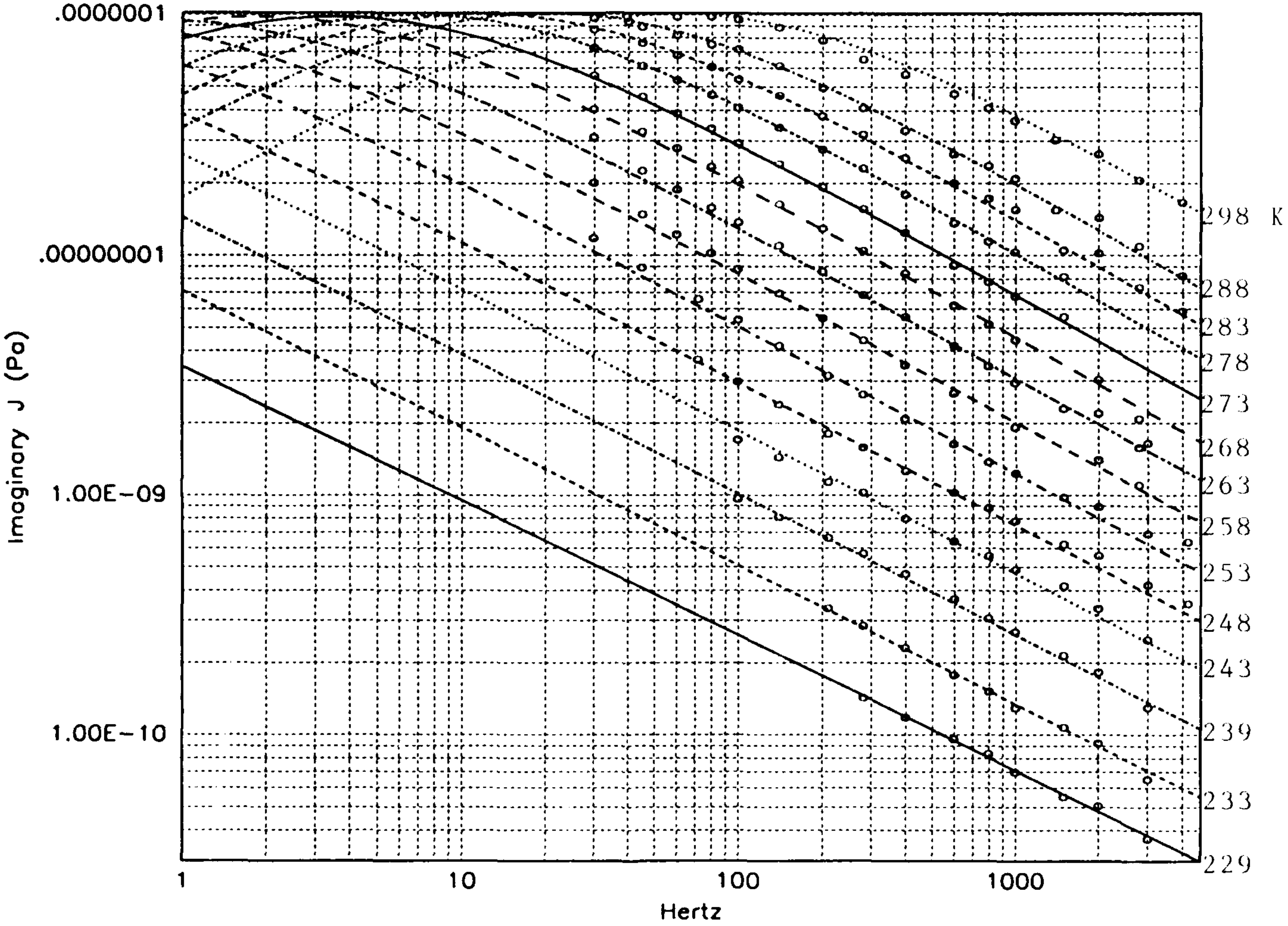

Fig 2. Compliance Modulus of Polyisobutylene (I)

each particular temperature evaluated by the model. The cutoff frequency represents the frequency point above which the model's predictions are questionable. Because of an approximation made in the development of the model, the fractional derivative constitutive law developed from the original hypothesis of the energy transitions in the

Table 1. Model Parameters for Polyisobutylene

Temperature (K)	Alpha	Beta	Cutoff Frequency
228.6	8.00e-05	0.565	115.24
232.8	2.80e-05	0.580	354.44
238.5	9.50e-06	0.590	1094.97
243.4	3.80e-06	0.600	2864.75
248.2	1.75e-06	0.600	6220.60
253.3	9.40e-07	0.620	12627.61
258.4	4.70e-07	0.630	26317.59
263.3	2.70e-07	0.640	47677.75
268.2	1.84e-07	0.660	75501.72
273.1	9.80e-08	0.660	141758.33
278.1	6.05e-08	0.670	238136.49
283.0	4.03e-08	0.677	366490.81
288.0	2.45e-08	0.680	609195.91
293.0	1.43e-08	0.680	1043727.27
298.2	7.80e-09	0.677	1893535.83
G zero=1.61E10 Pa			
G infinity=2.91E6 Pa			

molecular bonds contains a strong singularity. The approximation to overcome this shortcoming results in the following condition:

$$[\alpha(T)(i\omega)]^{\beta} \leq \frac{1}{5} \qquad (7)$$

The use of this condition is to insure the results of the model are valid [3:11]. The expression for the cutoff frequency is as follows:

$$f_c(T) = [\frac{1}{2\pi\alpha(T)}][.2]^{\frac{1}{\beta}} \qquad (8)$$

Greater detail on the model's development and the use of the approximation can be found in Reference 3 [3:15].

The curves at the bottom of Figure 1 and Figure 2 represent the viscoelastic behavior of polyisobutylene at the lowest temperature (228.6 K) and each curve above them represents the viscoelastic behavior of polyisobutylene at the next progressively higher temperature. To determine the accuracy of the model, the cutoff frequencies listed in Table 1 need to be compared to the model curves in the figures. For

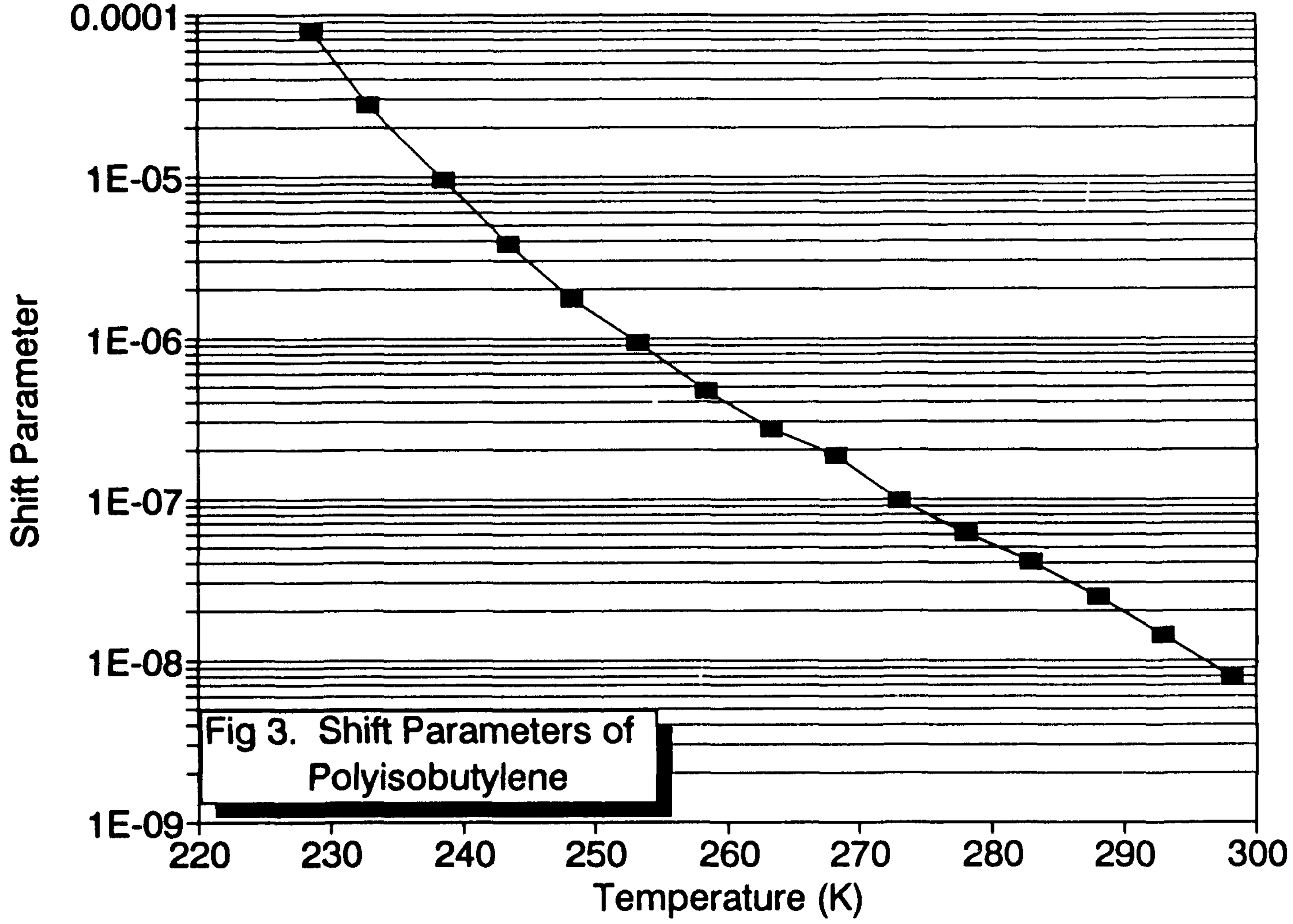

Fig 3. Shift Parameters of Polyisobutylene

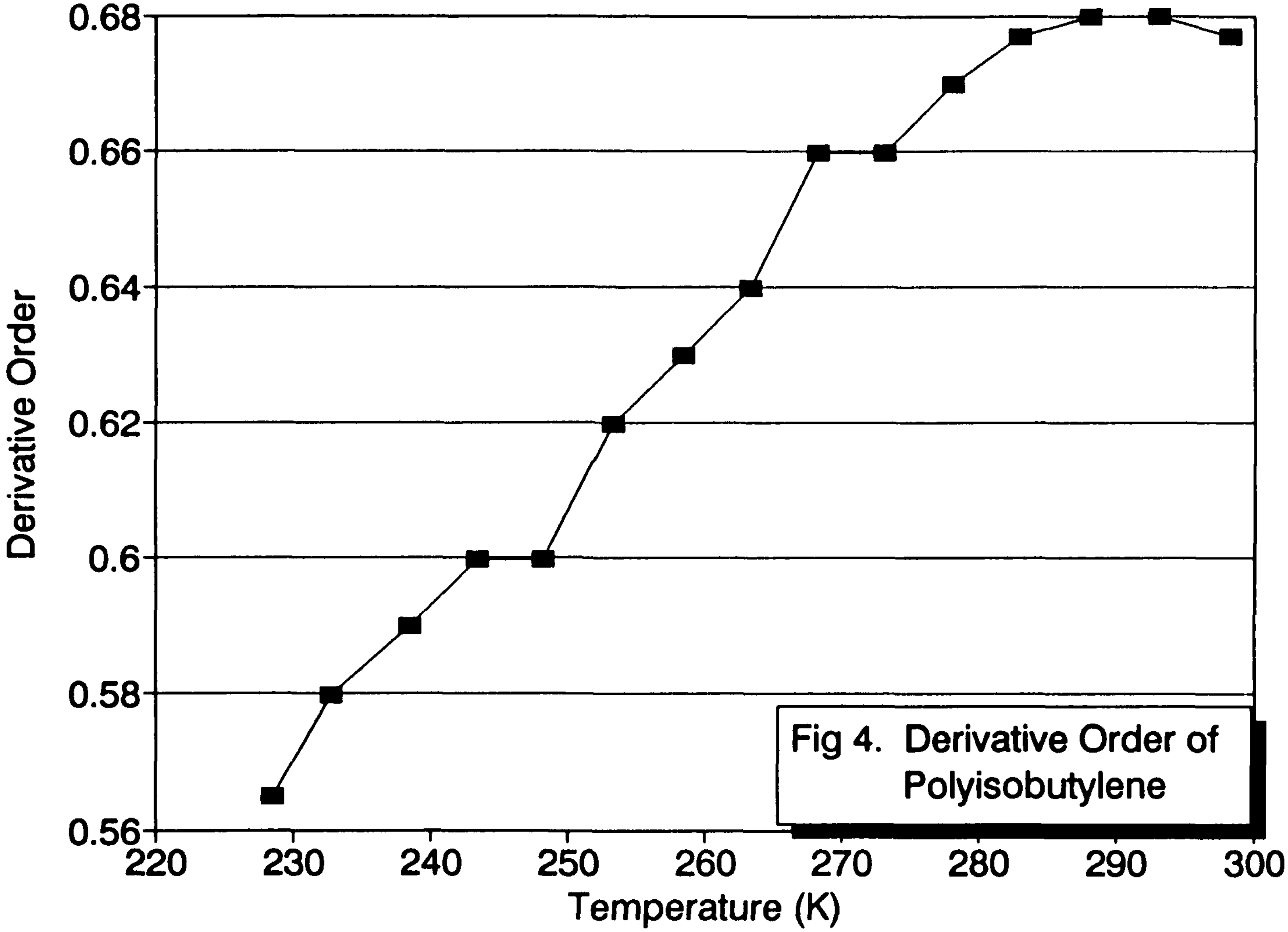

Fig 4. Derivative Order of Polyisobutylene

polyisobutylene, the cutoff frequencies only mildly affect the accuracy of the model. Actually, the model was very accurate for frequencies above the cutoff point, but in these cases the frequencies are only slightly above the cutoff point and only involve the four lowest temperatures, 228.6 - 243.4 K.

The affect of temperature on the parameters of the model can be observed in Figure 3 and Figure 4. The two figures show that the shift parameter and derivative order are indeed functions of temperature respectively.

<u>Polyvinyl Chloride Dimethyl Thianthrene</u> The next material, for which the model parameters were determined, was polyvinyl chloride dimethyl thianthrene. The data for this material was provided by Dr. David Jones of the Wright Laboratories' Flight Dynamics Directorate and is contained in Appendix B [7]. The results of the curve fits are shown in Figure 5 and Figure 6. This material was chosen for this thesis since its viscoelastic data suggested it exhibited thermorheologically complex behavior. The model parameters for this material are listed in Table 2. Unlike polyisobutylene, the top curves on Figure 5 and Figure 6 correspond to the lowest temperature. Each curve below the preceding curve reflects the affects of progressively higher temperatures. The difference in the position of the lowest temperature curve is explained by the

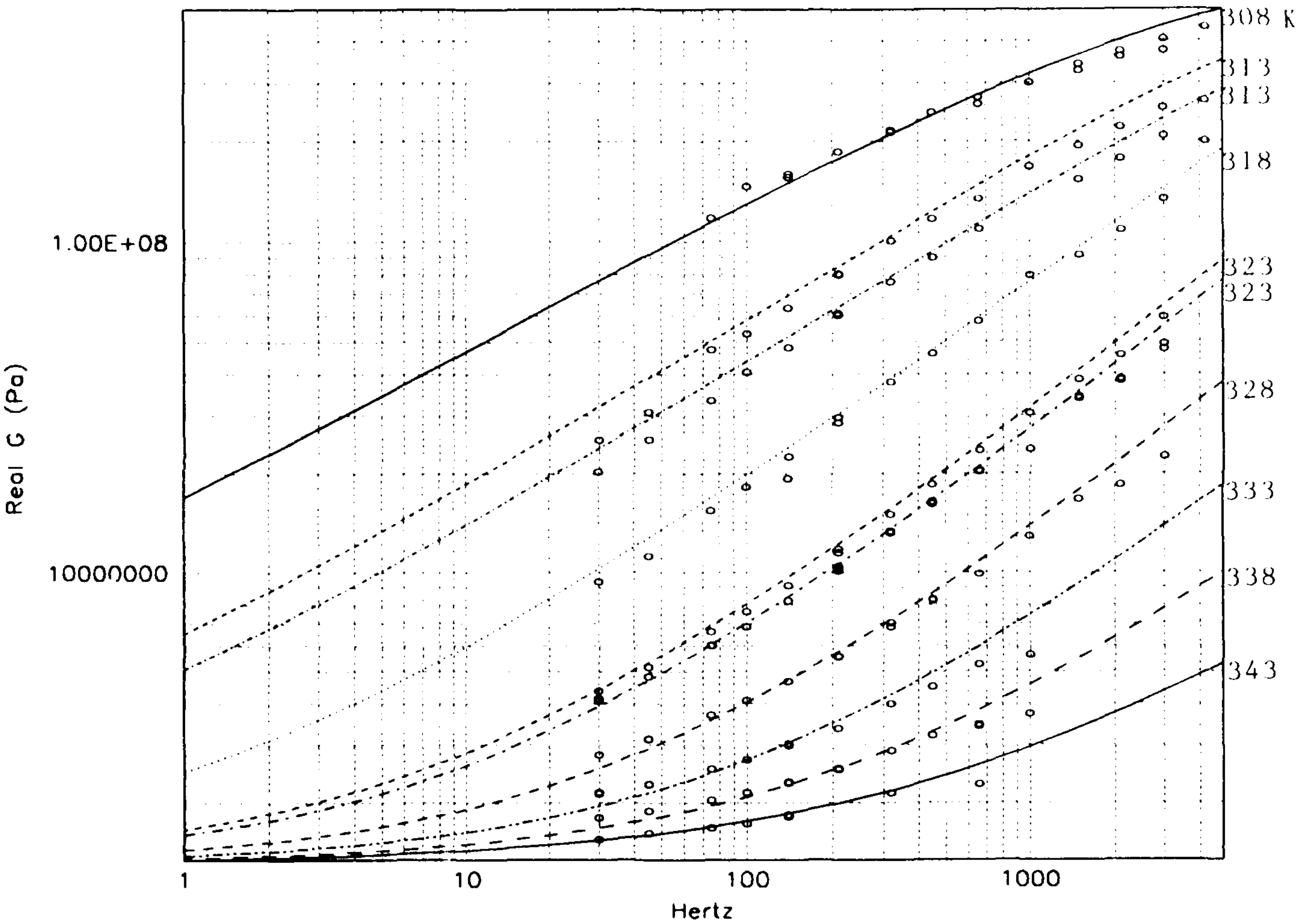

Fig 5. Modulus of Polyvinyl Chloride Dimethyl Thianthrene(R)

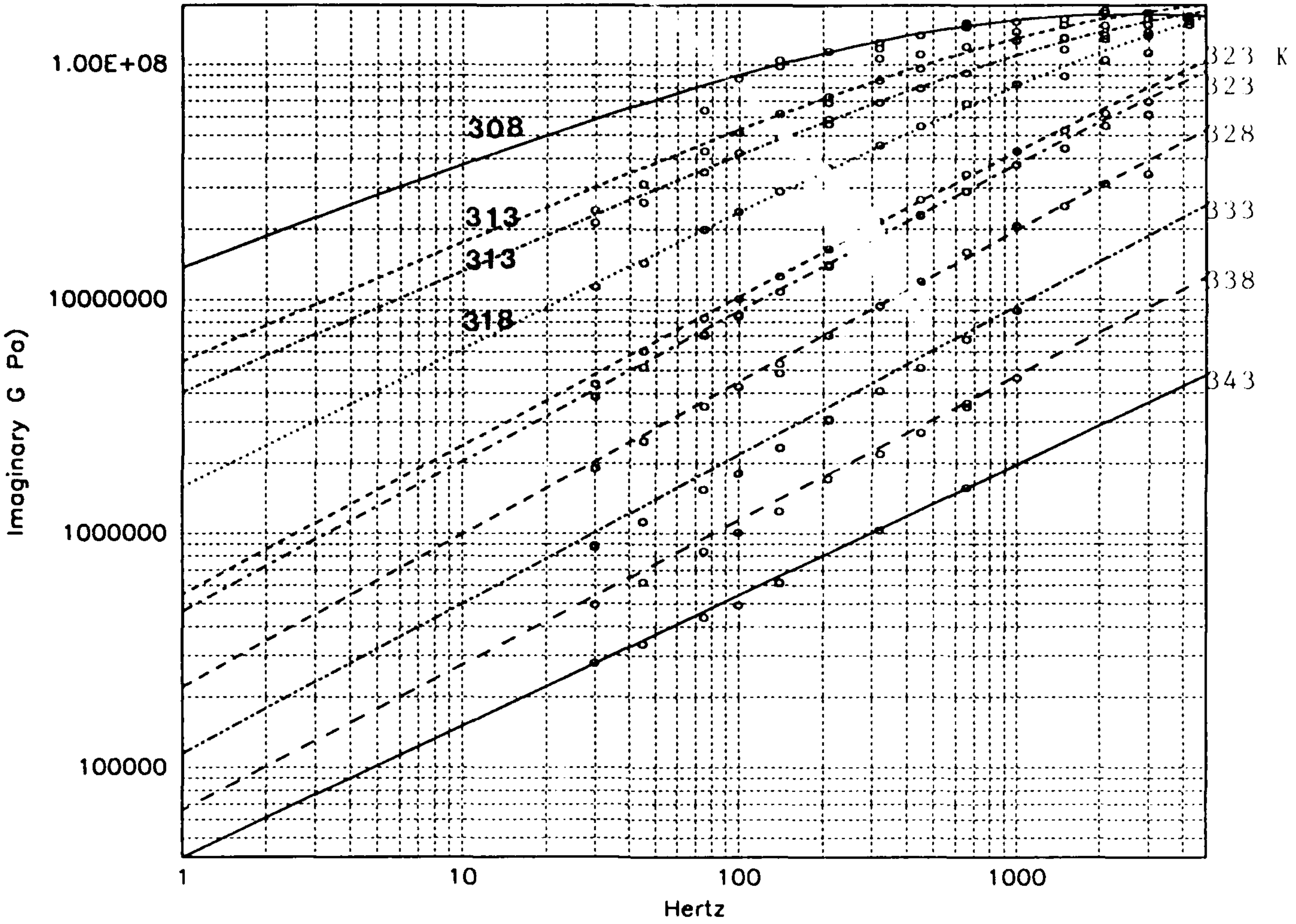

Fig 6. Modulus of Polyvinyl Chloride Dimethyl Thianthrene(I)

fact that the data and model curves presented for polyisobutylene were of the compliance modulus. The data and model curves presented for polyvinyl dimethyl thianthrene were of the shear modulus. The shear modulus will be presented for the remainder of the materials analyzed for this thesis. Again, it is also important to note the cutoff frequencies listed in Table 2 since they affect the four lowest temperature cases. The accuracy of the model is very good for most of the data, even at the frequencies above the cutoff point for the four lowest temperatures. Oddly, the accuracy starts to taper off at the higher frequencies and higher temperatures where conditions meet the requirements of Equation 7. This may suggest there are additional events happening at the molecular level during high frequency and/or high temperature conditions. These events affect the approximate and assumed equations governing the process of internal energy transitions and the underlying hypothesis of the fractional calculus model. These approximate and assumed equations, some of which are not directly testable at the molecular level, are based on theory themselves, but any influence on the equations by the environment is likely to influence the ability of the model to predict the viscoelastic behavior of a material accurately [3:5-8].

Table 2. Model Parameters for Polyvinyl Chloride Dimethyl Thianthrene

Temperature (K)	Alpha	Beta	Cutoff Frequency
307.61	6.200e-05	0.470	83.61
313.01	1.836e-05	0.520	392.44
313.03	1.102e-05	0.525	673.39
318.16	6.000e-06	0.595	1773.90
323.11	2.171e-06	0.640	5929.52
323.14	1.814e-06	0.645	7236.16
328.11	6.800e-07	0.655	20053.10
333.41	1.883e-07	0.640	68364.27
337.81	5.100e-08	0.620	232744.26
343.16	5.100e-09	0.560	1762338.11
G zero=8.5E8 Pa			
G infinity=1.31E6 Pa			

Examining the effects of temperature on the model parameters, Figure 7 and Figure 8 show the relationships of the shift parameter and the derivative order with temperature. The shapes of the curves of the shift parameter and derivative order as they vary with temperature are very similar to those of polyisobutylene. A pattern has started to develop and the pattern supports the idea of the thermorheologically complex material model.

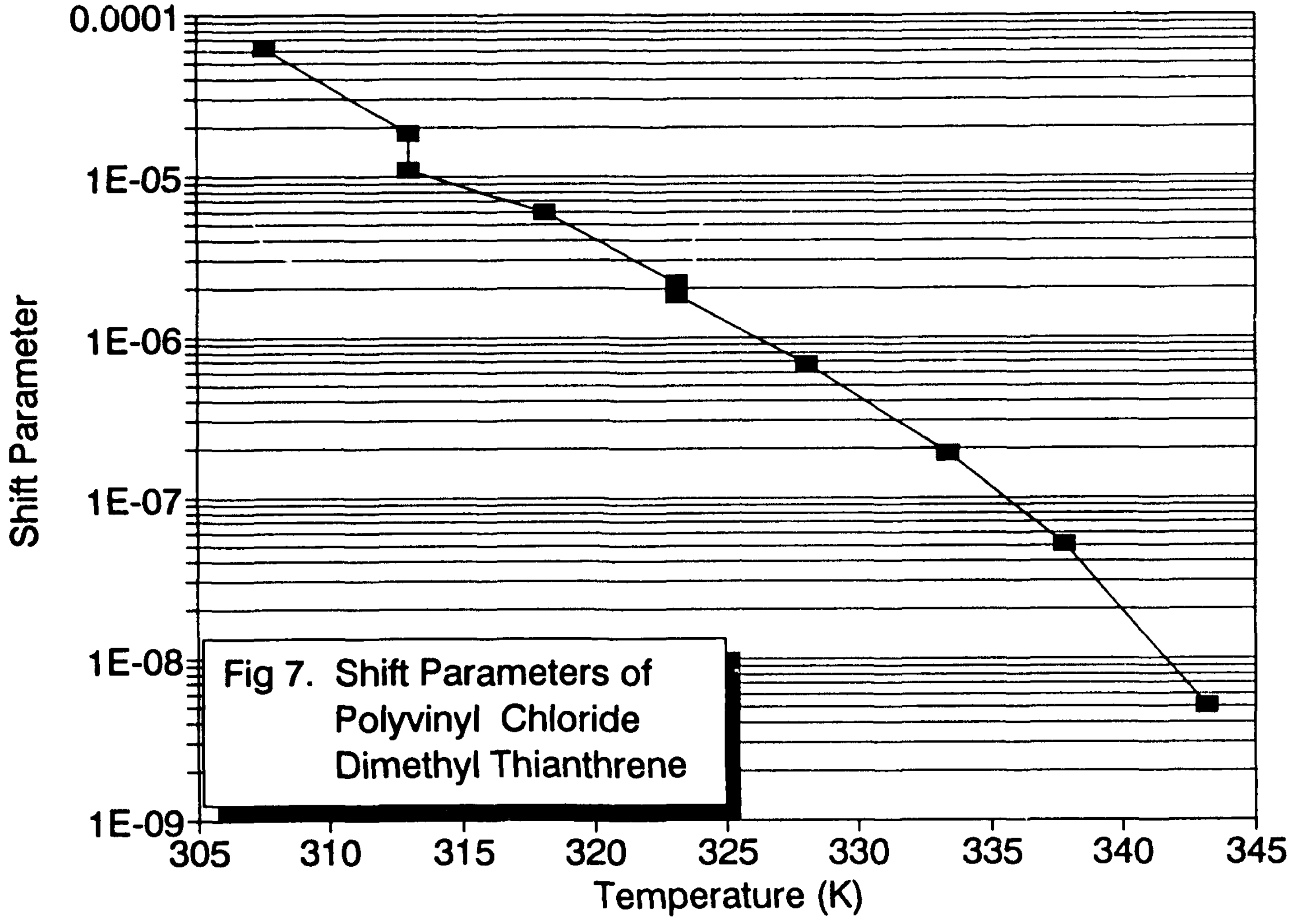

Fig 7. Shift Parameters of Polyvinyl Chloride Dimethyl Thianthrene

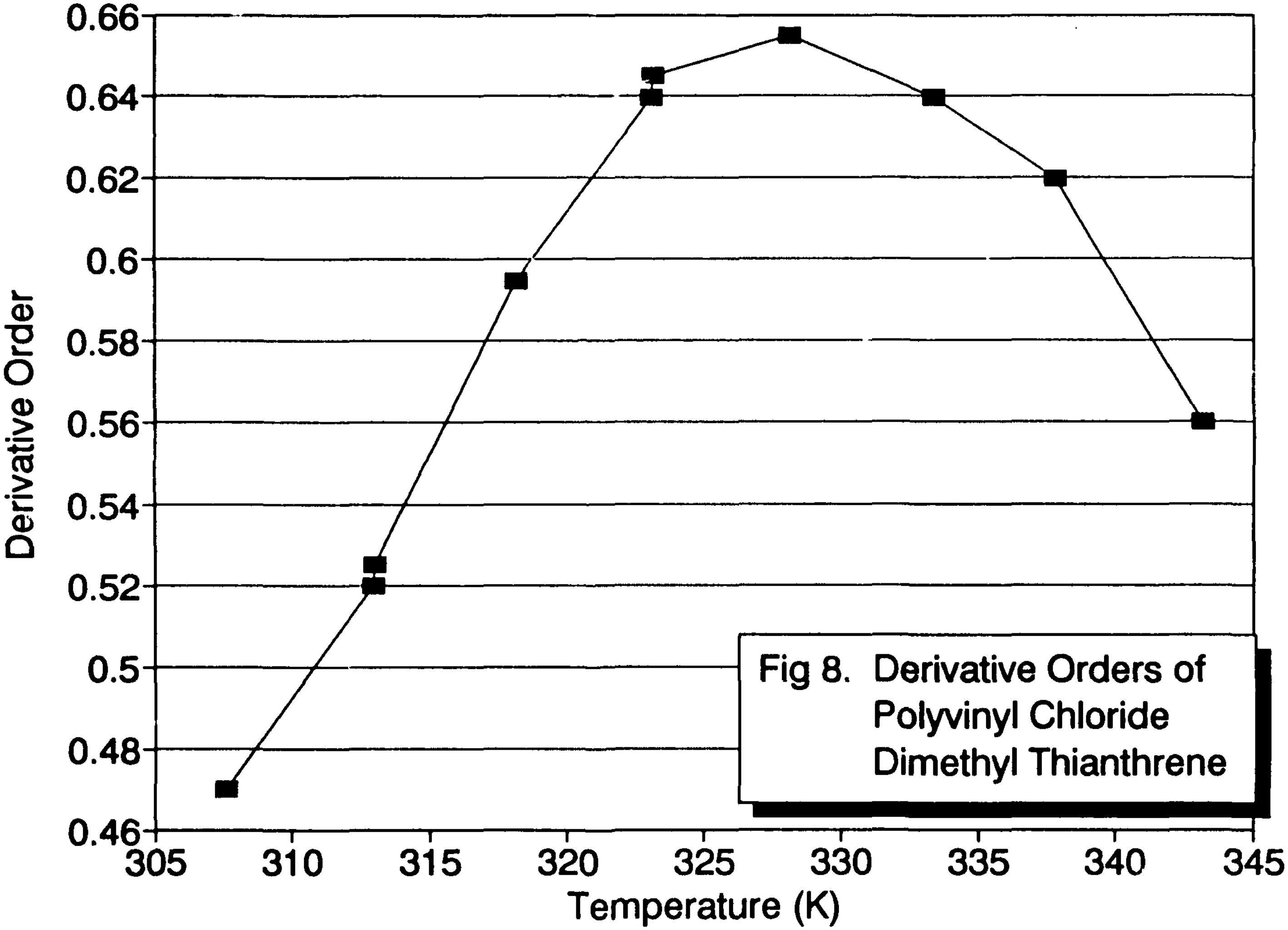

Fig 8. Derivative Orders of Polyvinyl Chloride Dimethyl Thianthrene

Atactic Polystyrene The next material analyzed was atactic polystyrene. Polystyrene was unique in the fact the modulus transitioned at a very low frequency. This is especially interesting since the available data suggests atactic polystyrene exhibits two distinct transitions with frequency. The other transition occurs at an even lower frequency range. This aspect of the data will be explored later. The analysis performed in this section deals with the data for the higher frequency transition. The data was obtained from Reference 1 [1:1237-1238].

Figure 9 and Figure 10 show the results of the curve fit performed with the atactic polystyrene viscoelastic data. Table 3 lists the parameters used to generate the model predictions shown in these figures. The accuracy of the model is good when the cutoff frequencies are observed, even though this double transition material is being modelled as a single transition material. The frequency dependent modulus of a double transition material increases from one modulus value to a higher value, stabilizes over a finite frequency range, and then increases to an even higher modulus value. For atactic polystyrene, the cutoff frequencies affects every temperature condition. At the peaks of the transition, the model departs significantly from the measured data, but the peaks all occur above the cutoff frequencies. Near the start of the

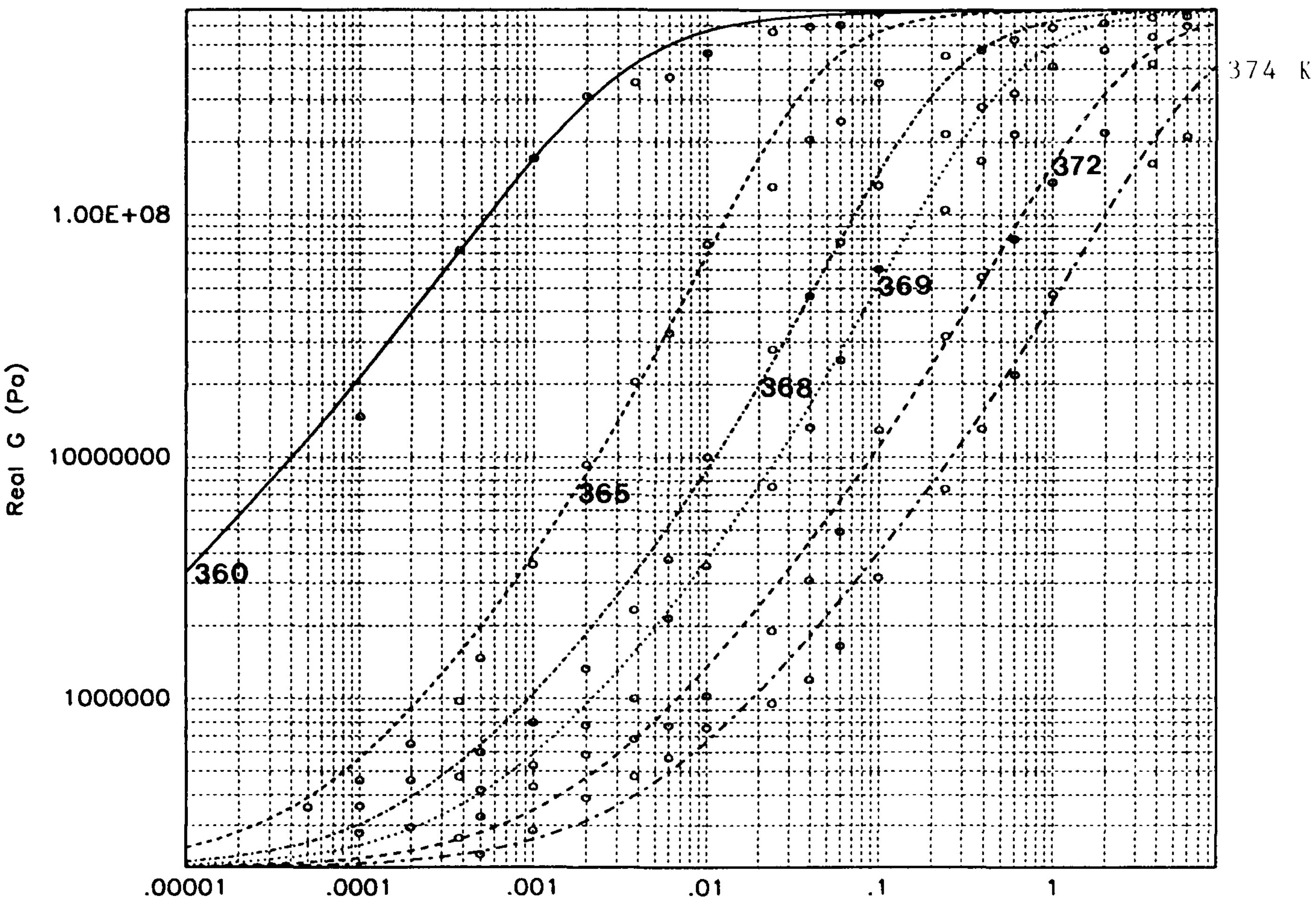

Fig 9. Shear Modulus of Atactic Polystyrene (R)

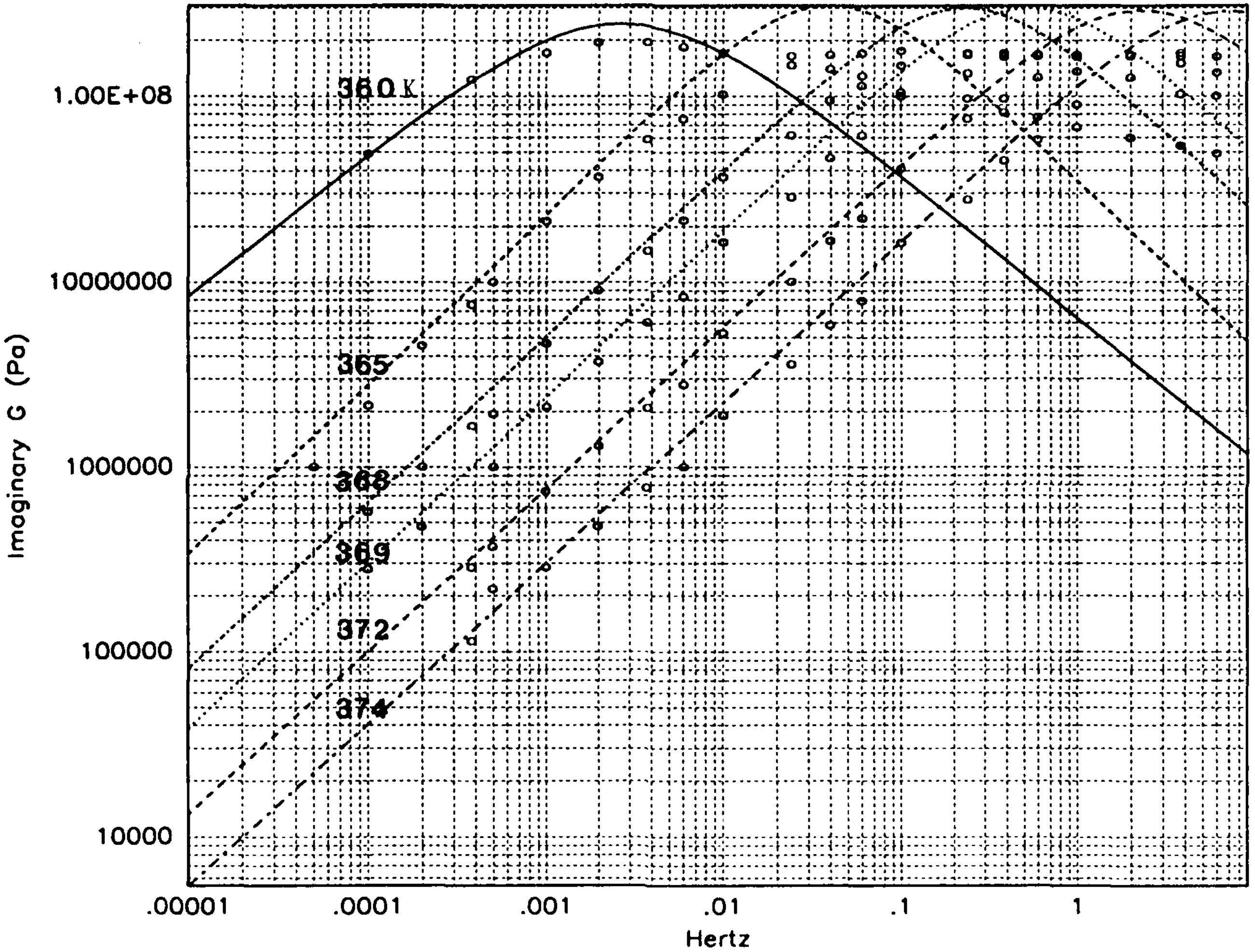

Fig 10. Shear Modulus of Atactic Polystyrene (I)

transition, the model also departs from the measured data generally more than in the two previous cases. This observation is probably explained by the fact that the start of the transition here is actually the end of another transition. Generally, the accuracy of the model is good outside of these trouble regions and the model always follows the trends of the data.

Table 3. Model Parameters for Atactic Polystyrene

Temperature (K)	Alpha	Beta	Cutoff Frequency
359.7	60.00000	0.780	0.00034
364.5	2.62560	0.920	0.01054
367.5	0.68570	0.900	0.03882
369.0	0.29710	0.900	0.08960
371.6	0.06991	0.880	0.36559
373.9	0.02259	0.872	1.11258
G zero=7.0E8 Pa			
G infinity=2.0E5 Pa			

The pattern noted earlier about the shape of the curves that describe the variation of the model parameters with temperature is also observed in atactic polystyrene. Figure 11 shows the relationship of the shift parameter with temperature exhibits the exponential behavior described earlier and Figure 12 shows the relationship of the derivative order with

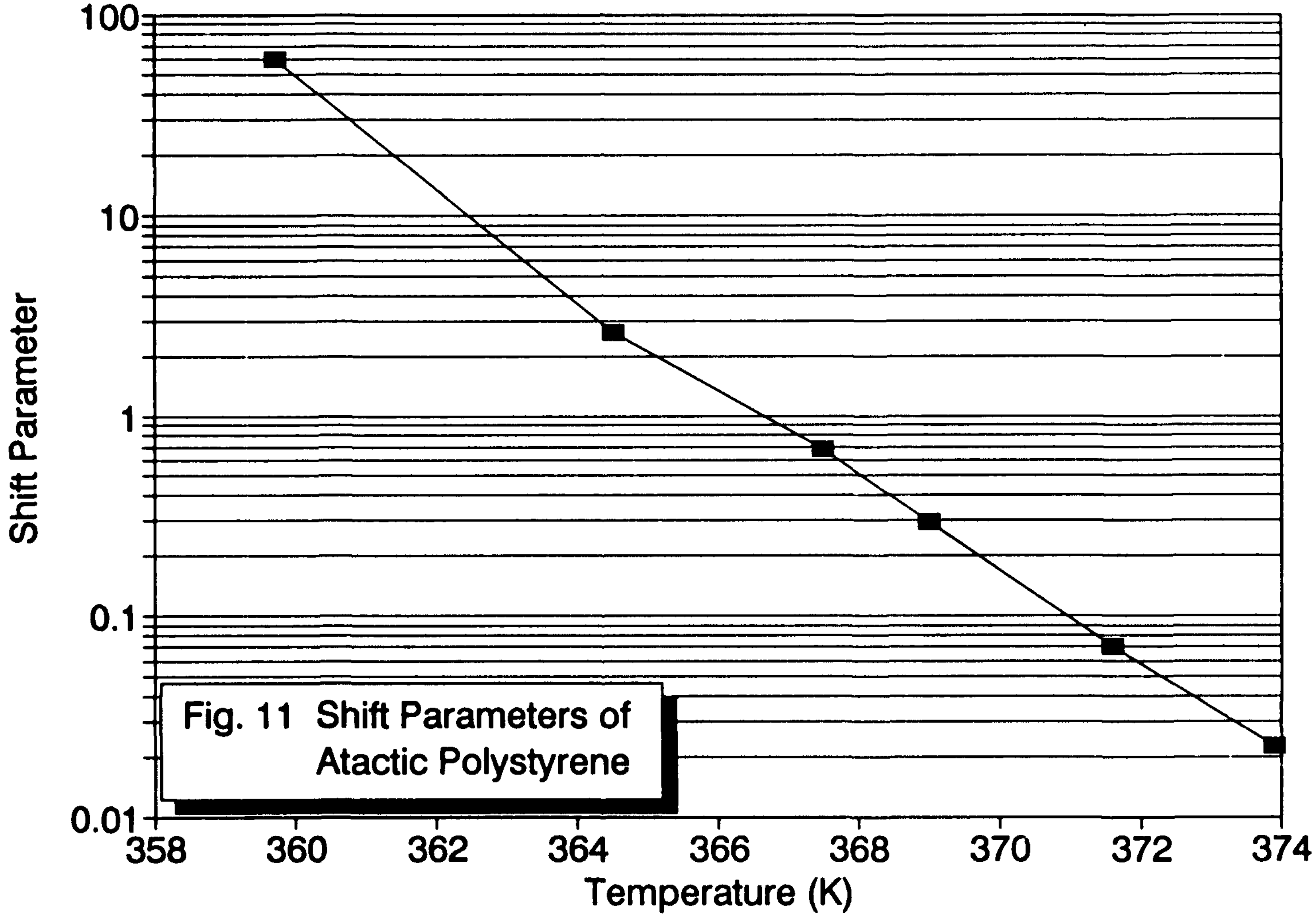

Fig. 11 Shift Parameters of Atactic Polystyrene

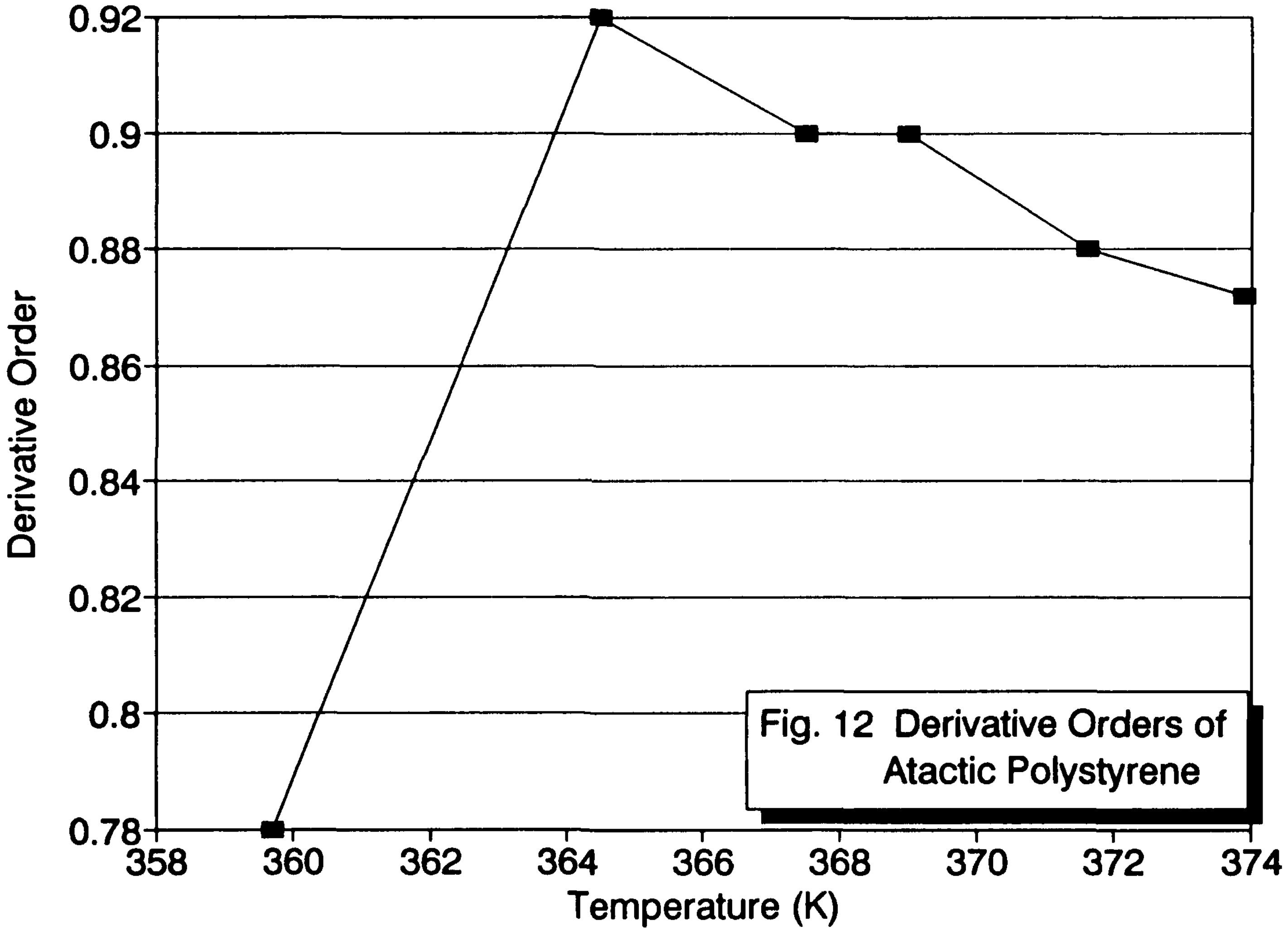

Fig. 12 Derivative Orders of Atactic Polystyrene

temperature resembles what may be a parabolic curve. The small number of temperature conditions is probably the reason the curve doesn't arc more, so additional data would be necessary to show conclusively that the pattern noted earlier is continued with atactic polystyrene. The pattern seems to hold clearly for the exponential behavior of the shift parameter. The varying of the parameters as a function of temperature continues to support the concept of the thermorheologically complex material.

C-1002 The final material analyzed was a material designated C-1002 and used by the Anatrol Corp. for specialized damping applications. The Mr. Paul Macioce of the Anatrol Corp. provided the data for the material, which is manufactured by the EAR Incorporated, Indianapolis, IN [8]. The data is listed in Appendix C. The results of the curve fits are shown in Figure 13 and Figure 14 and the model parameters are shown in Table 4. The measured data was unique because it seems to be data that is very close to the beginning of the transition region. Because of this condition, the imaginary portions of the moduli are noticeably curved as opposed to nearly straight lines as presented in the analysis of all of the other materials.

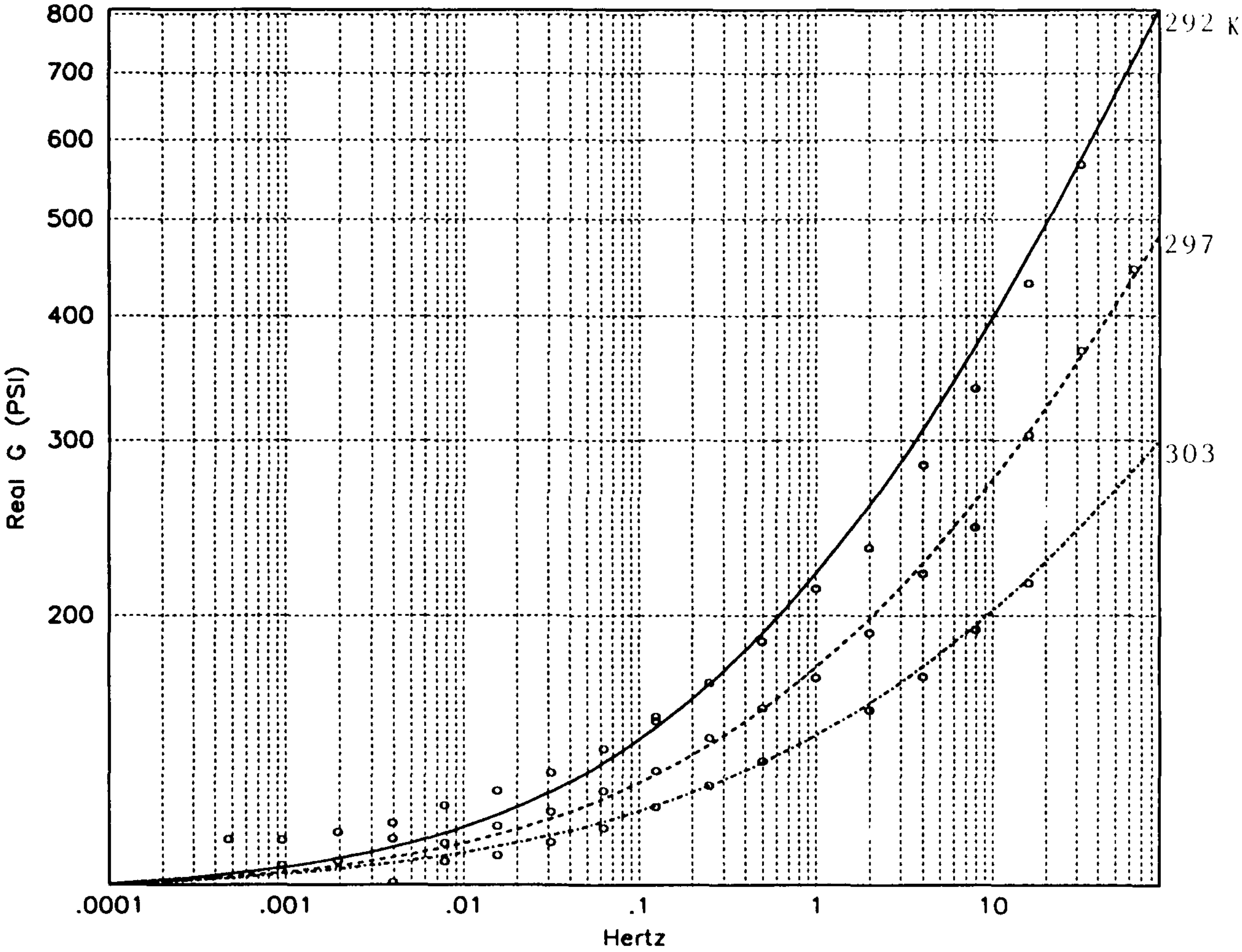

Fig 13. Shear Modulus of C-1002 (R)

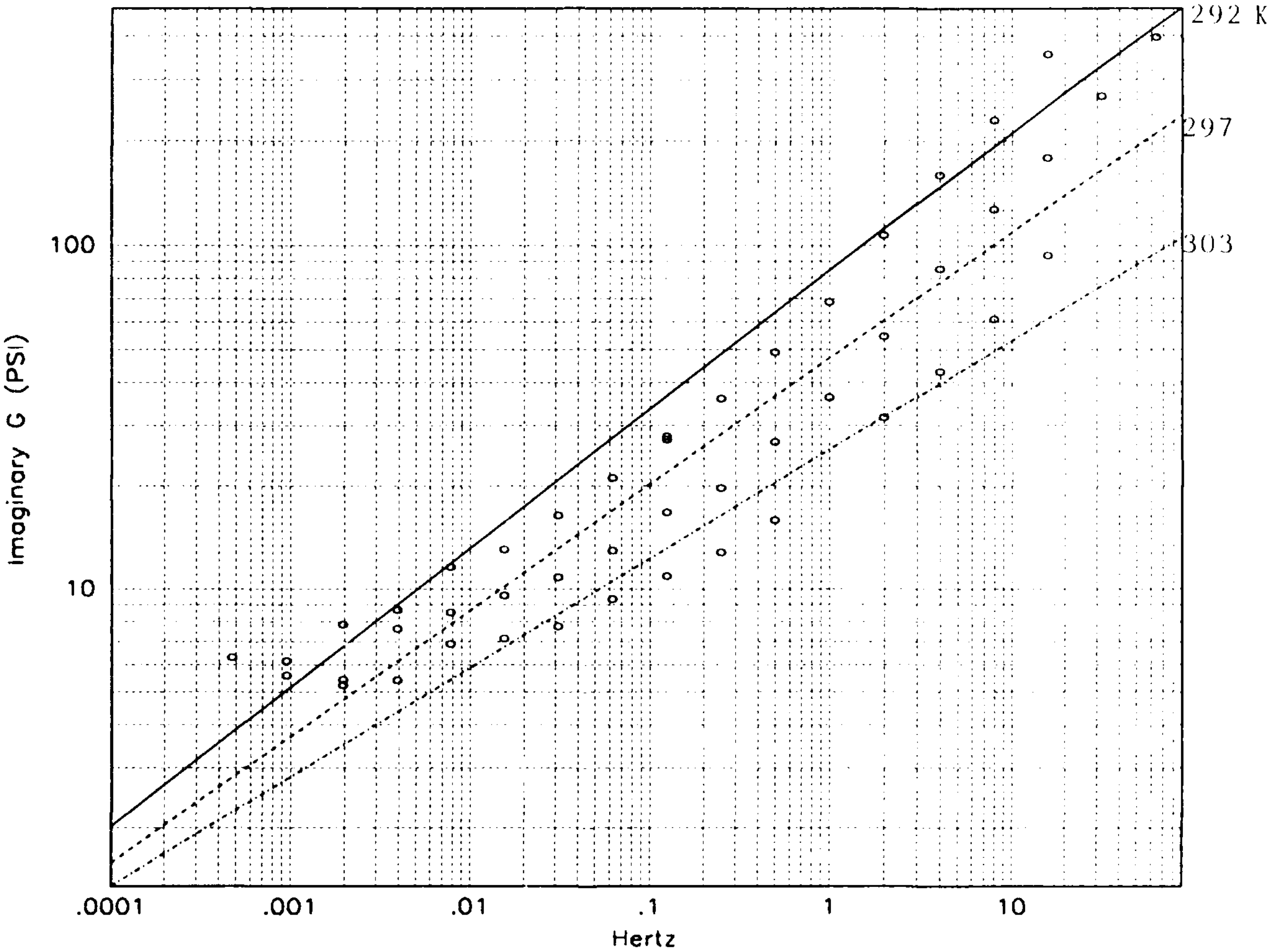

Fig 14. Shear Modulus of C-1002 (I)

Table 4. Model Parameters for C-1002

Temperature (K)	Alpha	Beta	Cutoff Frequency
292.0	2.925e-06	0.408	1053.25
297.0	2.410e-07	0.370	8525.01
303.0	6.500e-09	0.320	160186.35
G zero=12500 Psi			
G infinity=105 Psi			

The results of the curve fits are good for the real portion of the two highest temperature curves, but the accuracy of the prediction of the lowest temperature curves, which is the top curves of the figures, are not as good as what has been normally demonstrated by the model. In the imaginary portion of the curves, the model does not capture the curvature that is present in the measured data. The cutoff frequencies can be ruled out as an explanation since the frequency range analyzed in well below all of the cutoff frequencies. A possible hypothesis that explains the reduced accuracy of the results is that the data provided only represents one of the transitions the material exhibits. This material may have other transition regions above and below the frequency range presented in Figure 13 and Figure 14 that would explain the discrepancies. The single transition model was not developed to capture the effects of the other transition regions. It is important to note, when modelled using the fractional calculus transfer function, the predicted viscoelastic behavior of atactic polystyrene differs from the measured data slightly more than normal. This is more evidence to support the idea that events happening at lower frequency ranges are affecting the viscoelastic response of the material and therefore, the accuracy of the model. Another possible explanation is incorrect data, since one would expect the imaginary portion of the data to resemble a straight line based on an observation of the data of the other materials presented in this thesis.

Although there were only three temperatures analyzed for this material, the shapes of the model parameters curves as they vary with temperature were similar to those for the previous materials. They are shown in Figure 15 and Figure 16. Again, as noted in all the cases analyzed, the data supports the concept of the thermorheologically complex material.

Because the shapes of the curves of the shift parameter verses temperature and the derivative order verses temperature were similar for all of the materials modelled, there was an attempt to find analytical expressions to describe the relationships of both parameters have with temperature. Williams, Landel, and Ferry have derived an empirical equation to describe how the shift parameters of amorphous polymers

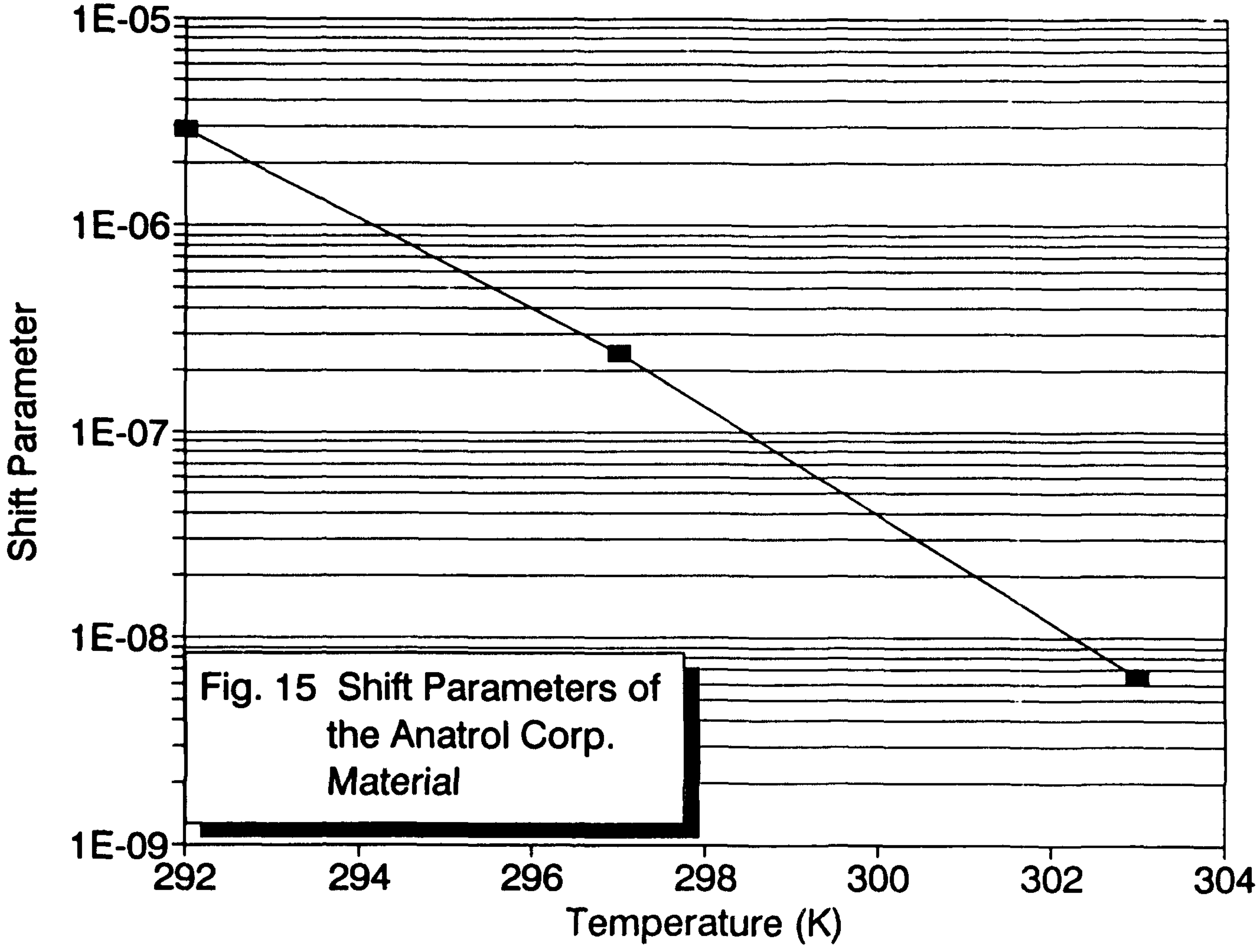

Fig. 15 Shift Parameters of the Anatrol Corp. Material

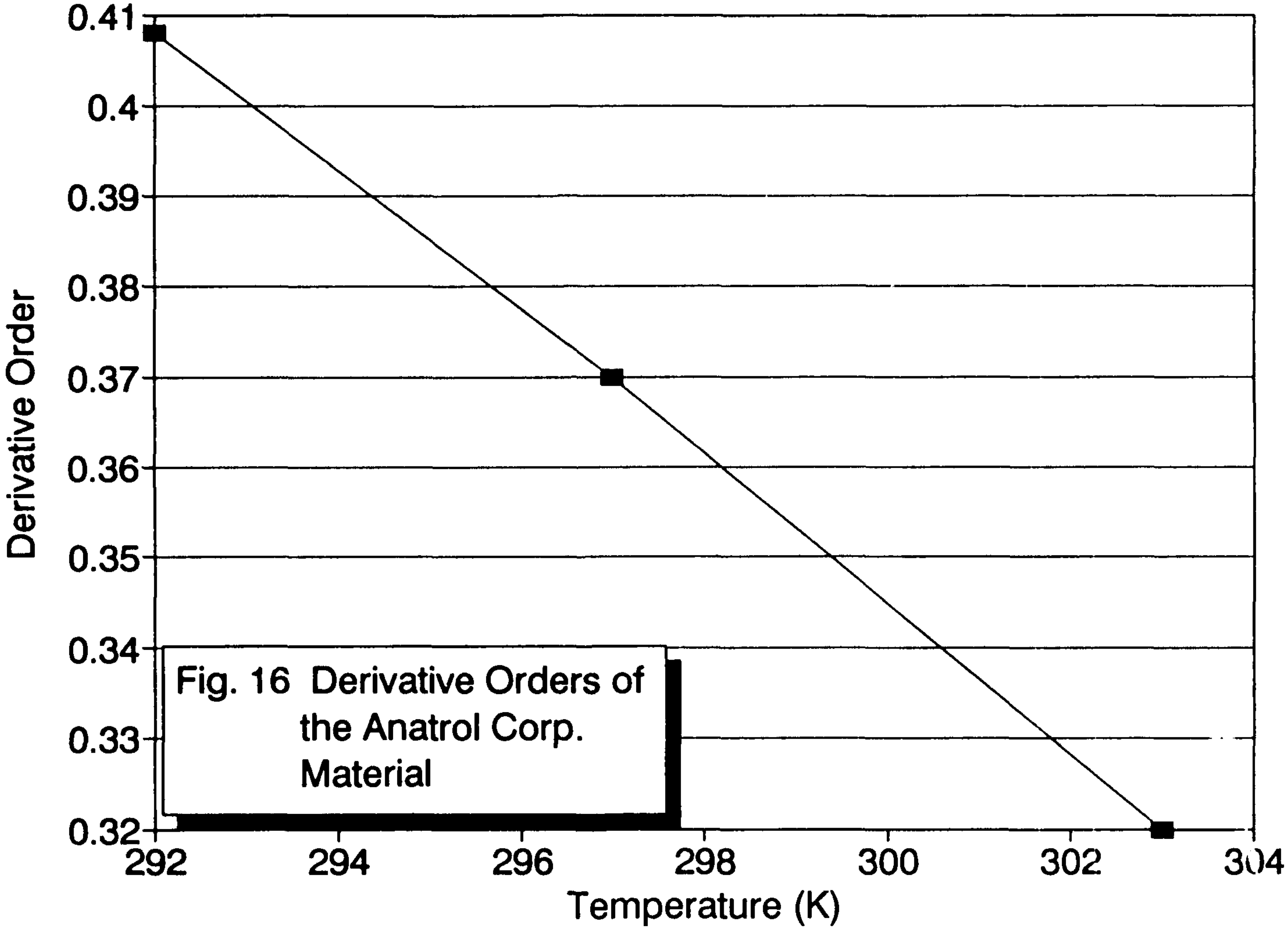

Fig. 16 Derivative Orders of the Anatrol Corp. Material

vary with temperature [9:3701]. The equation, referred to as the WLF equation is shown in Equation 9.

WLF Equation

$$\log\alpha = \frac{-8.86\,(T - T_s)}{101.6 + T - T_s} \qquad (9)$$

$$-50° < T - T_s < 50°$$

The equation assumes that there exist a reference temperature, T_s, that is constant and arbitrarily chosen [9:3701]. Using the parameters determined in this thesis within the WLF equation showed T_s was not constant for the system and the WLF equation did not provide a good analytical expression for how the shift parameter varies with temperature. Another possible analytical expression that describes how the shift parameter and the derivative order vary with temperature is the Arrhenius equation shown in Equation 10. The stress

Arrhenius Equation

$$\tau = \tau_o \exp\left(\frac{\Delta H}{RT}\right) \qquad (10)$$

relaxation time is τ, τ_o is a constant, ΔH is an activation relaxation time is τ, τ_0 is a constant, ΔH is an activation energy and R is the ideal gas constant. This equation is very similar to the transition rate parameter equation described in Reference 3 and shown in Equation 11 [3:5]. The transition

Transition Rate Parameter

$$\lambda_o = \nu(T)\exp\left(\frac{-\Delta}{kT}\right) \qquad (11)$$

rate parameter is λ_0, $\nu(T)$ is the energy barrier shape parameter, Δ is the energy barrier height parameter, and k is the Boltzman's constant. Comparing Equations 10 and 11, one will find that τ_0 of Equation 10 corresponds to λ_0 of Equation 11. Using this comparison and some additional relationships from Reference 3, shown in Equations 12 and 13, where $\theta(T)$ is the barrier distribution parameter, a modified Arrhenius relationship is hypotheized to exist. This expression,

$$\alpha^{\beta}(T) = \nu^{-\beta}(T)\Gamma(1+\beta)\Gamma(1-\beta) \qquad (12)$$

$$\beta(T) = \frac{T}{\theta(T)} \qquad (13)$$

shown in Equation 14, is very similar to an Arrhenius relationship. In the case of the thermorheologically complex material, the constant in the Arrhenius equation, τ_0,

Modified Arrhenius Equation

$$\tau = \tau_o(T)\exp\left(\frac{\Delta H}{RT}\right) \qquad (14)$$

can be described as a function of temperature. Unfortunately, because the transition rate parameter, τ_0 (λ_0), and the barrier energy, ΔH (Δ), change with temperature, it is not possible to check the Modified Arrhenius equation with just the parameter data resulting from the curve fits. The stress relaxation time, τ $(\nu(T))$, and the barrier distribution parameter, $\Theta(T)$, are easily calculated from Equations 12 and 13 respectively.

The results of the curve fitting task were very good. Most of the time, the model demonstrated the ability to predict accurately the viscoelastic behavior of the many different materials analyzed. The limitations of the model, specifically the cutoff frequency needs to be observed, but the model seems to be accurate well above the cutoff point. It is also important to recognize other significant conditions may be occurring that affect the equations used to govern the process of internal energy transformation in the material, an underlying hypothesis used by the model. These significant conditions and the influence of other transition regions over different frequency ranges may affect the accuracy of the model. The latter point will be examined in the following chapter. As stated earlier, the measured data for atactic polystyrene supports the idea that an additional transition region exists at a lower frequency range than examined during this analysis. The next chapter discusses the development of a double transition model as opposed to the single transition model used for this analysis.

V. Development of the Double Transition Model

For most physical phenomena in which a total understanding of the mechanisms that drive the process are unknown, one can find specimens that exhibit unexpected behavior if the examination of the phenomena is extensive enough. This situation exists in the viscoelastic behavior of certain materials. Materials that exhibit a frequency dependent modulus transition may actually exhibit multiple frequency dependent modulus transitions. The only method of learning if other transitions exists is by examining the viscoelastic behavior of the material in the frequency range of the transition, otherwise each transition appears distinct with its own "glassy" and "rubbery" modulus.

Atactic Polystyrene exhibits another frequency dependent modulus transition in the frequency range of 10^{-7} to 10^{-5} Hz. This frequency range equates to cycle periods from one day to four months. The data was obtained from Reference 1 along with the other atactic polystyrene data, but the data was provided at only one temperature (388 K) [1:1239-1240]. The remainder of this chapter discusses the development of a double transition viscoelastic model. This double transition model captured the viscoelastic behavior of atactic polystyrene over both of the modulus transition regions discussed previously.

Double Transition Model Development Equation 4 can be rewritten as:

Energy Transition Probability

$$\frac{E_{rel}(t) - E_{\infty}}{E_o - E_{\infty}} = \Phi(t) \qquad (15)$$

The probability that an energy transition has not occurred is, $\Phi(t)$ and it is defined by a β order Mittag-Leffler function. The probability is based on the assumption that the elevated internal energy states caused by the cyclic stressing of the material are randomly scattered throughout the material. When the elevated energy states transition to lower levels, they result in a slight temperature rise [3:9]. For the double transition model, the energy transition probability was assumed to be a linear combination of two Mittag-Leffler functions as shown in Equation 16. Equation 17 displays the restriction on the constants A1 and A2. The restriction forces a combination of the two Mittag-Leffler functions to represent the energy transition probability as opposed to multiples of the Mittag-Leffler functions representing the energy transition probability. Actually, the constants are easily determined from measured viscoelastic data. The constants represent the respective percentage of modulus change compared to the total modulus change over both transition regions.

Because the mathematical operations were easier, it

Double Transition Model

Energy Transition Probability

$$\frac{E_{rel}(t) - E_{\infty}}{E_{o} - E_{\infty}} = \Phi(t) = A1[E_{\beta_1}(-(\frac{t}{\alpha_1})^{\beta_1})] + A2[E_{\beta_2}(-(\frac{t}{\alpha_2})^{\beta_2})] \quad (16)$$

$$A1 + A2 = 1 \quad (17)$$

was more convenient to develop the model in the Laplace domain. Equation 18 shows the result of taking the Laplace transform of the relaxation modulus derived from Equation 16. Using the fundamental stress-strain relationship shown in

Laplace Domain Relaxation Modulus

$$E_{rel}(s) = \frac{E_{\infty}}{s} + (E_{o}-E_{\infty})\,[A1[\frac{s^{\beta_1-1}}{s^{\beta_1}+\alpha_1^{-\beta_1}}] + A2[\frac{s^{\beta_2-1}}{s^{\beta_2}+\alpha_2^{-\beta_2}}]] \quad (18)$$

Equation 19, an expression for the Young's modulus can be obtained. Shown along with Equation 19, Equation 20 is the Laplace domain form of the stress-strain relationship. The result of applying Equation 20 to Equation 18 is the Laplace

Fundamental Stress Strain Relation

$$\sigma(t) = \frac{d}{dt}\int_0^t E_{rel}(\tau)\,\varepsilon(t-\tau)\,d\tau \qquad (19)$$

Laplace Domain

Fundamental Stress Strain Relation

$$\sigma(s) = s[E_{rel}(s)\varepsilon(s)] \qquad (20)$$

domain Young's modulus expression shown in Equation 21. With a fair amount of algebra, Equation 21 can be rewritten into the form of a transfer function. This transfer function, displayed in Equation 22, is the double transition viscoelastic model. Equation 21 will be used later as the starting point for the thermodynamic analysis since it avoids the cross terms in Equation 22.

Laplace Domain Young's Modulus Equation

$$\frac{\sigma(s)}{\varepsilon(s)} = E(s) = E_\infty + A1(E_o - E_\infty)\frac{s^{\beta_1}}{s^{\beta_1}+\alpha_1^{-\beta_1}} + A2(E_o - E_\infty)\frac{s^{\beta_2}}{s^{\beta_2}+\alpha_2^{-\beta_2}} \qquad (21)$$

Double Transition Viscoelastic Model

$$E(s) = \frac{E_\infty[A2(\alpha_1^{\beta_1}s^{\beta_1} - \alpha_2^{\beta_2}s^{\beta_2}) + 1] + E_o[\alpha_1^{\beta_1}\alpha_2^{\beta_2}s^{\beta_1+\beta_2} + (1-A2)\,\alpha_1^{\beta_1}s^{\beta_1} + (2-A2)\,\alpha_2^{\beta_2}s^{\beta_2}]}{\alpha_1^{\beta_1}\alpha_2^{\beta_2}s^{\beta_1+\beta_2} + \alpha_1^{\beta_1}s^{\beta_1} + \alpha_2^{\beta_2}s^{\beta_2} + 1} \qquad (22)$$

Although the double transition model is similar to the previous model, the effect of the extra transition region added several higher order terms and increased the total number of model parameters to seven. Three of the model parameters, the "glassy" modulus, the "rubbery" modulus, and the A2 constant, are not temperature dependent and could be determined directly from measured viscoelastic data.

As a quick check to insure the model follows expected trends, the double transition viscoelastic model was examined at very low frequencies. Very low frequencies correspond to s approaching zero in the Laplace domain. It also was examined at very high frequencies. Very high frequencies correspond to s approaching infinity in the Laplace domain. At very low frequencies, the modulus should approach the "rubbery" modulus and at very high frequencies, the modulus should approach the "glassy" modulus. Both conditions held true for the case of the double transition model.

The same assumptions used for the single transition viscoelastic model were employed for the double transition model, so the restriction shown in Equation 7 is still applicable.

Because the model contained two sets of model parameters that consisted of a shift parameter and the derivative order, there existed two cutoff frequencies, one corresponding to each set. The set of parameters corresponding to the first transition region would be expected to have a lower cutoff frequency than that of the second transition region. For that portion of the frequency range that would be above the first cutoff frequency, a small amount of error would be introduced. Some error would be introduced in the second transition region as well since the viscoelastic behavior model was based on the effects of both transition regions and their effects on each other.

Curve Fit Procedure Changes Most the procedures used to curve fit the measured viscoelastic data with the single transition model were still used with the double transition model. The "glassy" and "rubbery" moduli were determined just as they were determined earlier. The A2 constant could be calculated by finding the change in the modulus from the beginning to the end of the second transition region and the total change in the modulus over both transition regions. The A2 constant is the fraction of the change in modulus over the second transition region divided by the total change in the modulus over both transition regions. The remainder of the parameters were determined using the same procedure described earlier. With the first shift parameter and derivative order corresponding to the first transition region and the second set of these parameters corresponding to the second transition region. The effects caused by varying theses parameters were the same as described earlier.

One major difference occurred while using the double transition model. The user had to consider that changes in one transition region would affect the other transition region. This complicated the curve fitting process and required more iterations than were performed using the single transition model to determine the model parameters.

Accuracy of the Double Transition Model As stated earlier, atactic polystyrene was the only material in which the measured viscoelastic data showed the material exhibited two frequency dependent modulus transitions. Although, many materials may have multiple modulus transition regions, the data necessary to learn if a material exhibited this viscoelastic behavior would normally be required to have a very wide frequency range and data such as this seems rare.

Because the data of atactic polystyrene at 388 K was the only data used to evaluate the accuracy of the double transition model, no real conclusions can be made from the

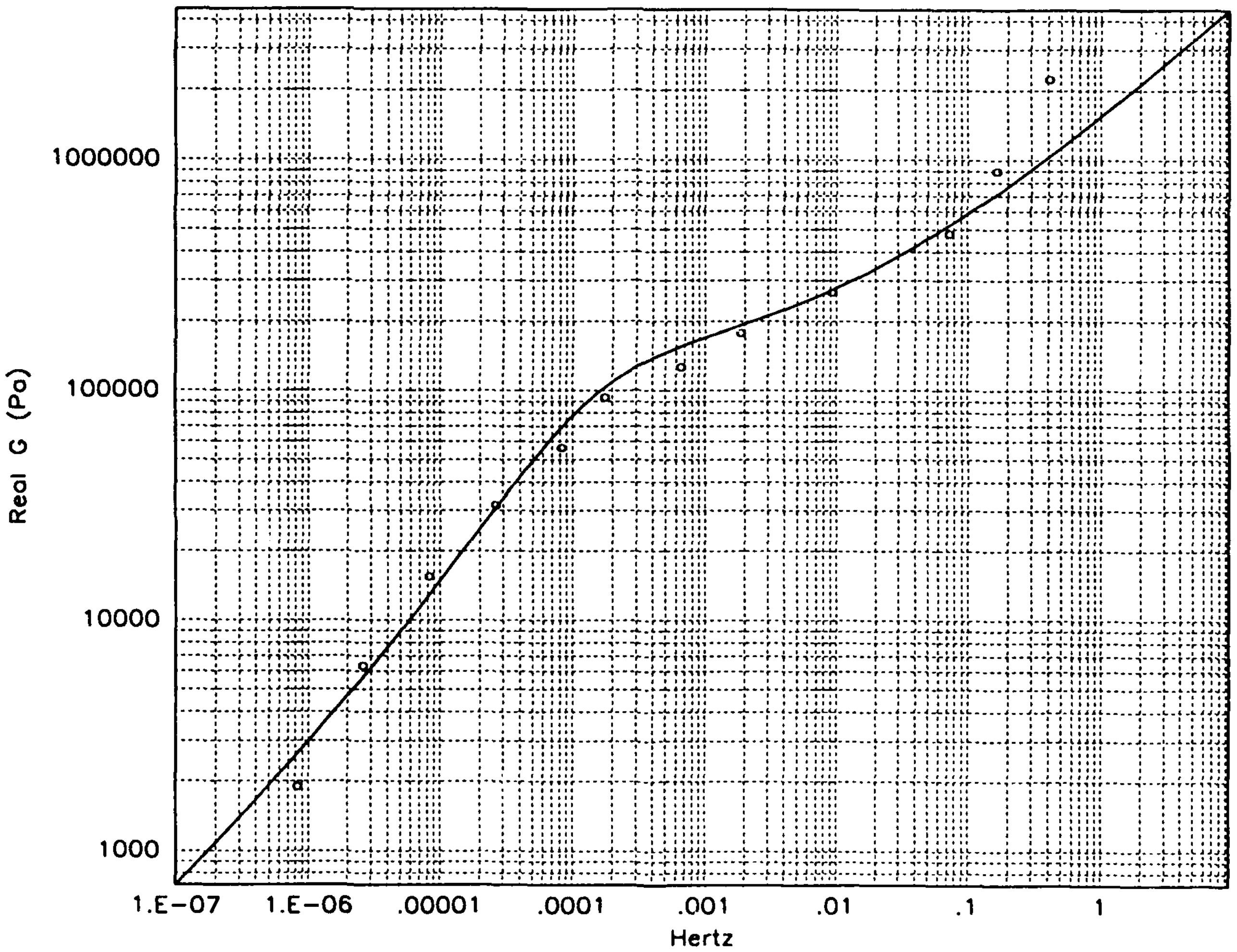

Fig 17. Shear Modulus of Atactic Polystyrene (2T-R)

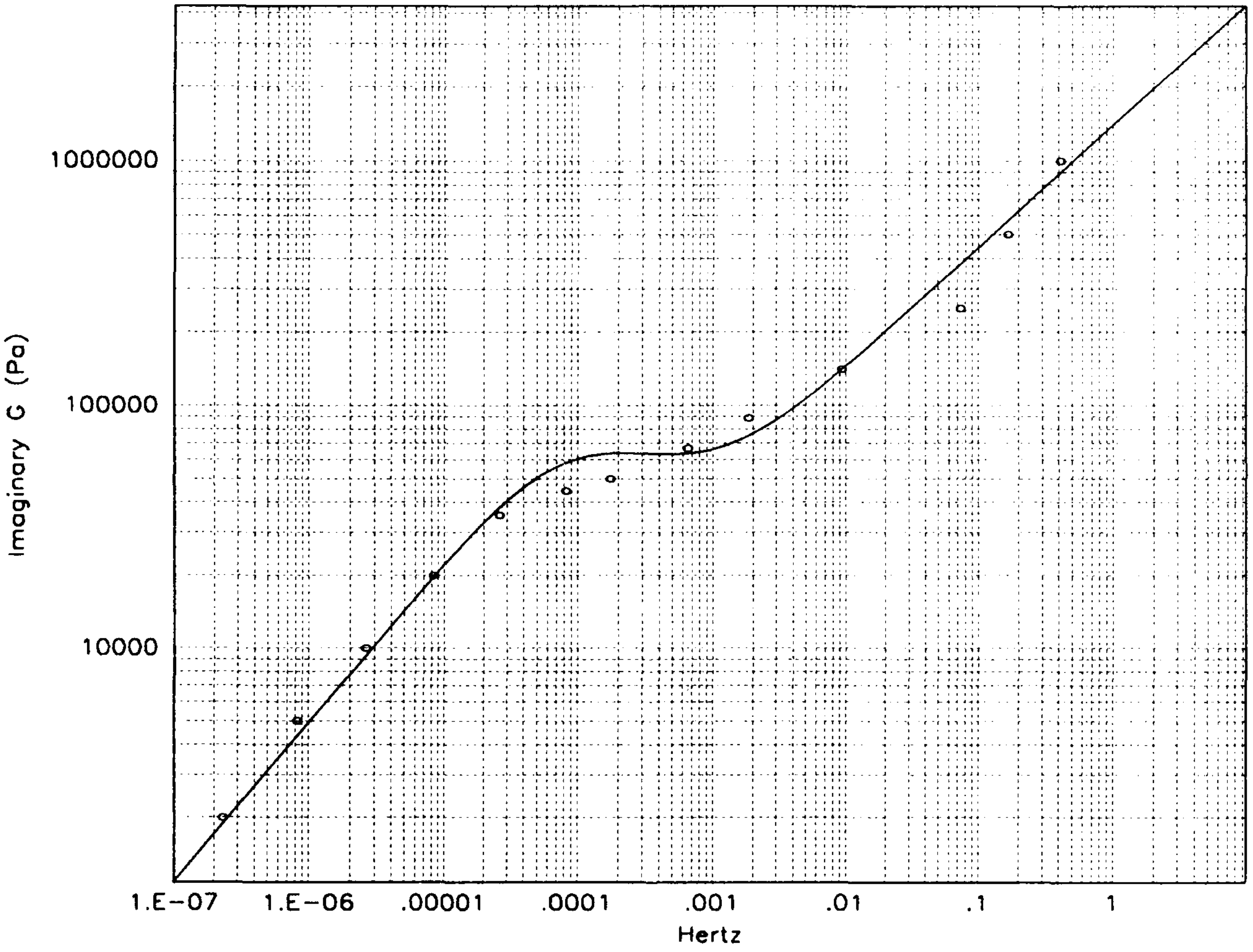

Fig 18. Shear Modulus of Atactic Polystyrene (2T-I)

results. Figure 17 and Figure 18 show the result of the curve fit performed using the double transition model. The model accurately predicts the viscoelastic behavior over the vast majority of the frequency range, but departs at the end of the frequency range for the real portion of the modulus. The prediction for the imaginary portion of the modulus was very good, even at the end of the frequency range. The parameters used to generate the model curves in Figure 17 and Figure 18 are shown in Table 5 . A significant portion of the data is above the first cutoff frequency, but all of the data is below the second cutoff frequency. Since there is only one set of data, it is impossible to tell if this curve fit is typical of the results achievable with this model, but considering the data covered over five decades of frequency, the performance of the model should be considered satisfactory for many applications.

Caution would force one to recognize this analysis was performed for only one material at one temperature. Caution would force one to also recognize the model results and the measured data diverged at the end of the frequency range for the real portion of the modulus, but the analysis did show some positive things as well. Although no conclusions can be made about the success of the extension of the single transition viscoelastic model to the double transition model, the model does accurately predict the viscoelastic behavior of atactic polystyrene over a wide frequency range. The model also followed expected trends for the low and high frequency conditions a material would experience while transitioning. These positive characteristics and the fact that the imaginary and the real portion of the modulus are obtained simultaneously using only the seven parameters in the model lends credibility to the double transition model. To examine further the validity of the double transition model, the next chapter will apply thermodynamic principles to the model to insure the results are realistic.

Table 5. Double Transition Model Parameters for Atactic Polystyrene

Temperature (K)	1st Alpha	2nd Alpha	1st Beta	2nd Beta	A1 Coefficient	1st Cutoff Frequency	2nd Cutoff Frequency
388.0	1348.0	6.4e-07	0.75	0.50	0.9998	0.00001	9947.18
G zero=7.0E8 Pa							
G infinity=0 Pa							

VI. Application of the Principles of Thermodynamics

Approach The approach taken examines the results of a viscoelastic material undergoing a sinusoidal strain. The temperature of the material will be assumed to be constant even with the external sources of heat and the dissipation of internal energy. It is possible for the temperature of a specimen of material to remain fairly constant if that material is undergoing a uniform, steady-state strain, the conductivity of the material is high, and the specimen is sufficiently small [10:138-139].

If the strain is sinusoidal, as defined by Equation 23,

Sinusoidal Strain

$$\varepsilon(t) = Sin\omega_o t \qquad (23)$$

then the resulting stress when the transients decay will be sinusoidal as well with an in phase portion and an out of phase portion that can be written in the form shown in Equation 24. The expression for the rate of internal work

Sinusoidal Stress

$$\sigma(t) = XSin\omega_o t + YCos\omega_o t \qquad (24)$$

shown in Equation 25 can then be determined from Equations 23

Rate of Internal Work

$$\sigma(t)\frac{d}{dt}[\varepsilon(t)] = X\omega_o Cos\omega_o t\ Sin\omega_o t + Y\omega_o Cos^2\omega_o t \qquad (25)$$

and 24 [10:139]. The Sin(ω_0t) in the first term results from the stress response and is apart of the component of the rate of work that is in phase with the strain. The Cos(ω_0t) in the second term, which also results from the stress response, represents the part of the rate of work that is out of phase with the strain. The phase difference in the two terms, ninety degrees, is equivalent to the phase difference between a purely real and purely imaginary value. In a direct comparison to the complex modulus, the in phase response to a real strain is the real portion of the modulus and it corresponds to the first term on the right side of Equation 25. The out of phase response to a real strain is the imaginary portion of the modulus and it corresponds to the second term on the right side of Equation 25. When the temperature of the material is constant, the expression is also equivalent, term by term, to the thermodynamic statement shown in Equation 26, which is a statement of the First Law of Thermodynamics, where d/dt(p)

1st Law of Thermodynamics

$$\frac{d}{dt}(p) = \frac{d}{dt}(\psi) + \delta \qquad (26)$$

is the rate of mechanical internal work, d/dt(Ψ) is the rate of change in the free energy, and δ is the rate of energy dissipated.

The results of this approach show the components of the complex modulus actually represent internal energy relationships. The real portion of the modulus represents the amount of internal energy stored by the material and the imaginary portion of the modulus represents the amount of energy dissipated by the material. By applying the Second Law of Thermodynamics to this concept of the modulus, it follows that the energy stored by the material and the energy dissipated by the material must both be positive quantities. To insure the double transition model meets the conditions that the stored and dissipated energies are positive quantities for all positive frequencies, the constraints shown in Equations 27a and 27b must be satisfied. Satisfying these constraints will lead to certain restrictions on the model parameters that will then force the model to predict viscoelastic behavior that is consistent with the Second Law of Thermodynamics.

Thermodynamic Constraints

$$Re[E(\omega)] \geq 0 \qquad (27a)$$

$$0 < \omega < \infty$$

$$Im[E(\omega)] \geq 0 \qquad (27b)$$

$$0 < \omega < \infty$$

Results The first step in analyzing the double transition model was to break the model into its real and imaginary components. Equation 21 was used as the starting point. This form of the frequency dependent modulus equation avoids the cross terms that would occur if the entire transfer function were separated into its real and imaginary components. The real and imaginary components were obtained by multiplying the numerator and denominator of each term by the complex conjugate of the denominator of that term. Since the denominators are always positive once multiplied by their conjugates, the thermodynamic constraints are satisfied by placing the restrictions on model parameters in the numerators of each term. Normally, it would be expected that the expression would be combined into the standard form of a transfer function. Because the entire transition region was assumed to be described by the linear combination of two

Mittag-Leffler functions and multiplication being a distributive operation, the terms in the model could remain separate for multiplication by the conjugate. Equation 28 shows the combined sum of the real components of numerator terms. Equation 29 shows the combined sum of the imaginary components of the numerator terms. The restrictions on the model parameters can easily be determined from these equations by examining two cases. The first case is the condition as the frequency becomes very small. Taking the limit of Equations 28 and 29 as frequency goes to zero leads to one of the restrictions on the model parameters. This restriction, shown in Equation 30, is necessary to satisfy the

Real Component of the Model

$$E_\infty + (E_o - E_\infty)\,[A1\alpha_1^{\beta_1}\omega^{\beta_1}Cos(\frac{\beta_1\pi}{2}) + A1\alpha_1^{2\beta_1}\omega^{\beta_1}$$

$$+A2\alpha_2^{\beta_2}\omega^{\beta_2}Cos(\frac{\beta_2\pi}{2}) + A2\alpha_2^{2\beta_2}\omega^{\beta_2}] \qquad (28)$$

Imaginary Component of the Model

$$(E_o - E_\infty)\,[A1\alpha_1^{\beta_1}\omega^{\beta_1}Sin(\frac{\beta_1\pi}{2}) + A2\alpha_2^{\beta_2}\omega^{\beta_2}Sin(\frac{\beta_2\pi}{2})] \qquad (29)$$

thermodynamic constraints. The next case is the condition at all other frequencies. To meet the thermodynamic constraints

Model Parameter Restriction - 1

$$E_\infty \geq 0 \qquad (30)$$

for this second case, all terms in both equations must remain positive for all positive frequencies. The assumptions listed in Equations 31a and 31b concerning the derivative orders of the model are important factors in the analysis of this case. Because of these two assumptions, the Cos($\beta_1\pi/2$), Sin($\beta_1\pi/2$), Cos($\beta_2\pi/2$), and Sin($\beta_2\pi/2$) terms are positive for all positive frequencies since the arguments of the trigonometric functions remain in the first quadrant. The remaining restrictions for the conditions of the second case can be determined by observation and are listed in Equations 32a through 32e. These restrictions insure all the terms in both the real and imaginary components remain positive. The model parameter restrictions shown in Equations 30 and 32 are necessary for the double transition model to predict viscoelastic behavior consistent with thermodynamic

Derivative Order Assumptions

$$0 \leq \beta_1 \leq 1 \qquad (31a)$$

$$0 \leq \beta_2 \leq 1 \qquad (31b)$$

constraints. It follows that the parameters used to model the viscoelastic behavior of atactic polystyrene in the previous

Model Parameter Restrictions - 2

$$E_o \geq E_\infty \qquad (32a)$$

$$A1 \geq 0 \qquad (32b)$$

$$A2 \geq 0 \qquad (32c)$$

$$\alpha_1 \geq 0 \qquad (32d)$$

$$\alpha_2 \geq 0 \qquad (32e)$$

chapter should and does meet the restrictions listed in Equations 30 and 32. This observation was obtained by comparing the model parameters of Table 5 to the model parameter restrictions. The ability of the model to meet the thermodynamic constraints adds support to the validity of the results obtained fr om the double transition model.

VII. Conclusions and Recommendations

The research presented by this thesis was to accomplish three objectives. The first objective was to validate the ability of a previously developed viscoelastic model to model accurately the frequency dependent viscoelastic behavior of thermorheologically complex materials. This model was based on a theory of energy transitions at the molecular level that led to a fractional derivative order model of viscoelastic behavior. The model assumes one transition between a steady state modulus value and a maximum modulus value that occurs when the material is in an excited state. The second objective involved extending the model described above to account for two distinct transitions between the steady state modulus value and the maximum modulus value. This second objective was caused by the observation that the measured viscoelastic data for atactic polystyrene, as frequency was varied, exhibited at least two transitions. The third and final objective of the thesis applied the First and Second Laws of Thermodynamics to the double transition model. By applying these thermodynamic principles to the double transition model, favorable results would add support to the validity of the model results.

The single transition model was used to predict the viscoelastic behavior of polyisobutylene, polyvinyl chloride dimethyl thianthrene, atactic polystyrene, and C-1002 with good results for most of the materials. The model also supported the concept of the thermorheologically complex material. Users of this model must remember that the model does involve some assumptions. The accuracy of some assumptions and therefore, the accuracy of the model may be affected by environmental conditions. The assumptions that need to be considered include the molecular energy theory used as the basis of the model and the restriction shown in Equation 7. There are several possible topics that arose for this objective that need to be addressed. The topics would include examining the affect of the assumed molecular energy distributions on the model while modeling additional materials to provide a larger sample on which to base the validity of the model. The ability of the model to predict the viscoelastic behavior of C-1002 was not as good as its ability to predict the viscoelastic behavior of the other materials. Causes for the discrepancies between the model and the measured data, which may include faulty data or other transition regions, need to be examined as well.

Possibly, the most important result from this thesis is the observation of the similarities between the parameter curves verses temperature for each material. Similarities were noted between the shift parameter curves for each material and the derivative order curves for each material. The fact that these similarities exist suggest there may be an analytical relationship between the parameters and temperature. This analytical relationship is worthy of examination since it may reduce the amount of experiment data necessary to model a particular material. The concept of the Modified Arrhenius equation provides a starting point for any effort in this area.

The double transition model produced a viscoelastic behavior prediction of atactic polystyrene that compared favorably with the measured data. Again, the user needs to note the assumptions embedded in the model, which are the same as those assumptions in the single transition model. Future efforts in this area should be focused on finding other materials that exhibit two modulus transitions as frequency varies and applying the model to these materials to validate the results. The search for materials that have multiple transition regions should begin with the other material analyzed in this thesis since they already exhibit thermorheologically complex behavior. However, the width of the frequency range necessary to identify materials with multiple transition regions may provide impractical test conditions.

The fact the model parameters met the restrictions that caused the model predictions to be consistent with the First and Second Laws of Thermodynamics lends credibility to the model results. The restrictions of the model parameters were very simple. The restrictions could be applied easily to the results of other temperature conditions or even predictions of the viscoelastic response of other materials.

Overall, the results of this thesis show there are candidate models or potential candidate models that would provide a compact engineering tool to use in predicting complicated viscoelastic behavior. The compactness of the models also would allow them to be used in adaptive control schemes where the nature of a thermorheologically complex material would influence the dampening characteristics of the system. Furthermore, the fractional derivative order of the model may be an insight into the underlying processes of nature.

Appendix A. Modplot.ex Executable File

The Curve Fit Routine The HERCULES computer system at the Air Force Institute of Technology was used for the vast majority of the calculations and plots. Instead of writing software in computer languages such as FORTRAN or PASCAL specifically for the model calculations and curve comparisons, several existing mathematics software packages were examined for use in this thesis. The MATRIX$_X$ package from Integrated Systems Inc. was chosen as the software package to use. The MATRIX$_X$ software package was selected because it already included an extensive mathmatics library and many useful algorithms, it works readily with complex numbers, it has plot routines incorporated that allow logarithmic scales, and most importantly, it can execute user-defined command files. These command files, defined as executable files by the MATRIX$_X$ package, resemble FORTRAN programs, but they also can include MATRIX$_X$ commands since they execute within the MATRIX$_X$ package. The program created for this thesis is run under the file, Modplot.ex. Because of the limitation of the MATRIX$_X$ package, which allows a maximum of 4096 characters on a line and the requirement that looped commands be performed on one line, the Modplot.ex executable file calls seven other executable files, which may call additional executable files themselves. The program was developed in two stages. In the first stage, the Modplot.ex program was developed to perform the calculations and plot the data curves and model curves for the fractional order time derivative viscoelastic model described above. In the second stage, the Modplot.ex program was modified to perform additional tasks. The additional tasks were required by the extension of the viscoelastic model to predict the viscoelastic behavior of materials that exhibit two transitions of modulus with frequency. The modifications preformed in the second stage of the modplot.ex program development will be discussed later. A complete listing of all of the executable files developed for this thesis is included in Appendix A. Setup.ex is the executable file that loads the mathematical viscoelastic model in the Modplot.ex program and initialize the variables. Modplot.ex is a menu driven program that is designed to give the user access to change or leave unchanged any model parameter for calculations. The Menu1.ex executable file lists the menu commands and asks the user for the desired command. The Modplot.ex executable file performs some menu tasks itself, but the larger more complicated tasks are performed by specialized executable files. The mathematical model is coded in a user defined function that is another type of MATRIX$_X$ executable file and is listed under the file name Modmodel.fun. The Inputfr.ex executable file allows the user to enter the desired frequency range for the model calculations in hertz or radians. Inputfr.ex also calculates frequency points at a user specified multiple of the previous frequency point. Frequency points separated by a multiple of the previous frequency provides for equal spacing of points plotted on a logarithmic scale. The Plotmod.ex and Pcomply.ex are executable files that plot the modulus data predicted by the model and compliance modulus data predicted by the model respectively. The Discurve.ex and Discomp.ex executable files respectively plot the modulus and compliance modulus data as well. They differ from the Plotmod.ex and Pcomply.ex executable files because they also plot experimental viscoelastic data on the same plots as the values predicted by the model. The experimental data files are created in a matrix format. The first column lists the values of frequency at which the data was taken, the second column lists the real portion of the measured data and the third column lists the imaginary portion of the measured data. All the columns must be of equal length. The Discurve.ex subroutine calls four additional executable files, Disc1.ex, Disc2.ex, Disc3.ex and Disc4.ex. These four additional files are the plot formats used in the Discurve.ex program. Pcurve.ex, Pcomply.ex, Discurve.ex, and Discomp.ex all call two other executable files, Hplot.ex and Dataset.ex. Hplot.ex stores user requested plots under a user defined filename and Dataset.ex stores the data used in those plots in an ASCII file named Hardout.dat.

The Modplot.ex program was designed to be very user friendly. Anyone with a small amount of knowledge about the fractional order time derivative viscoelastic model should be able to use the program effectively. The program was developed specifically as a tool for the research performed in this thesis and because of the specific nature of its development, a user's guide is not provided with the Modplot.ex program.

Modifications to Modplot.ex With the addition of the second set of model parameters, and the development of the double transition model, the Modplot.ex executable file was updated to adapt to the requirements caused by these additions. Additions were made to the Modplot.ex executable file to allow the user to input a second shift parameter, a second derivative order and the A2 constant. The double transition model was coded in a Matrix$_X$ user defined function called 2tmodmodel.fun. The Modplot.ex program was also modified to allow the user to choose between the single transition or the double transition model. With these changes integrated into the Modplot.ex program, modeling a material with two modulus transition regions was not anymore difficult than modeling a material with one modulus transition region.

Modplot.ex

```
//This Program Plots the Frequency Dependent,
//Modulus using a Fractional Calculus Model,
exec('setup.ex');//Initializes variables and requests data
```

```
format
//Running Menu Program,
While opt <> 15,...
      exec('menul.ex'),...//Menu Program
...
      if opt=1,...//Menu Item 1
         inquire ezero 'Input Glassy Modulus',...
      end;...//End if Optl
...
      if opt=2,...//Menu Item 2
         inquire einf 'Input Rubbery Modulus',...
      end;...//End if Opt2
...
      if opt=3,...//Menu Item 3
         inquire alpha 'Input Alpha Value',...
      end;...//End if Opt3
...
      if opt=4,...//Menu Item 4
         inquire alpha2 'Input 2nd Alpha Value',...
      end;...//End if Opt4
...
      if opt=5,...//Menu Item 5
         inquire beta 'Input Beta Value',...
      end;...//End if Opt5
...
      if opt=6,...//Menu Item 6
         inquire beta2 'Input 2nd Beta Value',...
      end;...//end if Opt6
...
      if opt=7,...
         inquire a2 'Input A2 Coefficient',...
      end;.../end if Opt7
...
      if opt=8,...
      exec('inputfr.ex'),...//Inputs frequency range
      end;...//End if Opt8
...
      if opt=9,...//Calculates modulus using one or two
                    transition model
         if transition=1,..
            [ereal,eimag,erealinv,eimaginv]=...
            freqmod(ezero,einf,alpha,beta,omega);...
         end;...//End if one transition
...
         if transition=2,...
            [ereal,eimag,erealinv,eimaginv]=...
freqmod2(a2,ezero,einf,alpha,alpha2,beta,beta2,omega);...
         end;...//End if two transition
      end;...//End if Opt9
...
```

```
      if opt=10,...
      exec('plotmod.ex'),...//Plots Complex Modulus
                              Calculations
      end;...//End if Opt10
...
      if opt=11,...
      exec('pcomply.ex'),...//Plots Complex Compliance Modulus
                              Calculations
      end;...//End if Opt11
...
      if opt=12,...//Input Data File to Curve Fit
         inquire datafile 'Input Data Filename (enclosed in
                          quotes)',...
         load (datafile),...
         inquire datavar 'Input Data Variable Name (no
                         quotes)',...
      end;...//End if Opt12
...
      if opt=13,...
      exec('discurve.ex'),...//Displays Data and Model Curves
                               for Curve Fit
      end;...//End if Opt13
...
      if opt=14,...
      exec('discomp.ex'),...//Displays Data and Model Curves
                              for Curve Fit
      end;...//End if Opt14
...
      if opt=15,...//Ends While Loop
         exit,...
      end;...//End if Opt15

end;//End While Loop
display ('Youe done?, If not you''re out of the program');
Return
```

Setup.ex

```
//This program is designed to fit in the Modplot.ex routine
//and initializes variables for the Modplot.ex routine and
  request data format
//
//Setting Default Values,
     Opt=0;//Option Default
     Counter=1;//Counter in Menu1.ex Default
     Hertz=1;//Frequency Units Flag
     Radians=0;//Frequency Unit Flag
     Axial=1;//Stress Type Flag
     Shear=0;//Stress Type Flag
```

```
     one=1;two=2;//Transition Number Flag
     y=1;yes=1;//Request Flag
     n=0;no=0;//Request Flag
//
//Defines Frequency Dependent,
//Modulus Transfer Functions, File on Disk,
  define 'modmodel.fun';
  define '2tmodmodel.fun';
//
//Requesting which units to plot
inquire whichunit 'What unit of frequency (hertz or radians)';
if whichunit=1,...//Determine which units to use
   display ('Units will be HERTZ');...
else,...
   display ('Units will be RADIANS');...
end;...//End Whichunit If
//
//Requesting which stress type is being used
inquire stresstype 'What type of stress (axial or shear)';
if stresstype=1,...//Determine which stress to use
   display ('Stress will be AXIAL');...
else,...
   display ('Stress will be SHEAR');...
end;...//End Stresstype If
inquire transition 'How many transitions does the material
                    exhibit (one or two)';
Return
```

Menu.ex

```
//This program is designed to fit in the Modplot.ex routine
//and displays the menu in which to operate to the Modplot.ex
  routine
display('Complex Modulus Plot    ')
choices=['1. Input Glassy Mod        2.Input Rubbery Mod
...
    3. Input Alpha Value   ';
         '4. Input 2nd Alpha Value   5. Input Beta
...
    6. Input 2nd Beta      ';
         '7. Input A2 Coefficient    8. Input Freq Range
...
    9. Calculate Modulus   ';
         '10. Plot Modulus           11. Plot Compliance Mod
...
    12. Input Data File    ';
         '13. Display Curve Fit      14. Compliance Curve
                                         Fit...
    15. Quit               '];
display(choices)
```

```
inquire opt 'Enter Menu Option',
counter=counter+1;
Return
```

Modmodel.fun

```
//[realmod,imagmod,invreal,invimag,modulus]=...
   Freqmod(glassmod,rubmod,bound,fractal,rate);
//This function calculates the frequency dependent modulus
//based on the fractional calculus model developed by Lt Col
  Bagley.
The outputs are:
//              realmod-real part of complex modulus
//              imagmod-imaginary portion of complex modulus
//              invreal-real part of the complex compliance
                        modulus
//              invimag-imaginary part of the complex
                        compliance modulus
//              modulus-total complex modulus
//the inputs are:
//              glassmod-glassy modulus or E infinity
//              rubmod-rubbery modulus or E zero
//              bound-energy boundary coefficent or alpha
//              fractal-fractional derivative order
//              rate-frequency in radians
//
[m,n]=size(rate);//Determine number of elements of frequency
vector
for i=1:m,...//Calculate modulus at each frequency
    x=bound*(jay*rate(i,1));...
    x=x**fractal;...
    modulus(i,1)=(glassmod+(rubmod*x))/(1+x);...
    realmod(i,1)=real(modulus(i,1));...
    imagmod(i,1)=imag(modulus(i,1));...
    invreal(i,1)=real((1/modulus(i,1)));...
    invimag(i,1)=imag((1/modulus(i,1)));...
end,//End For Loop
retf
```

2TModmodel.fun

```
//[realmod,imagmod,invreal,invimag,modulus]=...
   Freqmod2(coeff,glassmod,rubmod,bound1,bound2,fractal1,
            fractal2,rate);
//This function calculates the frequency dependent modulus
//based on the double transition fractional calculus model
//developed by Capt Victor Chambers referencing the model
  developed by Lt Col Bagley.
The outputs are:
//              realmod-real part of complex modulus
```

```
//              imagmod-imaginary portion of complex modulus
//                invreal-real part of the complex compliance
modulus
//                   invimag-imaginary part of the complex
compliance modulus
//              modulus-total complex modulus
//the inputs are:
//                 coeff-coefficient in derivation of A2 in
A1+A2=1
//              glassmod-glassy modulus or E zero
//              rubmod-rubbery modulus or E infinity
//             bound1-1st energy boundary coefficent or alpha
//             bound2-2nd energy boundary coefficent or alpha
//              fractal1-1st fractional derivative order
//              fractal2-2nd fractional derivative order

//              rate-frequency in radians
//
[m,n]=size(rate);//Determine number of elements of frequency
                   vector
a1=bound1**fractal1;a2=bound2**fractal2;
for i=1:m,...//Calculate modulus at each frequency
w1=((rate(i)*jay)**fractal1);w2=((rate(i)*jay)**fractal2);...
    w3=((rate(i)*jay)**(fractal1+fractal2));...
    x1=(a1*w1);x2=(a2*w2);x3=(a1*a2*w3);...
    c=(coeff*(x1-x2))+1;d=x3+((1-coeff)*x1)+((2-coeff)*x2);...
    y1=x1;y2=x2;y3=x3;y=(1+y1+y2+y3);...
    modulus(i,1)=(((rubmod*c)+(glassmod*d))/y);...
    realmod(i,1)=real(modulus(i,1));...
    imagmod(i,1)=imag(modulus(i,1));...
    invreal(i,1)=real((1/modulus(i,1)));...
    invimag(i,1)=imag((1/modulus(i,1)));...
end,//End For Loop
retf
```

Inputfr.ex

```
//This program is designed to fit in the Modplot.ex routine
//and allows the user to input the frequency range. It
//includes logic to account for use of hertz or radians
         clear cycles;clear omega;
         inquire x 'Input Initial Value of Frequency',
         inquire z 'Input Final Value of Frequency',
         inquire w 'Input Increment Multiplier of Frequency',
         nextfreq=x;counter2=0;...
         while nextfreq < z,...
               counter2=counter2+1;...
               omega(counter2)=nextfreq;...
               nextfreq=(w*nextfreq);...
         end;//End while
```

```
         if whichunit=1,...//Converts Cycles to Radians
         cycles=omega;...//Input was actually Cycles
         omega=(2*pi)*cycles;...
         end;//Convert Units
Return
```

Plotmod.ex

```
//This program is designed to fit in the Modplot.ex routine
//and plots the results of the Fractional Calculus Modulus
  model
      eimag=abs(eimag);...
              if whichunit=1,...
                 if stresstype=1,...

plot(cycles,ereal,'log/xlabel/Hertz/ylabel/...
                         Real E/report=1'),...
...
                    exec('hplot.ex'),...
...
                    pause,...

plot(cycles,eimag,'log/xlabel/Hertz/ylabel/...
                         Imaginary E/report=1'),...
                 else,...
...

plot(cycles,ereal,'log/xlabel/Hertz/ylabel/...
                         Real G/report=1'),...
...
                    exec('hplot.ex'),...
...
                    pause,...

plot(cycles,eimag,'log/xlabel/Hertz/ylabel/...
                         Imaginary G/report=1'),...
                 end;...//End if Stresstype
              else, ..
                 if stresstype=1,...


plot(omega,ereal,'log/xlabel/Radians/ylabel/...
                         Real E/report=1'),...
...
                    exec('hplot.ex'),...
...
                    pause,...

plot(omega,eimag,'log/xlabel/Radians/ylabel/...
                         Imaginary E/report=1'),...
```

```
                  else,...

plot(omega,ereal,'log/xlabel/Radians/ylabel/...
                          Real G/report=1'),...
...
                     exec('hplot.ex'),...
...
                     pause,...

plot(omega,eimag,'log/xlabel/Radians/ylabel/...
                          Imaginary G/report=1'),...
                  end;...//End if Stresstype2
                end;...//End if whichunit
...
       if ifhardout=1,...//Stores Plot File
          hardcopy(3,hardplot);...
          exec('dataset.ex'),...
       end;...//End if ifhardout
Return
```

Hplot.ex

```
//This program is designed to run inside the plot program for
//the MODPLOT.EX program. This program ask for a user defined
//filename and stores MatrixX plot files in that file.
inquire ifhardout 'Do You Want a Hardcopy (yes or no)',...

if ifhardout=1,...//Files in Hardout.dat and Hardplot.dat
   inquire  hardplot  'Enter  Plot  File  Name  (enclose  in
quotes)',...
   hardcopy(3,hardplot);...
end;...//End if ifhardout
Return
```

Dataset.ex

```
//This program is designed to be used in the Modplot.ex
//program to save data calculated using the program.
fsave 'hardout.dat' cycles omega ereal eimag erealinv eimaginv
return
```

Pcomply.ex

```
//This program is designed to fit in the Modplot.ex routine
//and plots the results of the Fractional Calculus Modulus
  model
      eimaginv=abs(eimaginv);...
      erealinv=abs(erealinv);...
              if whichunit=1,...
```

```
                  if stresstype=1,...

plot(cycles,erealinv,'log/xlabel/Hertz/ylabel/...
                          Real J/report=1'),...
...
                     exec('hplot.ex'),...
...
                     pause,...

plot(cycles,eimaginv,'log/xlabel/Hertz/ylabel/...
                          Imaginary J/report=1'),...
                  else,...
...

plot(cycles,erealinv,'log/xlabel/Hertz/ylabel/...
                          Real J/report=1'),...
...
                     exec('hplot.ex'),...
...
                     pause,...

plot(cycles,eimaginv,'log/xlabel/Hertz/ylabel/...
                          Imaginary J/report=1'),...
                  end;...//End if Stresstype
               else,...
                  if stresstype=1,...


plot(omega,erealinv,'log/xlabel/Radians/ylabel/...
                          Real J/report=1'),...
...
                     exec('hplot.ex'),...
...
                     pause,...

plot(omega,eimaginv,'log/xlabel/Radians/ylabel/...
                          Imaginary J/report=1'),...
                  else,...

plot(omega,erealinv,'log/xlabel/Radians/ylabel/...
                          Real J/report=1'),...
...
                     exec('hplot.ex'),...
...
                     pause,...

plot(omega,eimaginv,'log/xlabel/Radians/ylabel/...
                          Imaginary J/report=1'),...
                  end;...//End if Stresstype2
               end;...//End if whichunit
```

```
      if ifhardout=1,...//Stores Plot File
         hardcopy(3,hardplot);...
         exec('dataset.ex'),...
      end;...//End if ifhardout
Return
```

Discurve.ex

```
//This program is designed to fit into the Modplot.ex routine
//and plots experimental data over calculated data to
  determine curve fit
      eimag=abs(eimag);...
              if whichunit=1,...
                 if stresstype=1,...
                    exec('disc1.ex'),...
                 else,...
                    exec('disc2.ex'),...
                 end;...//End if Stresstype
              else,...
                 if stresstype=1,...

                    exec('disc3.ex'),...
                 else,...
                    exec('disc4.ex'),...
                 end;...//End if Stresstype2
              end;...//End if whichunit
       if ifhardout=1,...//Files in Hardout.dat and
                           Hardplot.dat
          hardcopy(3,hardplot);...
          exec('dataset.ex'),...
       end;...//End if ifhardout
Return
```

Disc1.ex

```
//Program called by curve fit plot routine

plot(cycles,ereal,'log/xlabel/Hertz/ylabel/...
                         Real E/report=1')
plot(datavar(:,1),datavar(:,2),'log,symbol mark 2/...
                         report=1/keep')
...
                    exec('hplot.ex')
...
                    pause
plot(cycles,eimag,'log/xlabel/Hertz/ylabel/...
                         Imaginary E/report=1')
plot(datavar(:,1),datavar(:,3),'log,symbol mark 2/...
                         report=1/keep')
```

Disc2.ex

```
//Progam called by curve fit plot routine

plot(cycles,ereal,'log/xlabel/Hertz/ylabel/...
                         Real G/report=1')
plot(datavar(:,1),datavar(:,2),'log,symbol mark 2/...
                         report=1/keep')
...
                    exec('hplot.ex')
...
                    pause

plot(cycles,eimag,'log/xlabel/Hertz/ylabel/...
                         Imaginary G/report=1')
plot(datavar(:,1),datavar(:,3),'log,symbol mark 2/...
                         report=1/keep')
```

Disc3.ex

```
//Progam called by curve fit plot routine

plot(omega,ereal,'log/xlabel/Radians/ylabel/...
                         Real E/report=1')
plot(datavar(:,1),datavar(:,2),'log,symbol mark2/...
                         report=1/keep')
...
                    exec('hplot.ex')
...
                    pause

plot(omega,eimag,'log/xlabel/Radians/ylabel/...

                         Imaginary E/report=1')
plot(datavar(:,1),datavar(:,3),'log,symbol mark2/...
                         report=1/keep')
```

Disc4.ex

```
//Program called by curve fit plot routine

plot(omega,ereal,'log/xlabel/Radians/ylabel/...
                         Real G/report=1')
plot(datavar(:,1),datavar(:,2),'log,symbol mark2/...
                         report=1/keep')
...
                    exec('hplot.ex')
...
```

```
                    pause

plot(omega,eimag,'log/xlabel/Radians/ylabel/...
                         Imaginary G/report=1')
plot(datavar(:,1),datavar(:,3),'log,symbol mark2/...
                         report=1/keep')
```

Discomp.ex

```
//This program is designed to fit into the Modplot.ex routine
//and plots experimental data over calculated data to
//determine curve fit for the Compliance Modulus
      eimaginv=abs(eimaginv);...
      erealinv=abs(erealinv);...
              if whichunit=1,...

plot(cycles,erealinv,'log/xlabel/Hertz/ylabel/...
                      Real J/report=1'),...
plot(datavar(:,1),datavar(:,2),'log,symbol mark 2/...
                      report=1/keep'),...
...
                 exec('hplot.ex'),...
...
                 pause,...

plot(cycles,eimaginv,'log/xlabel/Hertz/ylabel/...
                      Imaginary J/report=1'),...
plot(datavar(:,1),datavar(:,3),'log,symbol mark 2/...
                      report=1/keep'),...

              else,...

plot(omega,erealinv,'log/xlabel/Radians/ylabel/...
                      Real J/report=1'),...
plot(datavar(:,1),datavar(:,2),'log,symbol mark 2/...
                      report=1/keep'),...
...
                 exec('hplot.ex'),...
...
                 pause,...

plot(omega,eimaginv,'log/xlabel/Radians/ylabel/...
                      Imaginary J/report=1'),...
plot(datavar(:,1),datavar(:,3),'log,symbol mark 2/...
                      report=1/keep'),...
              end;...//End if whichunit
...
             if  ifhardout=1,...//Files  in  Hardout.dat  and
Hardplot.dat
             hardcopy(3,hardplot);...
```

```
                exec('dataset.ex'),...
                end;...//End if ifhardout
        Return
```

Appendix B. Viscoelastic Data for Polyvinyl Chloride Dimethyl Thianthrene

Table B-1. Polyvinyl Chloride Dimethyl Thianthrene Data

Temperature (K)	Frequency (Hz)	Modulus (MPa)	
		Real	Imaginary
307.61	75	118.16	63.86
307.61	100	147.02	86.93
307.61	140	156.47	98.39
307.61	140	159.58	104.33
307.61	210	186.61	113.59
307.61	320	213.765	116.98
307.61	320	216.01	124.14
307.61	450	244.13	132.88
307.61	660	259.41	144.7
307.61	660	271.52	150.2
307.61	1000	300.52	151.96
307.61	1500	325.88	146.96
307.61	1500	340.48	155.53
307.61	2100	357.6	164.09
307.61	2100	372.1	168.53
307.61	3000	373.71	155.71
307.61	3000	403.84	165.54
307.61	4200	438.69	160.64
307.61	5100	388.99	144.24
313.01	30	25.34	24
313.01	45	30.86	31.05
313.01	75	47.38	42.89

Table B-1 con't

Temperature (K)	Frequency (Hz)	Modulus	
		Real	Imaginary
313.01	100	53.05	51.36
313.01	140	63.35	61.63
313.01	210	79.46	70.055
313.01	210	80.35	68.92
313.01	320	100.665	85.34
313.01	450	117.06	96.18
313.01	660	134.53	119.34
313.01	1000	168.42	126.32
313.01	1500	194.13	129.785
313.01	2100	220.425	146.25
313.01	3000	251.4	146.44
313.01	4200	264.86	152.02
313.03	30	20.3	21.25
313.03	45	25.37	26.03
313.03	75	33.3	34.93
313.03	100	40.63	41.99
313.03	140	48.07	49.01
313.03	210	60.93	58.5
313.03	210	60.29	55.96
313.03	320	75.87	68.94
313.03	450	89.85	79.1
313.03	660	109.27	92.11
313.03	1500	153.95	115.74
313.03	2100	177.57	127.79
313.03	3000	207.92	132.53
313.03	4200	199.7	146.85

Table B-1 con't			
		Modulus	
Temperature (K)	Frequency (Hz)	Real	Imaginary
318.16	30	9.4	11.3
318.16	45	30.86	31.055
318.16	75	47.38	42.89
318.16	100	18.24	23.69
318.16	140	22.43	28.85
318.16	210	28.55	36.49
318.16	210	29.57	35.83
318.16	320	37.81	45.51
318.16	450	46.02	54.835
318.16	660	57.9	68.235
318.16	1000	79.43	82.58
318.16	1500	91.22	89.265
318.16	2100	108.15	104.32
318.16	3000	133.97	111.49
323.11	30	4.39	4.35
323.11	45	5.17	6.04
323.11	75	6.64	8.34
323.11	100	7.62	10.5
323.11	140	9.12	12.57
323.11	210	11.52	16.43
323.11	210	11.78	16.44
323.11	320	15.03	21.38
323.11	450	18.53	26.64
323.11	660	23.47	34.09
323.11	1000	30.45	42.91
323.11	1500	38.47	52.42

Table B-1 con't			
		Modulus	
Temperature (K)	Frequency (Hz)	Real	Imaginary
323.11	2100	45.47	61.76
323.11	3000	59.18	69.52
323.14	30	4.16	3.87
323.14	30	4.09	3.84
323.14	75	5.99	7.015
323.14	75	4.84	5.17
323.14	100	6.85	8.47
323.14	100	6.04	7.09
323.14	140	19.32	4.84
323.14	140	6.85	8.61
323.14	210	10.14	13.85
323.14	210	8.19	10.78
323.14	210	10.33	13.85
323.14	210	10.25	14.11
323.14	320	13.22	18.32
323.14	320	10.44	14.11
323.14	450	16.18	22.72
323.14	450	13.36	18.53
323.14	660	20.275	28.86
323.14	660	16.43	22.97
323.14	1000	23.67	37.36
323.14	1000	20.47	29.06
323.14	1500	34.09	44.01
323.14	1500	33.795	43.93
323.14	2100	38.12	54.77
323.14	2100	38.6	54.76

Table B-1 con't			
		Modulus	
Temperature (K)	Frequency (Hz)	Real	Imaginary
323.14	3000	47.46	61.28
323.14	3000	49.27	61.02
328.11	30	2.8	1.895
328.11	45	3.13	2.5
328.11	45	3.14	2.48
328.11	75	3.7	3.49
328.11	100	4.1	4.23
328.11	140	4.68	5.33
328.11	210	5.58	7
328.11	210	5.56	7.01
328.11	320	6.86	9.395
328.11	320	7.04	9.39
328.11	450	8.24	11.84
328.11	450	8.32	11.935
328.11	660	9.94	15.925
328.11	1000	12.87	20.61
328.11	1500	16.67	24.965
328.11	2100	18.42	31.1
328.11	3000	22.49	34.24
333.41	30	2.1555	0.885
333.41	30	2.13	0.87
333.41	45	2.275	1.12
333.41	45	2.29	1.12
333.41	75	2.54	1.54
333.41	100	2.71	1.8
333.41	140	2.99	2.32

Table B-1 con't			
		Modulus	
Temperature (K)	Frequency (Hz)	Real	Imaginary
333.41	140	3.02	2.32
333.41	210	3.37	3.09
333.41	210	3.36	3.03
333.41	320	4	4.06
333.41	450	4.51	5.1
333.41	660	5.26	6.72
333.41	1000	5.64	8.95
337.81	30	1.8	0.496
337.81	45	1.89	0.617
337.81	75	2.04	0.839
337.81	100	2.15	1
337.81	140	2.3	1.24
337.81	140	2.32	1.24
337.81	210	2.52	1.71
337.81	210	2.54	1.71
337.81	320	2.88	2.19
337.81	450	3.2	2.69
337.81	660	3.47	3.59
337.81	660	3.42	3.47
337.81	1000	3.73	4.61
343.16	30	1.54	0.278
343.16	45	1.62	0.336
343.16	75	1.68	0.435
343.16	100	1.73	0.493
343.16	140	1.82	0.611
343.16	140	1.84	0.619

Table B-1 con't			
		Modulus	
Temperature (K)	Frequency (Hz)	Real	Imaginary
343.16	320	2.14	1.03
343.16	660	2.28	1.57

Appendix C. Viscoelastic Data for the Anatrol Corp. Material

Table C-1. Anatrol Corp. Material Data			
		Modulus (PSI)	
Temperature (K)	Frequency (Hz)	Real	Imaginary
297	96	509.80	545.49
297	64	445.50	397.83
297	32	369.00	268.63
297	16	303.50	178.76
297	8	254.10	127.05
297	4	220.60	85.37
297	2	192.00	54.49
297	1	173.20	36.20
297	0.5	161.40	26.95
297	0.25	150.70	19.74
297	0.125	139.80	16.78
297	0.0625	133.40	12.94
297	0.03125	127.10	10.84
297	0.01563	123.00	9.58
297	0.00781	118.20	8.546
297	0.00393	119.40	7.64
297	0.00197	113.60	5.226
297	0.000954	112.20	6.17
297	0.000477	119.20	6.32
292	32	567.00	520.51
292	16	431.00	354.28
292	8	338.00	229.16
292	4	283.30	159.21

Table C-1 con't

Temperature (K)	Frequency (Hz)	Modulus	
		Real	Imaginary
292	2	234.00	106.94
292	1	213.00	68.59
292	0.5	188.40	48.98
292	0.25	171.12	35.94
292	0.125	156.70	27.89
292	0.125	158.20	27.37
292	0.0625	147.03	21.17
292	0.03125	139.10	16.41
292	0.0156	133.40	13.07
292	0.00781	129.00	11.61
292	0.00393	123.90	8.67
292	0.00197	121.20	7.88
292	0.000954	119.00	5.59
303	16	215.50	98.31
303	8	193.60	61.18
303	4	173.60	43.05
303	2	160.70	31.66
303	0.5	142.90	15.86
303	0.25	135.00	12.80
303	0.125	128.70	10.90
303	0.0625	122.40	9.36
303	0.03125	118.50	7.77
303	0.01563	115.00	7.18
303	0.00393	108.00	5.40
303	0.00197	106.30	5.42
303	0.00781	113.30	6.91

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The research presented here was accomplished in three parts. In the first part, a fractional order time derivative model of viscoelastic behavior was validated using experimental data for viscoelastic materials. Descriptions of internal energy loss at the molecular level led to the fractional order time derivative model. The fractional calculus stress-strain constitutive laws used in the model are easily applied to the temperature and frequency dependent moduli of viscoelastic materials. The second portion describes the extension of the above fractional order time derivative model to predict the viscoelastic behavior of thermorheologically complex materials that exhibit two modulus transitions with respect to frequency. The final portion determines the necessary restrictions on the parameters of the double transition viscoelastic model to insure the model doesn't violate thermodynamic principles.

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