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ACCELERATED CHARACTERIZATION OF GRAPHITE/EPOXY COMPOSITES

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ABSTRACT

A method to predict the long-term compliance of unidirectional off-axis laminates from short-term laboratory tests is presented. The method uses an orthotropic transformation equation and the time-stress-temperature superposition principle. Short-term tests are used to construct master curves for two off-axis unidirectional laminates with fiber angles of 10° and 90°. In addition, analytical predictions of long-term compliance for 30° and 60° laminates are made. Comparisons with experimental data are also given.

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INTRODUCTION

Advanced fiber reinforced composite laminates typically use epoxy resins for the polymer matrix component, which may result in time dependent laminate behavior. The viscoelastic response of polymer matrix composites has been studied by Halpin and Pagano [1], Lou and Schapery [2], Yeow, Morris and Brinson [3], Crossman and Flaggs [4], Renton and Ho [5], and others. Structural components made from graphite/epoxy or other polymer matrix laminates may become unserviceable over a period of time due to creep, relaxation, creep rupture, etc. It would be desirable to be able to measure these viscoelastic effects with short-term laboratory tests rather than perform long-term prototype studies. It would also be desirable to use analytical techniques to predict either short- or long-time behavior. As a result, a clear need exists for accelerated characterization techniques for laminates similar to those used for other structural materials.

A number of environmental factors such as temperature, humidity and stress level can strongly affect the viscoelastic response of a laminate. Furthermore, the history of the laminate prior to loading may be important through the effects of physical aging and curing/postcuring. Acceptable accelerated characterization methods must account for these variables in order to make valid predictions.

The best known accelerated characterization technique utilizes temperature as an accelerating factor, and is most often referred to as the time-temperature superposition principle [6]. Other methods may use stress [2], temperature and stress [7], or temperature and humidity [5] as accelerating factors. Implicit in the use of all techniques is the equivalence between time and each accelerating factor or combination thereof. For example, a short-term test at high temperature is equivalent to a long-term test at a lower temperature, other factors remaining constant.

The authors have elected to study the effects of temperature and stress as accelerating parameters. Master curves for creep compliance are constructed from short-term creep tests at various levels of stress and temperature for off-axis unidirectional T300/934 graphite/epoxy laminates. The use of the principal compliances to predict off-axis response is also discussed. The effects of temperature and stress level are given in the form of a combined temperature-stress shift factor. The use of the shift factor and how it is used in conjunction with the master curve for accelerated prediction of compliance is discussed.

The history of the material prior to loading is important. Evidence is given which shows that the specimen may additionally cure during testing at elevated temperature. Polymer systems are also susceptible to physical aging [8]. Therefore, attempts at accelerated predictions require proper knowledge of the physical aging process.

ACCELERATED CHARACTERIZATION METHODS

Procedures have been developed by which predictions of long-term time dependent laminate properties such as moduli and compliance could be made on the basis of short-term tests. The procedures are based upon the time-temperature superposition principle (TTSP) and the time-stress-temperature superposition principle (TSTSP).

Time-Temperature Superposition Principle

The TTSP for polymeric materials is well established. For a complete review, see Ferry [6]. Recently the method has been extended to composite materials [3]. To apply the TTSP, short-term creep tests were conducted on various off-axis unidirectional graphite/epoxy composites. The results of short term (15 min.) tests for a $[90°]_{8s}$ laminate are shown in Fig. 1. A vertical correction of the ratio of the absolute test temperature to an absolute reference temperature of the form given by Ferry [6] was applied to the short-term data prior to plotting. The reference temperature was selected as the glass transition temperature, T_g, and the short-term data was translated horizontally to form a smooth master curve, a portion of which is shown in Fig. 1. The amount each short-term curve is shifted horizontally is called the shift factor, log a_T, for that temperature. The beauty of the method is not so much that a master curve for a selected temperature can be found, but that when the appropriate vertical temperature correction and horizontal shift factor is applied to the master curve, a similar curve for any other temperature (within the temperature range of the short-term tests) can be found.

Other master curves were generated for tensile specimens whose fibers were at an angle other than 10° to the load direction [9]. Using master curves for fiber angles of 10° and 90°, the fact that no time or temperature effects were found for a fiber angle of 0°, and the visco-elastic analogue to the orthotropic transformation equation, the master curve for an arbitrary off-axis tensile specimen was predicted [3]. The predicted results are shown in Fig. 2 for a specimen whose fiber angle to load direction was 30°. Also shown is the master curve generated from short-term tests. As may be observed, the predicted master curve and experimentally determined master curve are in close agreement.

Continuous twenty-five hour creep tests were performed to verify the process of using master curves obtained from short-term tests and the analytical prediction procedures previously discussed. The results are also shown in Fig. 2. Close agreement exists between short-term, long-term, and predicted results. Results for other fiber angles may be found in [9].

Obviously, short-term results at one temperature can be used to predict long-term results at another temperature (accelerated characterization). All results discussed thus far have been for stress levels such that linear viscoelasticity was applicable. A material may behave in a nonlinear viscoelastic manner for sufficiently high stress levels. For this case an isothermal time stress superposition principle (TSSP) analogous to the TTSP has been used to produce master curves [7,10]. Both temperature and stress may be accelerating factors simultaneously as is discussed in the next section.

Time-Stress-Temperature Superposition Principle

In essence, the time-stress-temperature superposition principle (TSTSP) is a simultaneous application of the well known TTSP and the TSSP. The TSTSP was used by Daugste [11] to predict the nonlinear viscoelastic behavior of a 45° glass reinforced unidirectional composite.

There are several advantages to the TSTSP over other approaches such as that of Lou and Schapery [2]. First, it is easier to apply than the other nonlinear theories investigated. Second, it offers a convenient way in which any of the other accelerating environmental effects might be handled. For example, effects of stress and moisture could be studied through an analogous time-stress-moisture superposition principle. A general outline of the TSTSP is given below.

For illustrative purposes hypothetical transient creep compliance vs. log time is shown in Fig. 3 for several stress and temperature levels. The data from Fig. 3a for each temperature level may be shifted to obtain the σ_1 master curve shown in Fig. 3c using the TTSP. Similarly, master curves may be formed for stress levels σ_2, σ_3 and σ_4. An outcome of this procedure will be the temperature shift factor, log a_T, and its corresponding stress dependence. In this instance, T_1 was arbitrarily chosen as the reference temperature. The data from Fig. 3b for each stress level may be shifted to obtain the T_1 master curve shown in Fig. 3d using the TSSP. Similarly, master curves may be formed for temperature levels of T_2, T_3 and T_4. This procedure will yield the stress shift factor, log a_σ, and its associated temperature dependence. The master curves in Fig. 3c or the master curves in Fig. 3d may now be shifted to obtain the unified master curve for a stress σ_1, and a temperature T_1, as shown in Fig. 3e. This unified master curve can now be shifted to determine a unified master curve for any temperature and/or stress level within the range of data. The degree to which the TTSP and TSSP master curves combine to form a smooth unified curve is thought to be a good indication of the validity of the method. Of course, proof of the TSTSP method can only be obtained by comparison of predictions and experimental measurements. For the nonlinear TSTSP characterization to be useful in composites, the method must be able to predict the time/stress/temperature dependence of off-axis modulus or compliance of unidirectional laminates. More will be said about this later.

EXPERIMENTAL RESULTS AND DISCUSSION

In our earlier work on T300/934 graphite/epoxy laminates we found no dependence of the T_g on thermal cycling [3]. However, for more recently acquired batches of material we have found such a dependence. Apparently, over a period of a couple of years, the manufacturer has omitted a rather crucial postcuring cycle. Figure 4 shows thermal expansion measurements prior to and after post cure, with corresponding values of T_g of 180°C (356°F) and 194°C (381°F), respectively. Details of the experimental procedures may be found in [12].

Another effect of postcuring is seen in Figs. 5 and 6. Figure 5 shows that compliances were significantly reduced by postcuring (thermal conditioning). Furthermore, additional curing led to significant decreases in the time dependent response of the composite. Figure 6 shows the effects of postcuring on master curves produced from Fig. 5. Master curves are practically identical for short times, but the deviation between the curves increases for increasing values of time. Thus, even though master curves can be produced from short-term tests, postcuring of a specimen (for example, during long-term tests) can lead to over predictions of compliance.

Thermal conditioning specimens for 36 hours at 199°C (390°F) all but eliminated postcuring effect with respect to creep compliance [12]. Consistent temperature and stress effects were obtained after the above postcuring sequence. It should be noted that specimens were slowly cooled (several °F/hour) from the postcure temperature of 199°C to room temperature [12] to avoid possible effects of physical aging [8].

Using the procedures illustrated in Fig. 3, compliance master curves were formed for unidirectional laminates with fiber angles of 90° and 10°, as shown in Figs. 7 and 8, respectively. Horizontal as well as vertical shifting was required in master curve formation to eliminate temperature and/or stress dependence of initial compliance. The stress-temperature shift function surface for a 90° specimen is shown in Fig. 9.

Also shown in Figs. 7 and 8 is the correlation between long-term (150 hours) test data and the master curves formed from short-term data. As may be seen, good agreement was obtained.

The goal in producing 90° and 10° compliance master curves was to use them to predict master curves for a lamina with an arbitrary fiber angle such that lamination theory might then be used in turn to predict the long time response of an arbitrary laminate. As previously stated, the TSTSP, in conjunction with the orthotropic transformation equation, may be used to predict the time/stress/temperature dependence of off-axis compliance of a lamina. The orthotropic transformation equation may be written as,

$$S_{xx} = S_{11} \cos^4 \theta + S_{22} \sin^4 \theta + (2S_{12} + S_{66}) \cos^2 \theta \sin^2 \theta \qquad (1)$$

From 0° specimens it has been found [12] that S_{11} and S_{12} were practically independent of time and temperature, and thus were considered constant.

The long-term compliances of 30° and 60° specimens were obtained using constant values for S_{11} and S_{12}, the stress dependent master curves for S_{22} and S_{66} at a constant temperature of 320°F (160°C), and Eq. (1). The results are shown in Figs. 10 and 11, along with long-term experimental data. The maximum deviation between predictions and long-term data is about 10%.

Unlike previous results [3], the off-axis predictions must account for the stress dependent nature of the master curves. That is, the applied uniaxial stress must be transformed into stress components in the principal material directions. The master curves for stresses associated with these directions are then used, along with Eq. (1), to predict off-axis compliance, such as shown in Figs. 10 and 11.

SUMMARY AND CONCLUSIONS

A method to predict the long-term compliant behavior of unidirectional off-axis laminates from short-term laboratory tests has been presented. The method makes use of the TSTSP and an orthotropic transformation equation, and accounts for the effects of time, stress, and temperature.

It has been shown that postcuring was necessary in order to obtain repeatable results. The TSTSP has been used to construct master curves from short-term tests of 10° and 90° unidirectional laminates. The master curves are in good agreement with long-term tests. In addition, analytical predictions of long-term compliance for 30° and 60° laminates have been made; experimental data agrees reasonably well with the predictions.

It is concluded that the TSTSP, along with the orthotropic transformation equation, is a viable method to predict long-term compliance of off-axis unidirectional laminates. Methods are underway to extend the method to more complex laminates.

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REFERENCES

1. Halpin, J. C. and Pagano, N. J., "Observations on Linear Anisotropic Viscoelasticity," Journal of Composite Materials, Vol. 2, Jan. 1968, pp. 68-80.

2. Lou, Y. C. and Schapery, R. A., "Viscoelastic Characterization of a Nonlinear Fiber-Reinforced Plastic," Journal of Composite Materials, Vol. 5, April 1971, pp. 208-234.

3. Yeow, Y. T., Morris, D. H. and Brinson, H. F., "The Time-Temperature Behavior of a Unidirectional Graphite/Epoxy Composite," Composite Materials: Testing and Design (Fifth Conference), ASTM STP 674, 1979, pp. 263-281.

4. Crossman, F. W. and Flaggs, D. L., LMSC-D33086, Lockheed Palo Alto Research Laboratory, November 1978.

5. Renton, W. J. and Ho, T., ATC Report No. B-92100/8CR-105, Vought Corp. Advanced Technology Center, August 1978.

6. Ferry, J. D., Viscoelastic Properties of Polymers, John Wiley and Sons, Inc., New York, 1970.

7. Cessna, L. C., Jr., "Stress-Time Superposition of Creep Data for Polypropylene and Coupled Glass-Reinforced Polypropylene," Polymer Engineering and Science, Vol. 11, May 1971, pp. 211-219.

8. Strick, L. C. E., Physical Aging in Amorphous Polymers and Other Materials, Elsevier Scientific Publishing Co., New York, 1978.

9. Yeow, Y. T., "The Time-Temperature Behavior of Graphite Epoxy Laminates," Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA, May 1978.

10. Urzhumtsev, Y. S. and Maksimov, R. D., "Time-Stress Superposition in Nonlinear Viscoelasticity," Polymer Mechanics, Vol. 4, No. 2, 1968, pp. 318-320.

11. Daugste, C. L., "Joint Application of Time-Temperature and Time-Stress Analogies to Constructing Unified Curves," Polymer Mechanics, Vol. 10, No. 3, 1974, pp. 359-362.

12. Griffith, W. I., Morris, D. H. and Brinson, H. F., "The Accelerated Characterization of Viscoelastic Composite Materials," Virginia Polytechnic Institute and State University, Report VPI-E-80-15, April 1980.

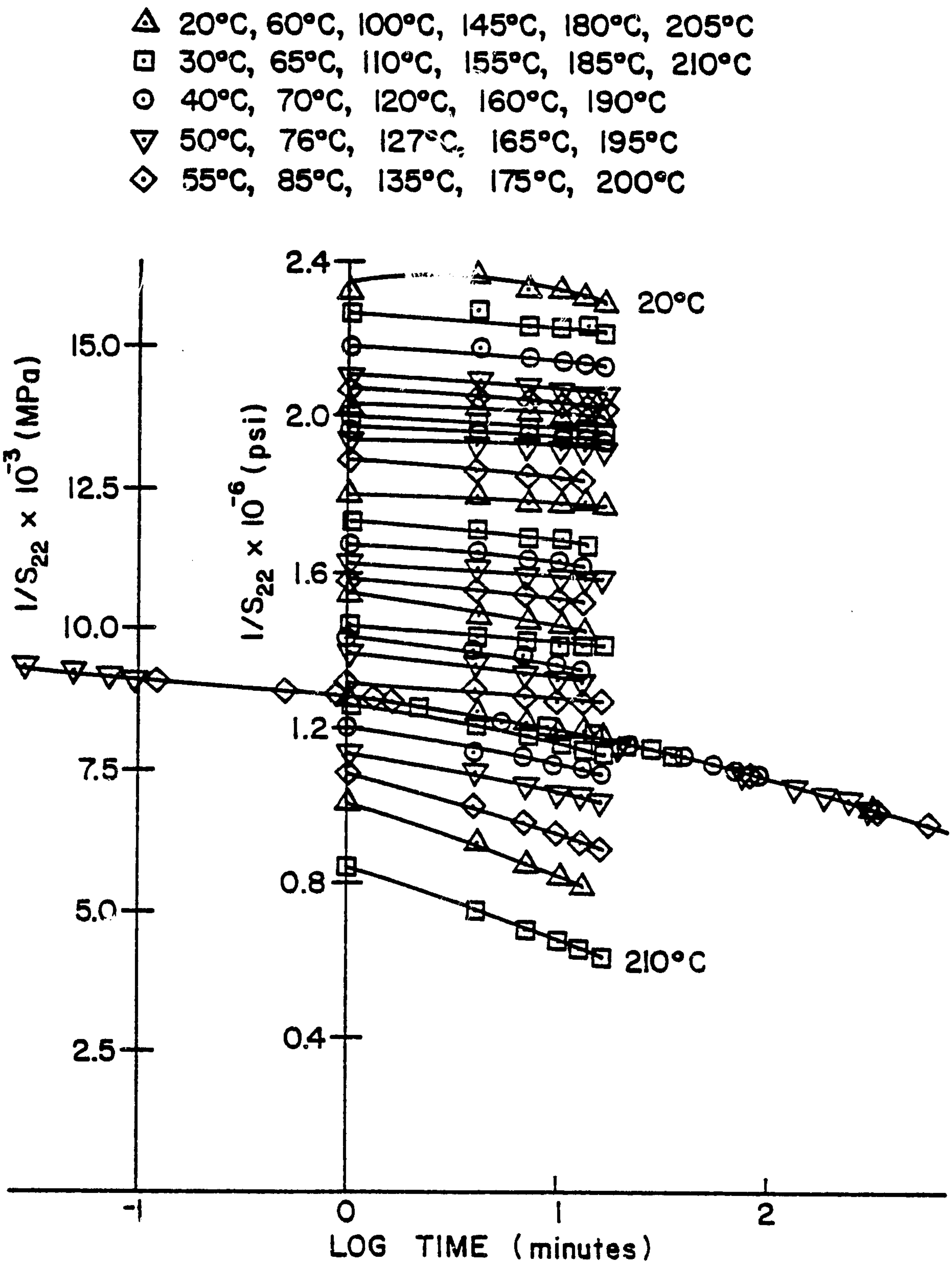

Fig. 1. Reduced Reciprocal of Compliance and Portion of 180°C Master Curve for $[90]_{8s}$ Graphite/Epoxy Laminate

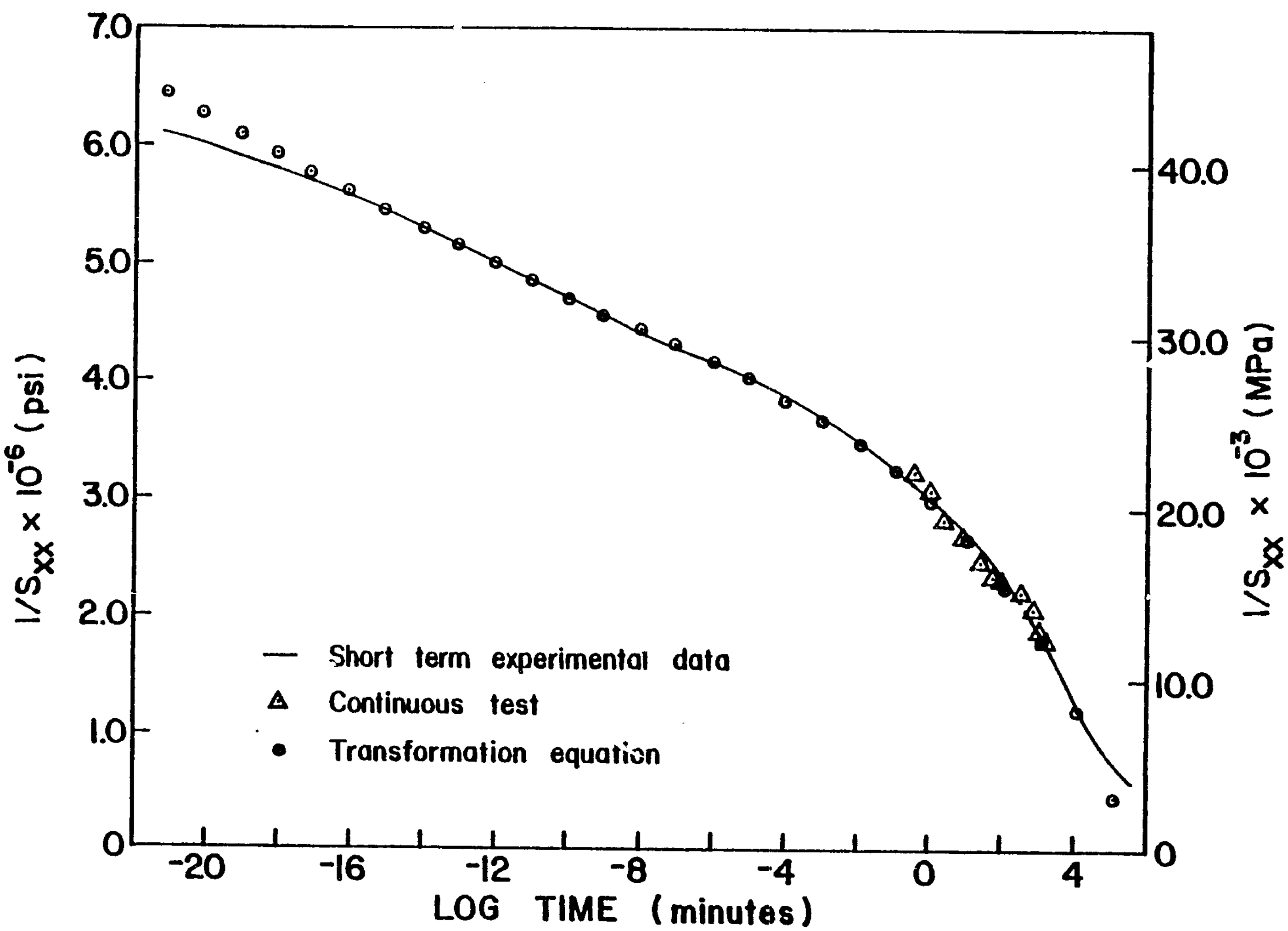

Fig. 2. Master Curve of the Reciprocal of Reduced Compliance of $[30°]_{8s}$ Laminate at 180°C

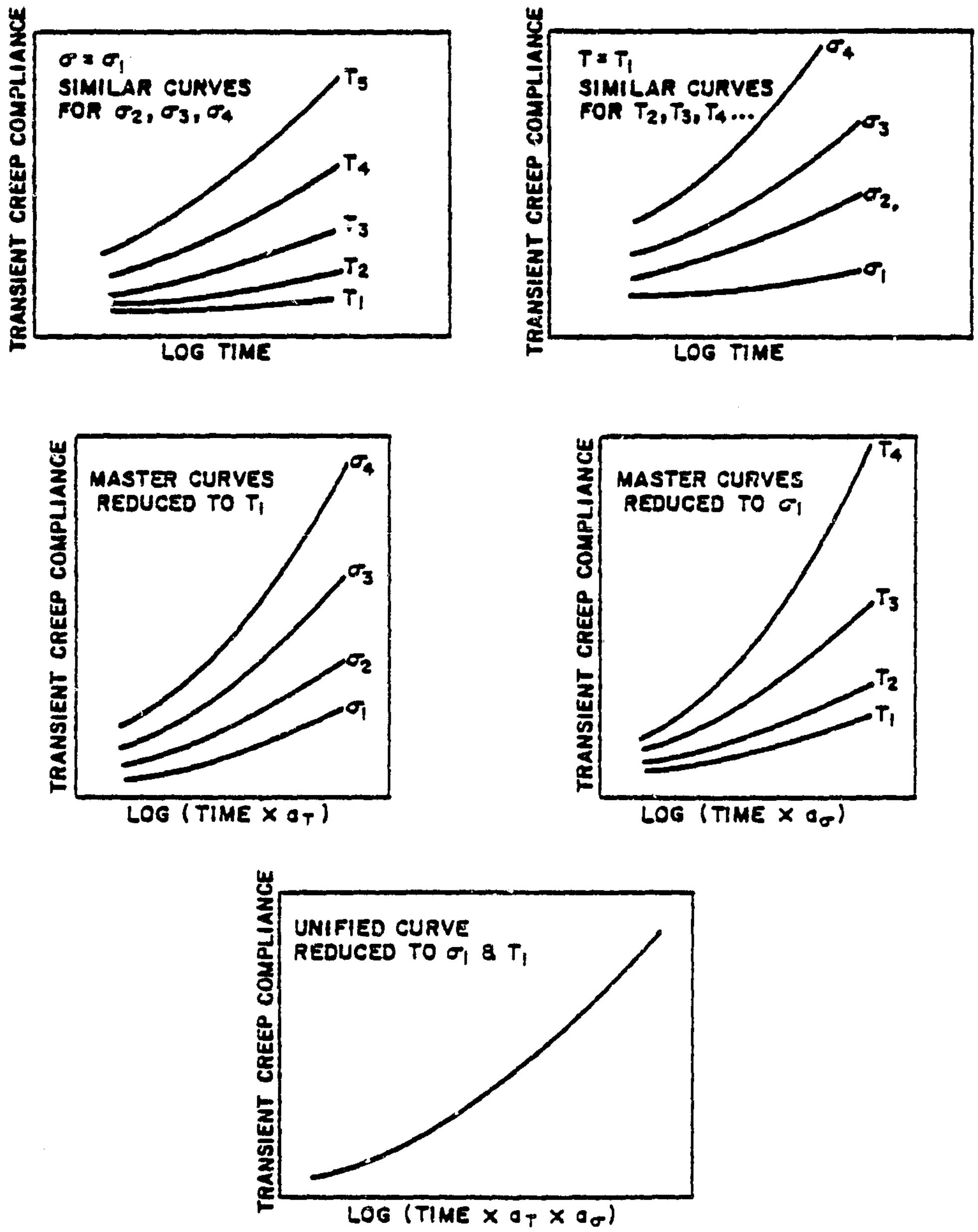

Fig. 3. Schematic Diagram to Illustrate the Time-Stress-Temperature Superposition Principle

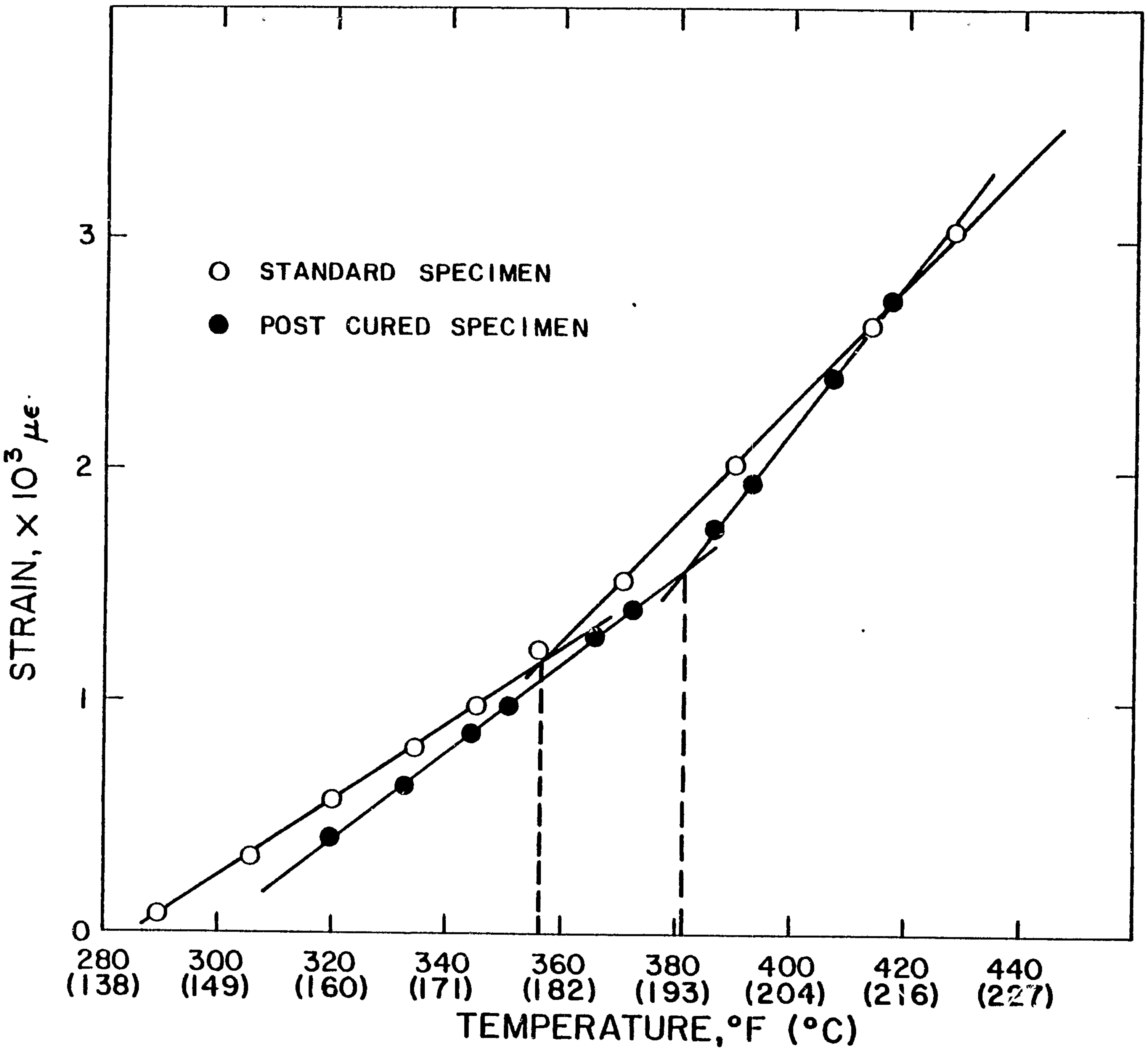

Fig. 4. Thermal Expansion Before and After Post Cure

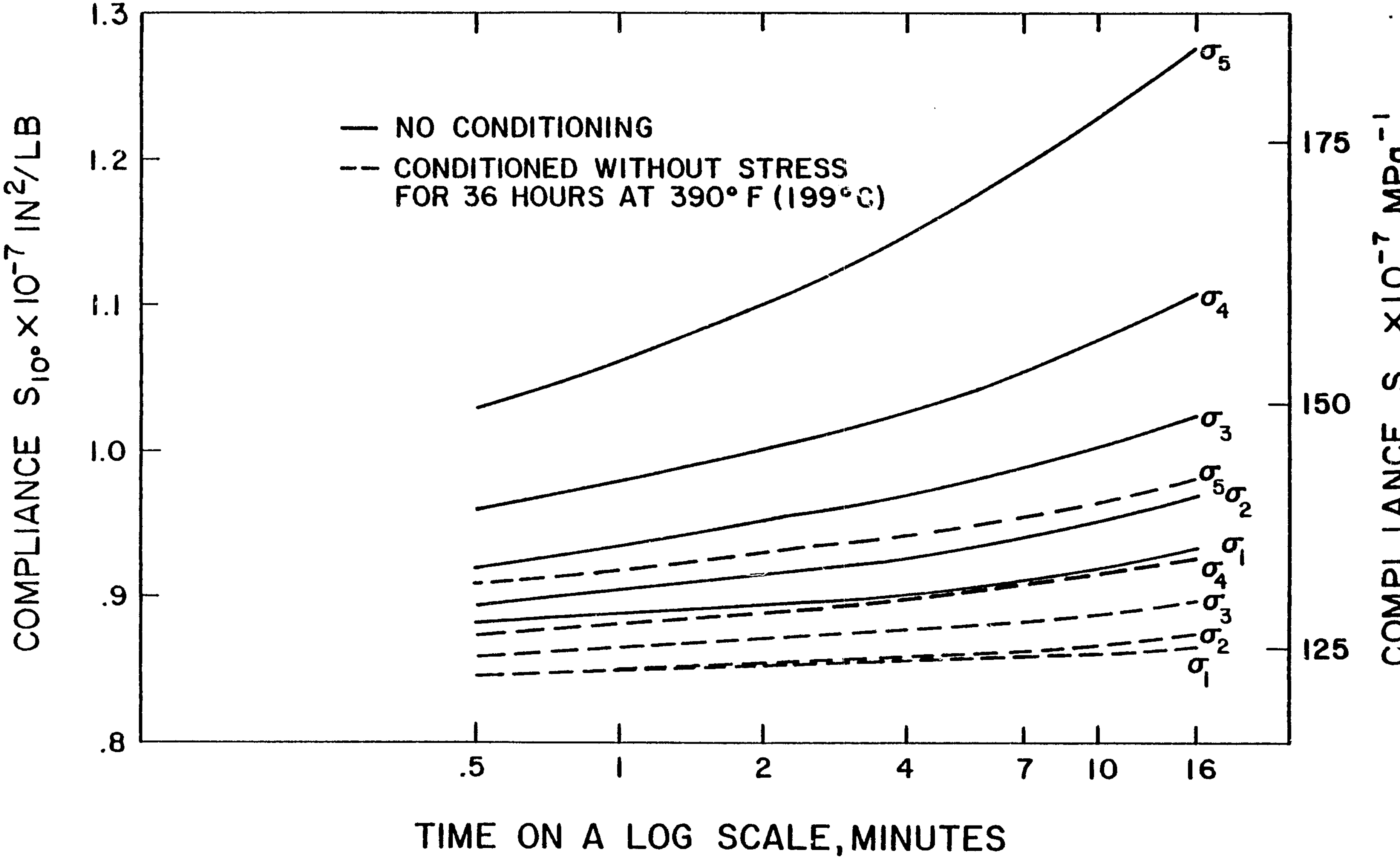

Fig. 5. Comparison of $S_{10°}$ Compliance at 290°F (143°C) With and Without Thermal Conditioning

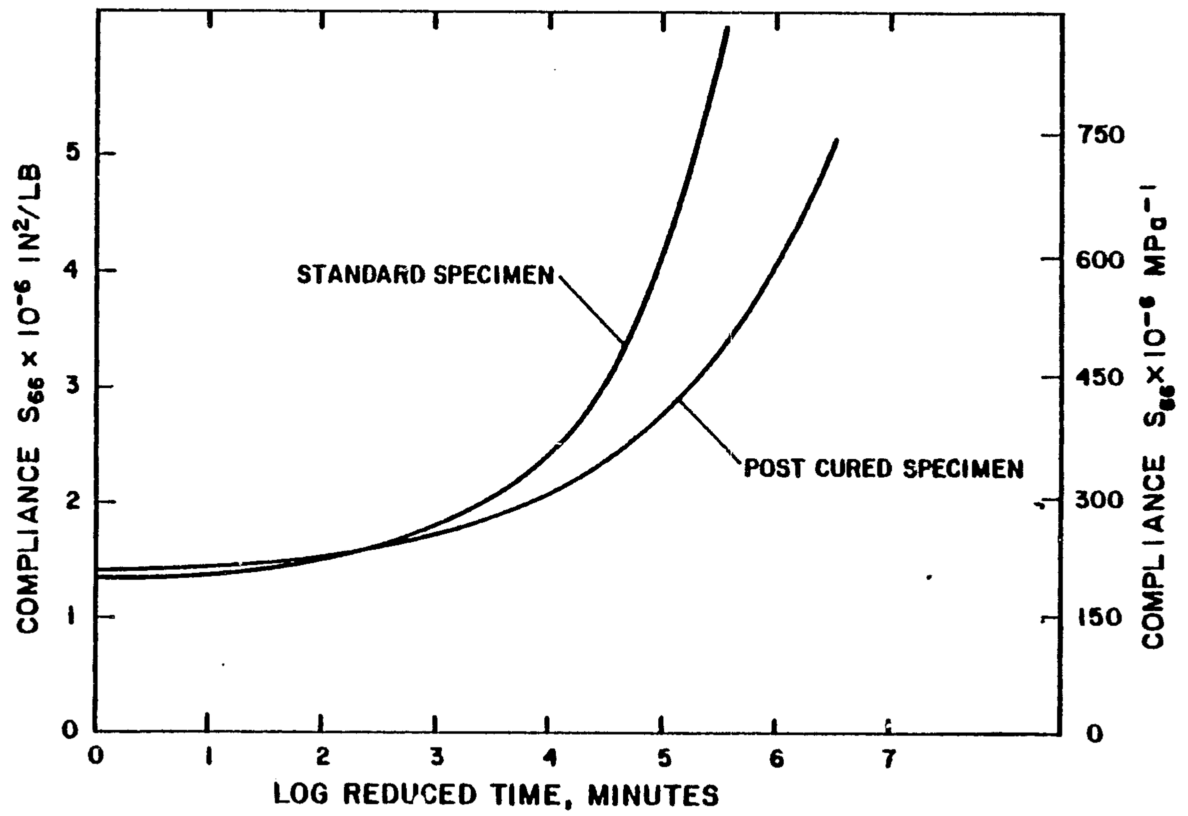

Fig. 6. Comparison of S_{66} Master Curves at 290°F (143°C) With and Without Thermal Conditioning

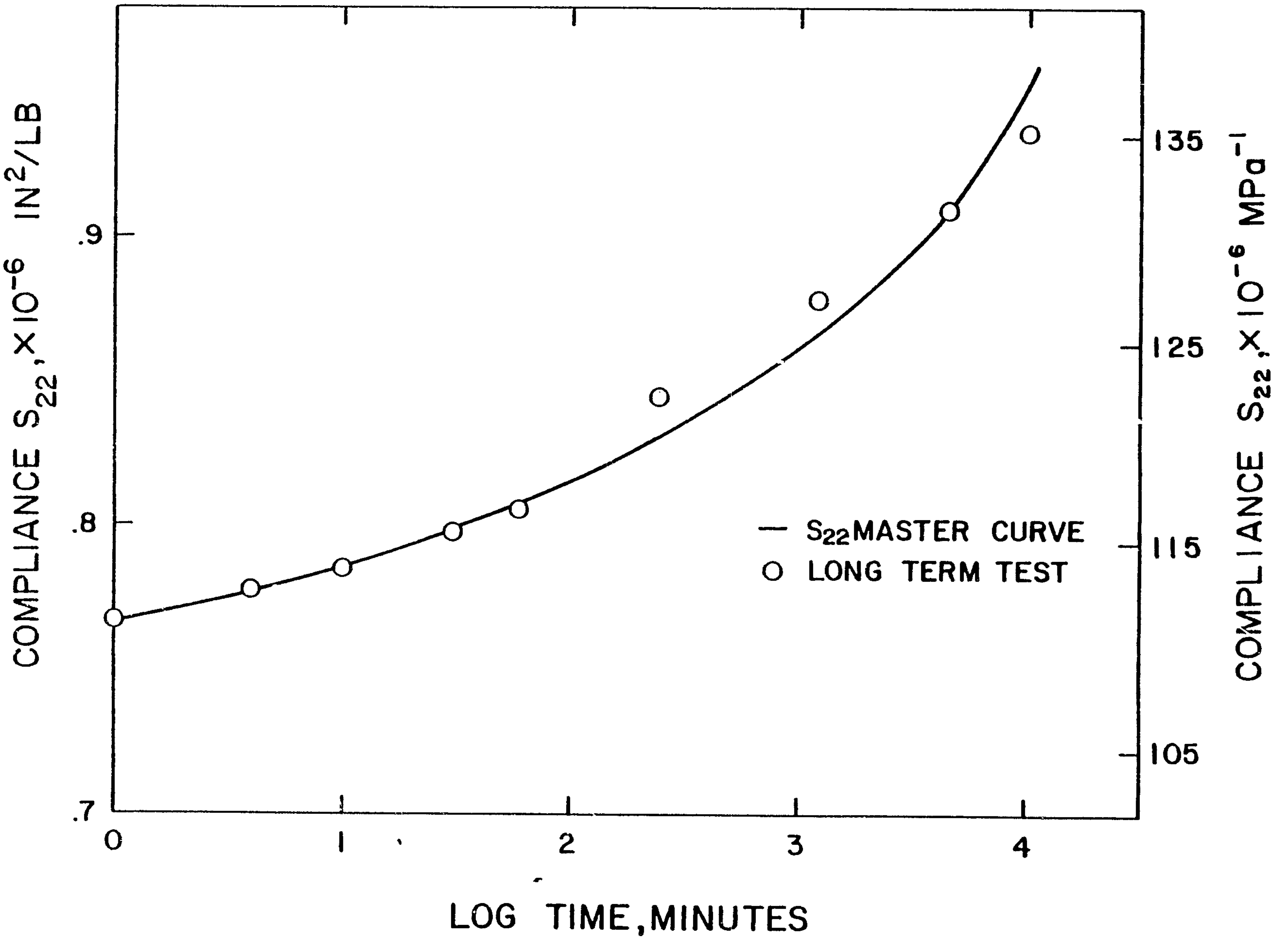

Fig. 7. Comparison of S_{22} Master Curve With a Long Term Test at 320°F (160°C) and 2,750 psi (19 MPa)

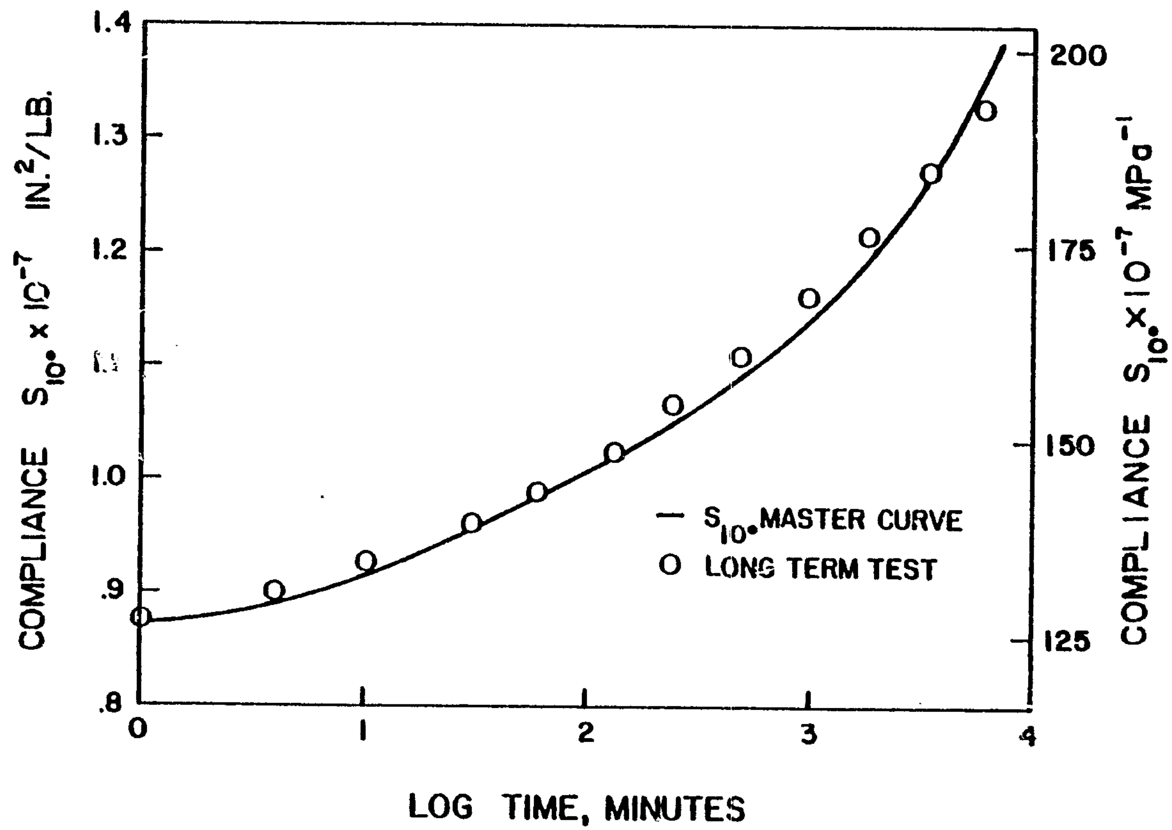

Fig. 8. Comparison of $S_{10°}$ Master Curve With a Long Term Test at 320°F (160°C) and 19,500 psi (134 MPa)

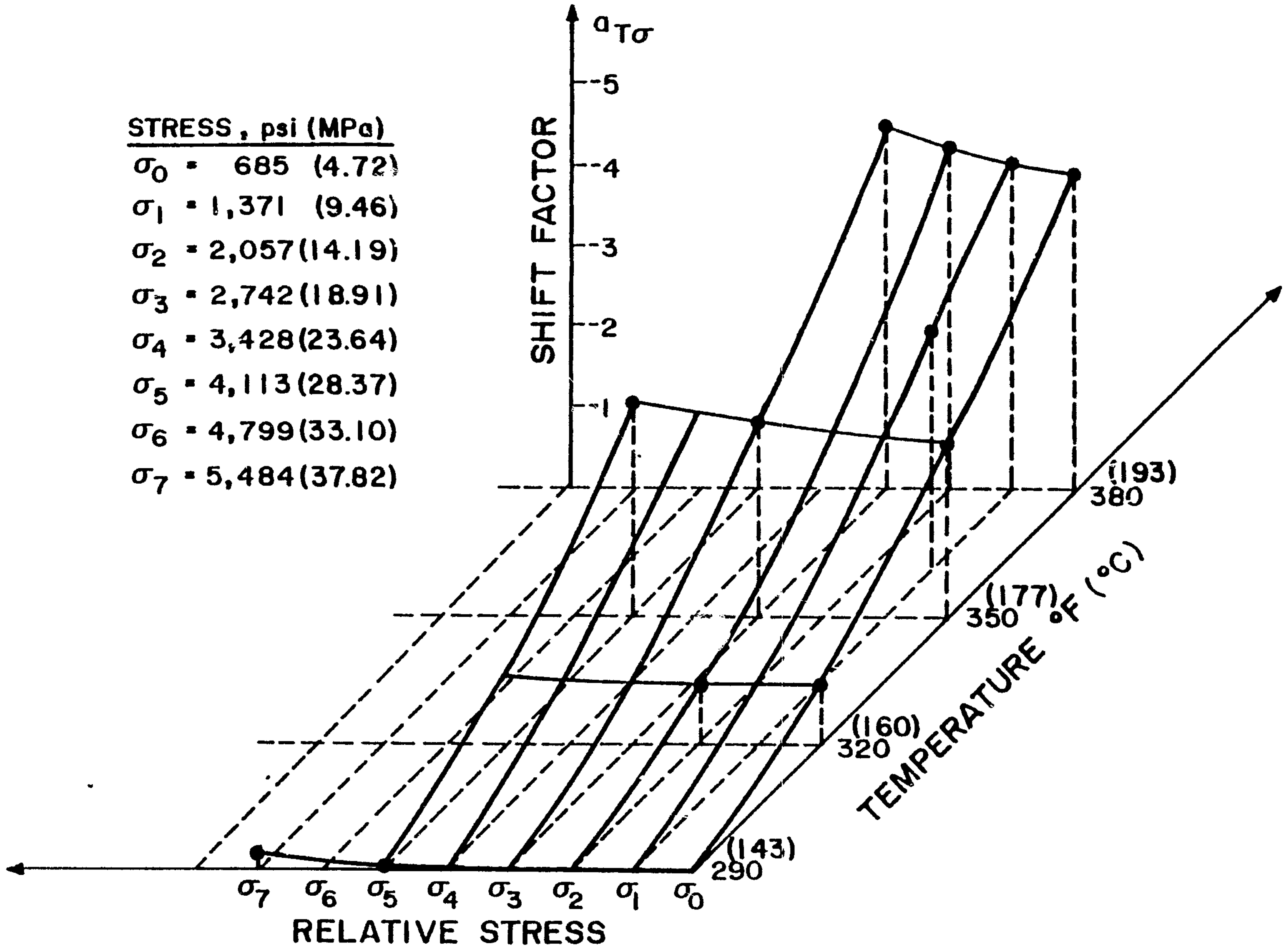

Fig. 9. Shift Surface for Combined Shift Factor for S_{22} (Post Cured Specimen)

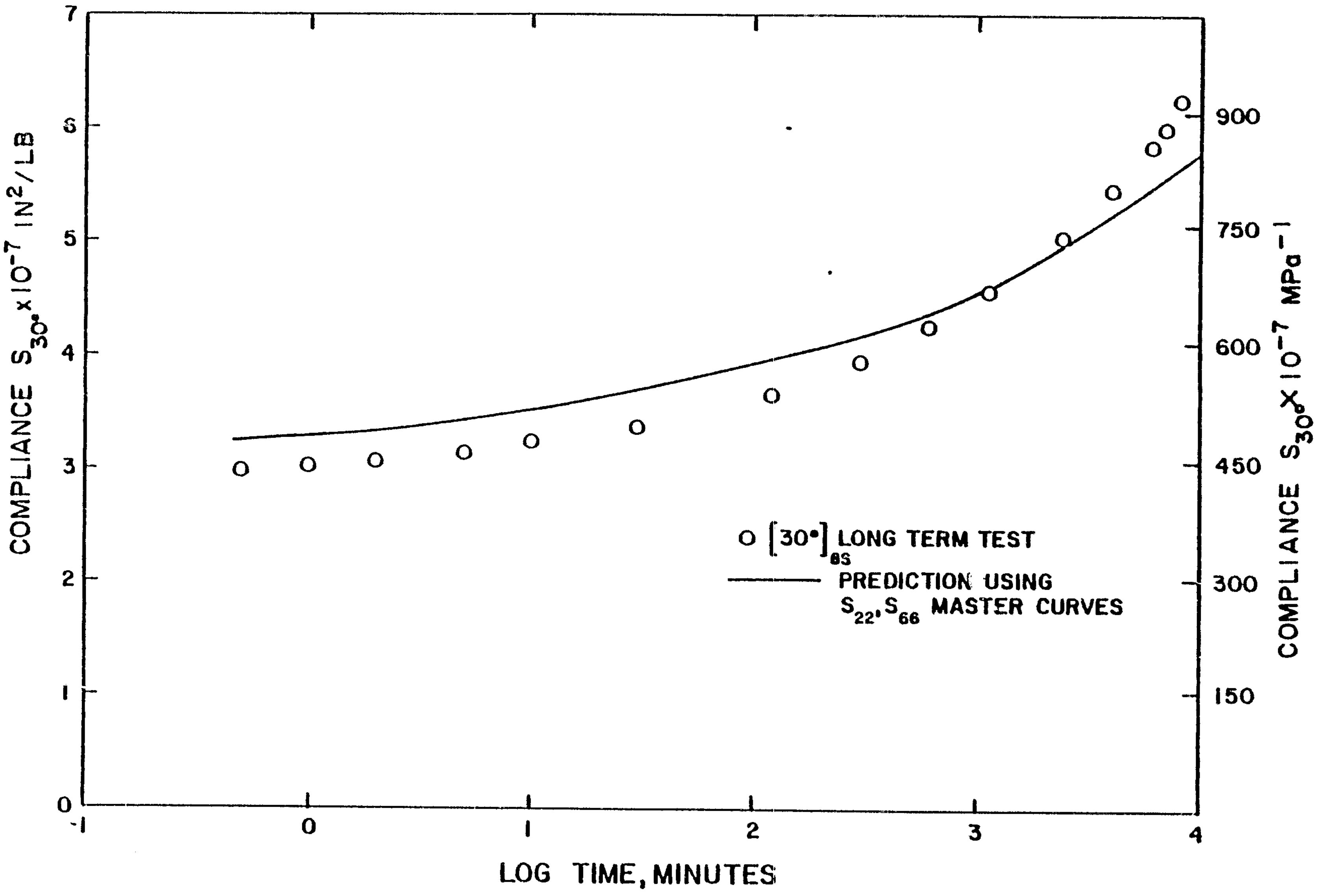

Fig. 10. Comparison of Predicted and Measured $S_{30°}$ Compliance at 320°F (160°C)

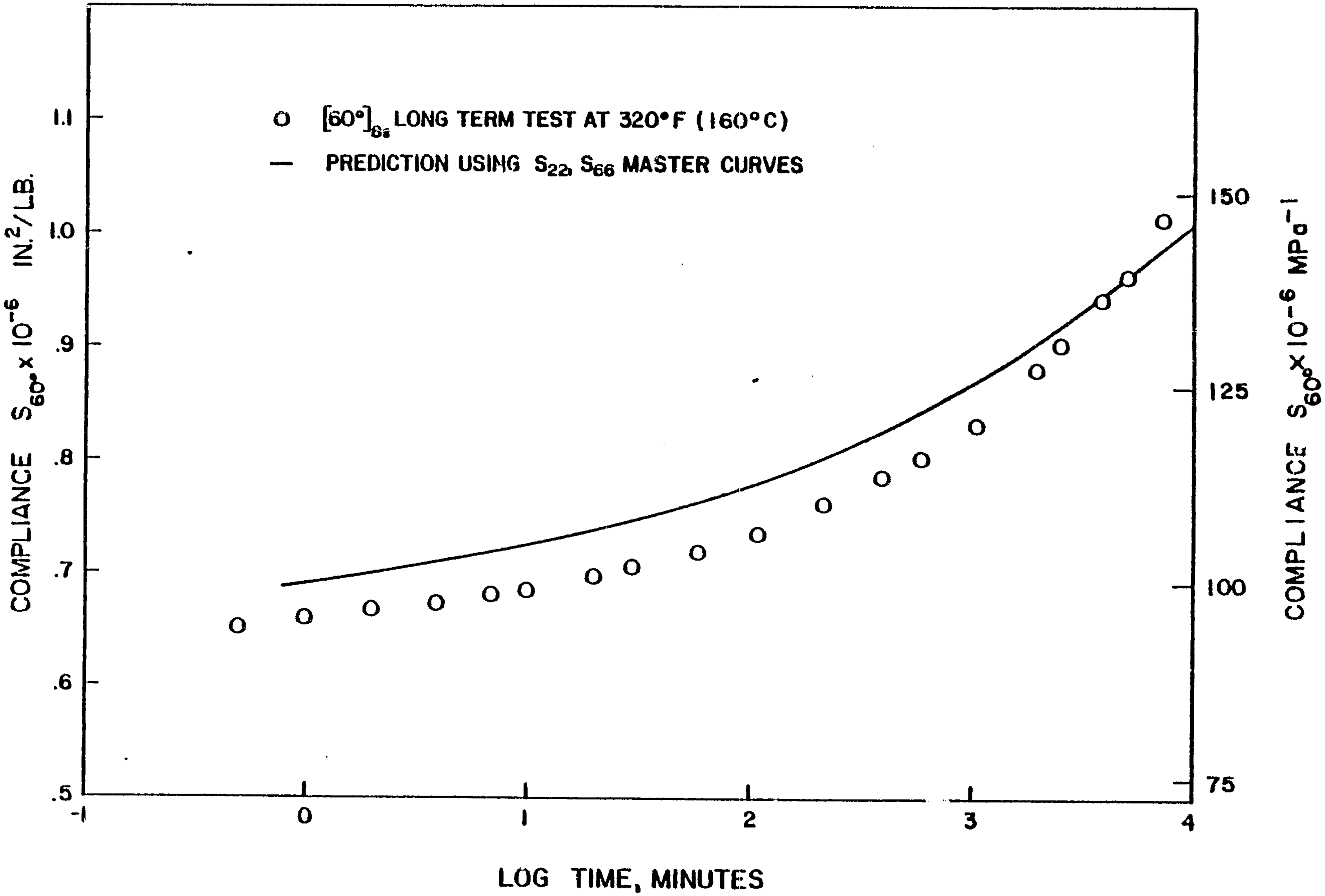

Fig. 11. Comparison of Predicted and Measured $S_{60°}$ Compliance at 320°F (160°C)