MATERIAL CHARACTERIZATION
OF VISCOELASTIC
POLYMERIC MOLDING COMPOUNDS

A Thesis
Presented in Partial Fulfillment of the Requirements for
the Degree Master of Science in the
Graduate School of The Ohio State University

by
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For My Family
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LIST OF SYMBOLS

\( \sigma \)  Stress
\( \varepsilon_i \)  Induced Strain
\( E(t) \)  Relaxation Modulus
\( \dot{\varepsilon} \)  Strain-Rate
\( t \)  Time
\( T \)  Temperature
\( a_T \)  Horizontal Shift Factor
\( t_r \)  Reduced Time
\( T_R \)  Reference Temperature
\( T_g \)  Glass-Transition Temperature
\( E_o \)  Short Time Relaxation Modulus
\( E_i \)  Prony Series Coefficients
\( \kappa_i \)  Characteristic Relaxation Times
\( \sigma_u \)  Ultimate Stress
\( \varepsilon_f \)  Failure Strain
CHAPTER I
INTRODUCTION

The emphasis today in microelectronic package manufacturing focuses on reducing the size of the devices. Typically, these electronic packages are encapsulated within a polymeric molding compound to protect the device from environmental and other effects. Previously, the size of the devices was large enough that mechanical effects on the molding compound were not considered in the design of the package. However, as the size of the device decreases, the stress levels in the molding compound become large and can not be neglected.

Also, during the assembly process, a technique known as solder-reflow subjects the package to large, rapid temperature changes. Because the matrix component of molding compounds is usually a polymer, its material characteristics can change as a function of temperature. This leads to further complication of the package design process; in order to design smaller yet durable electronic packages, the molding compound used must be fully characterized to allow the inclusion of both thermal and mechanical effects in the design.

Nitto-Denko MP7100 is a polymeric molding compound for use in electronic packaging. Additionally, MP7100 exhibits viscoelastic behavior. Therefore, the material characteristics of MP7100 are time and temperature
dependent, and the characterization of the molding compound must consider these time related effects.

**VISCOELASTIC CHARACTERIZATION**

In determining the viscoelastic properties of a polymer, several different experimental methods are used, each determining a different material parameter. Some of these tests are creep-compliance, stress-relaxation, and constant strain-rate testing. Here, only stress-relaxation and constant strain-rate testing were used.

The stress relaxation test is used to determine the relaxation modulus of a material as a function of time $t$. In its idealized form, the test involves inducing a known strain instantaneously in a specimen and subsequently holding that strain constant. The stress is then measured, indirectly through the load, as it decays over time. See Figure 1. For a uniaxial stress-relaxation test, we define the relaxation modulus as:

$$E(t) = \frac{\sigma(t)}{\varepsilon_o}$$  \hspace{1cm} (1)

where:

- $\varepsilon_o = \text{induced constant strain input}$, and
- $\sigma(t) = \text{resulting stress as a function of time}$

The results are typically plotted as logarithmic relaxation modulus versus logarithmic time.

Constant strain-rate testing is used to determine the elastic modulus of a material and the effects of load-rate on the material behavior. Here, the strain input is ramped at a constant strain-rate. As the strain is ramped the
Stress Relaxation Testing

Constant Strain Rate Testing

Figure 1  Schematic of Ideal Viscoelastic Tests
stress is measured again indirectly through the load. See Figure 1. The measured stress is then plotted against the strain.

**THERMORHEOLOGICALLY SIMPLE MATERIAL**

The time-temperature superposition principle, first noted by Leaderman, allows us to broaden the time scale of a relaxation (or creep-compliance) curve while still utilizing a relatively narrow experimental window [5]. Leaderman found that creep-compliance curves obtained at various temperatures could be shifted horizontally along the log t axis to create a smooth, continuous compliance curve known as a master curve [1]. Materials which exhibit this behavior are known as thermorheologically simple materials, or TSM. This principle also applies equally well to stress-relaxation curves.

Using a family of stress-relaxation curves obtained at various temperatures with identical strain inputs, one temperature is chosen as the reference temperature, \( T_R \). The remaining curves are then shifted along the log t axis relative to the curve obtained at \( T_R \) until they overlap and form a continuous master curve. The amount of horizontal shift at each temperature is known as the horizontal shift factor, \( a_T \). This shift factor is generally determined empirically, and is a function of temperature only.

Qualitatively this means that a change in temperature has the effect of changing the time scale of the material. Thus, using Leaderman's work, it can be shown that at time t, for some temperature \( T_1 \), the relaxation modulus, \( E(t, T_1) \), is the same as the relaxation modulus at a reference temperature, but at the reduced time \( t_R \); i.e., \( E(t, T_R) \) where:
\[ t_r = \frac{t}{a_T} \quad (2) \]

Here, the time has been scaled by an amount given by the shift factor, \( a_T \). By using the reduced time the log \( t \) axis of the shifted relaxation curve becomes:

\[ \log(t_r) = \log\left(\frac{t}{a_T}\right) = \log(t) - \log(a_T) \quad (3) \]

Because the reference curve is not shifted, \( a_T = 1 \) for \( T = T_R \). The shift factor will increase as temperature decreases and will decrease as temperature increases. This implies that relative to the reference temperature, processes accelerate for higher temperatures and decelerate for lower temperatures. Thus, relative to a particular reference temperature, elevated temperatures extend the reference data to longer times, while data from reduced temperature tests extend the reference data toward shorter times. In the present case, the resulting master curves at the reference temperature extend from \( 10^{-7} \) sec to \( 10^{12} \) sec.

**PROBLEM DESCRIPTION**

Increasingly severe operating conditions and smaller electronic packaging lead to greater sophistication in package design. Because of this, the time-dependent properties of the package materials must be considered in a package reliability analysis. Therefore the viscoelastic properties of the molding compound must be obtained before such an analysis can be performed. This research is generally meant to provide a model for time-dependent material property data characterization, while at the same time developing a specific data base for a commonly used molding compound, Nitto-Denko MP7100.
Specifically, stress-relaxation tests were performed and are discussed in Chapter II. Several strain levels and temperatures from ambient (24°C nominal) to 150°C were investigated. From these tests, master relaxation curves were developed using horizontal shifting. The shift factors are presented as functions of temperature and various forms of curve fitting were investigated to characterize the shift factors. A Prony series was then used to fit the master curves.

Also, constant strain-rate testing was performed at temperatures again ranging from room temperature to 150°C. Various strain-rates were also used to examine the effects of both strain-rate and temperature on the stress-strain behavior of MP7100. In addition, a master curve relating the material's secant modulus as a function of temperature and strain-rate was produced to investigate whether time-temperature superposition is valid for this material. These results are presented in Chapter III. Data and figures relevant to each appropriate section are presented in the text. Experimental data for all tests are presented in the appendices.
CHAPTER II
STRESS-RELAXATION TESTING

In characterizing a viscoelastic material, stress-relaxation tests are used to determine the relaxation modulus, $E(t)$, of the material. In these tests, a material specimen is subjected to a constant strain, and the stress is measured as it decays over time. The stress in the specimen must be measured indirectly through the load.

SPECIMEN DESCRIPTION AND TEST CONDITIONS

The specimens used were molded dog bone type IV tensile specimens conforming to ASTM D 638-91 and having a rectangular cross-section with nominal dimensions of 0.25 in. by 0.125 in. in the test section. The specimens were 4.5 in. in the overall length. The specimens were molded by INTEL Corporation and were subjected to a post mold cure at 175°C for 5 hours. A 0.25 in. hole was machined into each end to allow a pin connection with the testing apparatus. See Figure 2.

Stress relaxation tests were conducted at three strain levels: 0.25%, 0.5%, and 1.0% strain. The temperatures used for the strain levels were varied between ambient (24°C) and 150°C. A matrix of all stress-relaxation test conditions is shown in Table 1.
Figure 2       Test Specimen (actual size)
Essentially the test conditions were determined by the physical limits of the extensometer. The temperature operating range of the extensometer limited tests to a maximum of 150°C. Also, stress-relaxation strains below 0.25% were not attainable because strains of this magnitude and smaller approached the limits of the extensometer’s resolution.

Table 1  Matrix of Stress-Relaxation Test Conditions

<table>
<thead>
<tr>
<th>Strain Input</th>
<th>Test Temperatures (°C)</th>
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<tr>
<td></td>
<td>24 50 75 100 110 120 135 150</td>
</tr>
<tr>
<td>0.25%</td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>24 50 75 87 100 112 125 137 150</td>
</tr>
<tr>
<td>1.0%</td>
<td></td>
</tr>
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</table>

PROCEDURE

To induce the constant strain input on the specimen, an MTS servo-hydraulic test machine was used. The machine was operated in uniaxial strain control and the strain was measured using an MTS extensometer (model 632.85B-05) with a range of ± 5.0% strain over a 1 in. gage length. The load was measured using either a 200lb or 500lb capacity load cell (Lebow model 3169-108), depending upon the particular test conditions. Test temperatures were achieved using an MTS oven mounted on the frame of the servo-hydraulic machine. Extension rods and clevises were attached to the MTS actuator and crosshead to allow the use of the oven. A Data
Translations 12-bit A/D board was used in conjunction with an IBM/PC to record elapsed time, load, stroke, and strain.

With the MTS machine off, a specimen was inserted into the clevises and secured in place with steel pins. The extensometer was then attached to the specimen and the oven was activated. The system was allowed to reach thermal equilibrium for a minimum of one hour. A schematic of the experimental setup is shown in Figure 3.

To prevent a large load "bump" of the specimen, the MTS machine was then activated under stroke control. While in stroke control, the slack was removed from the system. The entire setup was then allowed to sit for several minutes until the output voltages had stabilized. At this point, the MTS machine was switched from stroke to strain control. This process usually resulted in the specimen being briefly subjected to a small load (<5 lbs). Once the machine was in strain control, the data acquisition software was activated and the test was begun. In all cases, the desired strain input was ramped in 1 second.

A chart recorder was used during the first seconds of the test to provide a real-time record of the initial strain ramp. This was done to allow verification that the desired strain level had been achieved.

**RESULTS**

In an ideal case, the strain input would have been induced by an instantaneous step function, as in Figure 1. In reality, the strain input was induced over a finite time span at a finite strain rate. In the tests conducted
Figure 3  Schematic of Test Setup
here, all strain inputs were ramped in 1 second as mentioned above. The
effect of this ramp time is that, initially, the relaxation modulus of the
material undergoing an actual test will not agree with that of an ideal test.
However, it can be shown that for times greater than 5t, where t is the ramp
duration, the difference between ideal and actual conditions is generally less
than 1% (see Appendix A of reference [6]). Based on this, the first 5 seconds
of each test data was removed before the data was reduced.

The relaxation modulus was determined by calculating the
engineering stress using the load data and the known initial cross-sectional
area. Then the relaxation modulus was determined from equation (1).
The relaxation modulus was then plotted as logarithmic E(t) against
logarithmic time. This test procedure was repeated at various temperatures
for strain inputs of 0.25%, 0.5%, and 1.0%. By performing the tests indicated
in Table 1, a family of stress-relaxation curves was generated for each strain
input. These families for 0.25%, 0.5%, and 1.0% strain are shown in Figures
4, 5, and 6 respectively. To illustrate the high level of reproducibility
possible, a replicate test is shown for $\varepsilon_o = 0.5\%$ and $T = 75^\circ C$. No tests were
conducted for $T<100^\circ C$ at a strain level of 1.0% because it was found that the
specimens repeatedly failed during the strain ramp at these lower
temperatures.

ANALYSIS

MP7100 has two distinct regions of behavior which are dependent
upon the temperature. At lower temperatures the material is said to exhibit
"glassy-type behavior". This is characterized by relatively high elastic
Figure 4 Stress-Relaxation Curve Family for $\varepsilon_0 = 0.25\%$ Strain
Figure 5  Stress-Relaxation Curve Family for $\varepsilon_0 = 0.5\%$ Strain
Figure 6  Stress-Relaxation Curve Family for $\varepsilon_0 = 1.0\%$ Strain
moduli for temperatures in this region. At higher temperatures, the material undergoes "rubbery-type behavior", where the elastic modulus is greatly reduced with respect to the glassy region. "The region where the modulus ... has the greatest dependence upon temperature is called the transition region. The corresponding temperature, or narrow temperature range, is designated as the glass-transition temperature $T_g$" [1]. In the transition region the material can undergo drastic changes in its mechanical behavior over a very small change in temperature.

This phenomenon can best be seen in Figures 4 and 5. For the lower test temperatures (e.g. 24°C, 50°C, 75°C), the material’s modulus exhibits only a modest dependence on temperature illustrated by the almost horizontal stress-relaxation curves. This is also true for the higher test temperatures (e.g. 135°C to 150°C). However, in the transition temperature region (100°C to 125°C) the modulus has a much larger dependence on temperature. This is illustrated by the relatively large vertical changes in the stress-relaxation curves at these temperatures. In this transition region the curvature of the stress-relaxation curves changes from concave-down to concave-up at a temperature of approximately 110°C. This temperature can be taken as a measure of the glass-transition temperature which compares with values if 120°C - 130°C quoted by Nitto-Denko.

Examination of the curve families revealed that, in all three cases, the curves could be shifted horizontally to produce smooth, continuous master curves. Thus MP7100 is a thermorheologically simple material. A reference temperature of $T_R = 100°C$ was arbitrarily selected because it was the lowest
temperature at which a 1.0% strain was attainable without failure of the specimen. These master curves are shown in Figure 7.

Examination of the 0.25% strain and 0.5% strain master curves in Figure 7 illustrates two distinct regions: an upper shelf for short times, and a lower shelf at longer times separated by the steeper, transition region. In this transition region the relaxation modulus has its strongest dependence on time. The data in this transition region were acquired at or near the glass-transition temperature and are very susceptible to slight thermal variations. This can introduce discrepancies in the relaxation curves which manifest themselves as incoherent regions on the master curve. This is the case particularly in the 0.25% strain master curve at approximately Log t = 3.

The master curves shown in Figure 7 show that MP7100 exhibits non-linear viscoelastic behavior within the range of strain tested here. This is evident because the relaxation modulus is dependent upon the imposed strain $\varepsilon_0$.

For each of the master curves generated, the horizontal shift factors are functions only of temperature. Because of this, the shift factors versus temperature for all three cases are plotted for a 100°C reference temperature. See Figure 8. Some error is to be expected in obtaining these shift factors. The main sources of this error can be attributed to error in estimating the shift of the individual stress-relaxation curves themselves. This is of special concern when shifting the curves obtained at the low and high temperatures. Unlike the curves obtained near the transition temperature, these curves are relatively flat. Because of this, there is some measure of ambiguity in the locality of their overlap. It is this source of error which could account for the
Figure 7 Stress-Relaxation Master Curves at $T_R = 100^\circ C$ (for all $\varepsilon_o$)
Figure 8  Log $a_T$ versus Temperature for $T_R = 100^\circ$C (for all $\varepsilon_0$)
spreading of the shift factors at both ends of the curve illustrated in Figure 8. To quantify this error, an equation discussed by Kenner, Knauss, and Chai can be used [4]. This equation is given by

$$\delta \log a_T = 2 \delta \log E \left( \frac{\Delta \log t}{\Delta \log E} \right)$$

(4)

where $\delta \log a_T$ = possible shifting error, $\delta \log E$ = vertical error in relaxation curve, and $\left( \frac{\Delta \log t}{\Delta \log E} \right)$ = inverse of the slope of the relaxation curve. For a derivation of equation (4) see Reference [4].

The shift factor error decreases the closer the test temperature is to the transition temperature. This is due to the increasing slope of the curves in this region. Conversely, shifts occurring at temperatures well above or below the transition temperature will have larger errors due to the smaller slopes of the curves involved. Examination of the replicate tests in Figure 5 reveals a $\delta \log E$ of approximately 0.03 which corresponds to approximately 8% error. Taking this value to be the “worst case” vertical error in the stress-relaxation curves, calculating the straight-line slopes of the individual stress-relaxation curves, and by applying equation (4), error bars can be applied to the shift factors as in Figure 8. Although these bars would suggest large errors for the extreme temperatures (on the order of 6 decades for $T = 24^\circ$C), it is not felt that such large error is actually present in the shift data. This is merely the quantification of the possible error and not a reflection of the actual error.

This plot is then fitted using the WLF equation, a straight line, and the Arrhenius equation. It was observed that the shift factor undergoes a noticeable change in slope as it passes through the glass-transition
temperature. Because of this, the shift factor was fitted separately both above and below this temperature.

The WLF equation was first proposed by Williams, Landel, and Ferry to relate the horizontal shift factor and temperatures for polymers [2]. The form of this equation is given by

$$\log a_T = -\frac{c_1(T - T_R)}{c_2 + T - T_R}$$

where $T_R$ = the reference temperature. In attempting to fit the data using the WLF equation, it was found that the fit curves were concave-down, which is opposite in nature to what would normally be expected. This means that the resulting coefficients, $c_1$ and $c_2$, have no physical significance and the WLF equation was therefore rejected as a possible fit method.

The Arrhenius equation is given by:

$$\log a_T = A + \frac{B}{T_{\text{ABS}}}$$

where $T_{\text{ABS}}$ = absolute temperature and the constants $A$ and $B$ were found to be:

$A = -39.03$

$B = 14232 \, (^{\circ}K)$ for $T < T_g$

$A = -64.63$

$B = 23993 \, (^{\circ}K)$ for $T > T_g$

Although both the straight-line and Arrhenius equations provided usable fits, upon examination the Arrhenius fit was chosen to be the best approximation of the horizontal shift factor as a function of temperature. This form was used both above and below the glass-transition temperature. This fit to the shift factor data is shown in Figure 8.
A Prony series was used to fit the master relaxation modulus curve for each of the strain levels. This series is of the form
\[ E(t) = E_o - \sum_{i=1}^{n} E_i \left( 1 - \exp^{-\frac{t}{\kappa_i}} \right) \]  
(7)
where \( E_o \) = long-term relaxation modulus, \( E_i \) = Prony coefficients, and \( \kappa_i \) = characteristic relaxation times. In fitting the master curves, the reference temperature was taken as \( T_R = 100^\circ C \), and the characteristic relaxation times were taken at every even decade on the log-time axis. Table 2 shows the Prony coefficients obtained from fitting the 0.25% strain master curve. This master curve and the fit obtained are shown in Figure 9. Table 3 contains the Prony series fit coefficients for the 0.5% strain master curve, while Figure 10 illustrates the 0.5% strain curve fit. Table 4 and Figure 11 show the fit data and actual curve fit for the 1.0% strain master curve. In all cases the Prony series provides an excellent fit to the stress-relaxation master curves.

Stress-relaxation data for all tests conducted are given in Appendix A.
Table 2  Prony Coefficients for 0.25% Strain Master Curve

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<th>$E_i$ (MPa)</th>
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<td>21</td>
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$E_0$ (MPa) 21434.5
Figure 9  0.25% Strain Stress-Relaxation Master Curve with Prony Series Fit
Table 3  
Prony Coefficients for 0.5% Strain Master Curve

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$E_0$ (MPa) 17203.7
Figure 10 0.5% Strain Stress-Relaxation Master Curve with Prony Series Fit
Table 4  Proney Coefficients for 1.0% Strain Master Curve

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$E_0$ (MPa) 2980.3
Figure 11  1.0% Strain Stress-Relaxation Master Curve with Prony Series Fit.
CHAPTER III
CONSTANT STRAIN-RATE TESTING

Constant strain-rate testing is used to determine the influence of loading rate on the behavior of a material. In a constant strain-rate test, a material specimen is subjected to uniaxial strain which is ramped at a constant rate. The resulting stress is measured indirectly through the load.

SPECIMEN DESCRIPTION AND TEST CONDITIONS

The material specimens used for constant strain-rate testing were identical to the specimens used in the stress-relaxation tests (see Figure 2). Constant strain-rate tests were performed at strain-rates of $10^{-4}$ s\(^{-1}\), $10^{-5}$ s\(^{-1}\) and $10^{-6}$ s\(^{-1}\). Temperatures were varied between ambient (24°C) and 150°C to examine the effects of both strain-rate and temperatures on the mechanical behavior of MP7100. Of particular interest was the initial elastic modulus $E$, as well as the maximum stress. A matrix of the constant strain-rate test conditions is shown in Table 5. As stated in Chapter 2, the test temperatures were limited to $T<150$°C because of the operating range of the extensometer. Strain-rates of $10^{-4}$ s\(^{-1}\), $10^{-5}$ s\(^{-1}\) and $10^{-6}$ s\(^{-1}\) were arbitrarily chosen to provide a variety of strain-rates which would produce usable data.
Table 5  Matrix of Constant Strain-Rate Test Conditions

<table>
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<tr>
<th>$\dot{e}$ (s$^{-1}$)</th>
<th>Test Temperatures ($^\circ$C)</th>
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<td>10$^{-4}$</td>
<td>24</td>
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<td>10$^{-5}$</td>
<td>24</td>
</tr>
<tr>
<td>10$^{-6}$</td>
<td>24</td>
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PROCEDURE

The test equipment and software used, as well as the procedure for mounting a test specimen, was identical to the stress-relaxation testing.

Following startup of the MTS machine and the subsequent mode switch to strain control, (see Chapter II, Procedure) the data acquisition software was activated, and the strain began ramping at the preselected rate. Here, the chart recorder was employed throughout the test to allow a real-time plot of the load versus strain curve being generated by the specimen.

RESULTS

For each test, the engineering stress was calculated and plotted against strain. The plots were then used to produce families of curves to illustrate the effects of temperature and strain-rate on the material.

To examine the effect of temperature on the mechanical behavior of MP7100, Figure 12 contains the stress-strain curves generated at a strain-rate of 10$^{-4}$ s$^{-1}$ for all temperatures. Similarly, Figure 13 contains the curves for a strain-rate of 10$^{-5}$ s$^{-1}$ and Figure 14 corresponds to a strain-rate of 10$^{6}$ s$^{-1}$. 

Figure 12  Effect of Temperature on Tensile Response
Strain-Rate = $10^{-4}$ s$^{-1}$
Figure 13  Effect of Temperature on Tensile Response
Strain-Rate = 10^{-5} \text{ s}^{-1}
Figure 14  Effect of Temperature on Tensile Response
Strain-Rate = 10^{-6} \text{ s}^{-1}
To demonstrate the high level of reproducibility in the constant-strain rate tests, a replicate test is shown for a strain-rate of $10^{-5}$ s$^{-1}$ at $T = 100^\circ$C.

The effects of strain-rate are illustrated in the following Figures:

- Figure 15 .................................. 24°C
- Figure 16 .................................. 50°C
- Figure 17 .................................. 75°C
- Figure 18 .................................. 100°C
- Figure 19 .................................. 125°C
- Figure 20 .................................. 150°C

In all cases, all three (3) strain-rates are represented at a single temperature.

A dramatic decrease in the initial, elastic modulus of the material can be seen to occur as temperatures increase beyond 100°C for all strain-rates (see Figures 12, 13, 14). This can be attributed to the material passing through its glass-transition temperature and entering the “rubbery” regime. The nature of the glass-transition was discussed in Chapter II, Analysis.

Generally the strain to failure increases with increasing temperature until a maximum value is reached at $T = 125^\circ$C. This effect can also be attributed to the glass-transition temperature. As the material nears the transition temperature, its behavior is slowly becoming more “rubbery”. This allows greater strains to be reached, while the elastic modulus decreases. At $T_g$, there is a large decrease in the modulus and the material rapidly becomes “rubbery”, allowing even larger strains to be achieved, while the modulus has decreased even further. As the temperature increases well beyond the transition temperature, the material begins to move further into the “rubbery” region and loses tensile strength. As this happens the material becomes very soft and the failure strain begins to decrease as temperature increases further.
Table 6 contains the elastic modulus, the ultimate stress, and the failure strain determined from each constant strain-rate test conducted. All constant strain-rate test data are given in Appendix B.
Figure 15  Effect of Strain-Rate on Tensile Response  
T = 24°C
Figure 16: Effect of Strain-Rate on Tensile Response
T = 50°C
Figure 17  Effect of Strain-Rate on Tensile Response
\( T = 75^\circ C \)
Figure 18  
Effect of Strain-Rate on Tensile Response 
$T = 100^\circ C$
Figure 19  Effect of Strain-Rate on Tensile Response
T = 125°C
Figure 20  Effect of Strain-Rate on Tensile Response
T = 150°C
Table 6  Constant Strain-Rate Test Results

<table>
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<th>Strain Rate:</th>
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<tr>
<td>E = 21.8x10^3 MPa</td>
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E: elastic modulus
σ_u: ultimate stress
ε_f: failure strain
ANALYSIS: Secant Modulus Master Curve

Ferry noted that for time-temperature superposition to be valid, the shift data for different tests must agree for the same material [2]. As a check on the stress-relaxation modeling of MP7100, the ability to create a master curve using secant modulus data was investigated. The secant modulus is defined to be the slope of a line on a stress versus strain curve drawn from the origin to the point on the curve that corresponds to a specified strain level. For all 18 constant strain-rate tests, the 0.2% strain secant modulus was determined. The logarithmic secant moduli were plotted versus logarithmic strain-rate for each test temperature. Figure 21 illustrates this family of curves.

It was then investigated whether these curves could be shifted horizontally on the logarithmic strain-rate axis to form a smooth, continuous master curve, as was done with the stress-relaxation data. Only horizontal shifting was considered in order to remain consistent with the method used to generate the stress-relaxation master curves. Using a reference temperature of $T_R = 100^\circ$C, shift factors for each temperature were determined by using the Arrhenius equations developed in Chapter II. Using these shift factors, the log secant modulus curves in Figure 21 were shifted horizontally by replacing $\dot{e}$ with $\dot{e}/a_r$. Upon shifting the curves, it was found that a master curve began to take shape. Although not continuous, the master curve in Figure 22 has a shape that could be construed as smooth.

Further experimentation is needed to fully populate the secant modulus master curve, but from the available data, the shift data appears to
be consistent between the stress-relaxation master curves and the secant modulus master curve. Since the shift factors used to generate the secant modulus master curve were determined from the straight line equations used to characterize the stress-relaxation master curve shift factors, time-temperature superposition principle appears to be valid for MP7100.
Figure 21  Log Secant Modulus versus Log Strain-Rate
Figure 22  
Secant Modulus Master Curve at $T_R = 100^\circ C$
CHAPTER IV
PREDICTION OF STRESS/STRAIN BEHAVIOR

The behavior of a material during constant strain-rate testing can be predicted by using the results of the stress-relaxation testing. Assuming the material to behave in a linearly viscoelastic manner, we make use of the constitutive relation:

$$\sigma(t) = \int_{-\infty}^{t} E(t-\tau) \frac{d\varepsilon}{d\tau} \, d\tau$$  \hspace{1cm} (8)

We can integrate this expression over a desired time-span to obtain the resulting stress as a function of time [1]. Here, we define our strain history to be the constant strain-rate ramp used in the constant strain-rate tests. Therefore, (8) becomes:

$$\sigma(t) = \int_{-\infty}^{t} E(t-\tau) \dot{\varepsilon} \, d\tau$$  \hspace{1cm} (9)

Recognizing that in all cases the strain rate is a constant, we can factor it out of the integral. Also, because we assume the modulus to be zero for \( t \leq 0 \), we can further simplify the limits of integration. Therefore:

$$\sigma(t) = \dot{\varepsilon} \int_{0}^{t} E(t-\tau) \, d\tau$$  \hspace{1cm} (10)

In Chapter II the modulus of the material was modeled using a Prony series of the form given by equation (7). Substituting (7) into (10), we obtain upon integrating:
\[
\sigma(t) = E_t \left[ E_i t - \sum_{i=1}^{n} E_i \left( t - \kappa_i \left( 1 - \exp^{-\kappa_i} \right) \right) \right]
\] (11)

Recall that \( E_i \) and \( \kappa_i \) were obtained from fitting a master curve generated at a reference temperature of \( T_R = 100^\circ C \). To make use of equation (11) at temperatures other than the reference temperature, we simply multiply each \( \kappa_i \) by the resulting shift factor corresponding to the different temperature. Here, these shift factors were obtained from the Arrhenius fits developed in Chapter II.

The accuracy of equation (11) in predicting the stress-strain behavior of the material is a test of the linear model used for the constitutive relation. By using equation (11) and each of the three Prony series generated for the master curves, three stress versus strain curves were calculated for comparison with experimental data. The constant strain-rate tests performed at 24\(^\circ\)C, 100\(^\circ\)C, and 150\(^\circ\)C at a rate of 10\(^{-4}\) s\(^{-1}\) were used for comparison. Each experimental curve along with the three predictions based on the three stress-relaxation master curves are shown in Figures 23, 24, and 25 for 24\(^\circ\)C, 100\(^\circ\)C, and 150\(^\circ\)C respectively.

At all three temperatures, the best prediction of the experimental curve is provided by the 0.25\% strain master curve data. This is to be expected because a linear constitutive model should provide a better approximation for smaller strains. Some viscous effects can be seen in the prediction curves, as their slopes are not constant, but decrease with increasing strain.

The best overall prediction is that of the 0.25\% strain master curve data at \( T = 24^\circ C \). Here, the predicted response for small strains nearly
Figure 23  Comparison of Experimental and Predicted Stress-Strain Behavior for $T = 24^\circ C$
Figure 24  Comparison of Experimental and Predicted Stress-Strain Behavior for $T = 100^\circ C$
Figure 25  Comparison of Experimental and Predicted Stress-Strain Behavior for $T = 150^\circ C$
matches the experimental curve. The other predictions underestimate the actual material response, with the 0.5% strain data better than the 1.0% strain data by far. The prediction for room temperature behavior based upon the relaxation modulus for 1% strain must be considered suspect because of the lack of short term data at this temperature (24°C nominal). Recall form Chapter II that no actual test data were attainable at a strain level of 1% for temperatures less than 100°C. The Prony fit to the relaxation data in Figures 9, 10, and 11 provide an extrapolated short-term modulus which is represented by the left-most point in each fit. The extrapolated value from Figure 11 (1% strain) is approximately 20% of the extrapolated short-term modulus from Figure 9 (0.25% strain). In reality, the short-term modulus for 1% strain is probably more than twice the value indicated in the Prony fit.

In the 100°C case, the predicted results are somewhat lower in magnitude for relatively small strains than the experimental curve. At 100°C the material is in the transition region between “glassy” and “rubbery” behavior. It is in this transition region that the non-linear effects are most evident. Because of this, the large discrepancies between the predicted and the experimental responses seen in Figure 24 can be attributed to the non-linear behavior of the material which the linear model cannot accommodate. Because a linear model was used, the predictions underestimate the response for smaller strains while overestimating the response for larger strains.

For T = 150°C the predicted curves all provide decent representations of the experimental curve. At this temperature the rate processes are greatly accelerated and the long-term moduli (represented by the right-most point
of the fit in Figures 9, 10, and 11) begin to dominate the predictions much sooner. Hence the difference between the predictions and the experimental response are relatively small because the non-linear effects are reduced at large times.

**QUASI-NON-LINEAR PREDICTION ANALYSIS:**

In a constant strain-rate test, lower strain levels will obviously occur at shorter times. As time increases so does the strain in the material. However, because MP7100 exhibits viscoelastic behavior, the modulus of the material, and thus the stress-strain response, varies with time. Additionally, MP7100 is a non-linear viscoelastic material, therefore its modulus also has a dependence on the strain level.

At room temperature, the material’s initial response is governed by its short-time, low strain level modulus. For the data gathered here, this corresponds to the “upper-shelf” of the 0.25% master curve. As time progresses the strain level increases. Eventually the material’s behavior is better characterized by the 0.5% strain master curve. As time progresses further, the strain level continues to rise and the material’s modulus behaves like the 1.0% strain master curve. All of these master curves are illustrated in Figure 7.

At 100°C, the material’s initial response is governed by its glass-transition region, low strain level modulus. Here this corresponds to the transition region of the 0.25% strain master curve. The modulus in this region of the curve is lower than that in the “upper-shelf” region. At 100°C we would expect the modulus of the material to be lower than the modulus
of the material at 24°C. As the strain increases the material behavior
becomes like the transition region of the 0.5% strain master curve, followed
by the 1.0% master curve.

At 150°C the material's initial response will be that of the “rubbery”
region, low-strain level modulus. This corresponds to the “lower-shelf” of
the 0.25% strain master curve. As above, when the strain increases, the
material response becomes like the 0.5% strain master curve and then the
1.0% strain master curve. The predicted response never levels off to an
asymptotic value because the stress-relaxation models always indicate a
non-zero modulus for very large times.

In performing a quasi-non-linear prediction of the stress-strain
response, we will make use of all three sets of stress-relaxation data to
formulate a single prediction at a given temperature. First, we produce the
three separate linear response predictions from each set of stress-relaxation
data as outlined in the previous section. Then on each prediction curve, we
mark a point which corresponds to the stress at the strain at which that
particular prediction data was acquired (i.e., 0.25% strain for the 0.25% strain
master curve data, 0.5% strain for the 0.5% strain master curve data, etc.). We
will begin to see that these data points create a curve that is in relatively
good agreement with the experimental response.

This procedure was applied to the room temperature case and can be
seen in Figure 23. Here, at 24°C, the 1.0% strain master curve data was not
applicable for the reasons discussed in the previous section concerning
extrapolation of the short-time modulus. However, using just the two data
sets yields a prediction that is relatively accurate. Figure 24 shows the
prediction for $T = 100^\circ C$. Here all three data sets were employed and the resulting prediction is quite good. The quasi-non-linear prediction does underestimate the actual response for larger strains (larger times). At $T = 150^\circ C$ the quasi-non-linear prediction is accurate initially, but it too underestimates the actual response at larger strains. This can be seen in Figure 25.
CHAPTER V
CONCLUSIONS

Nitto-Denko MP7100 is a molding compound currently available for use in the design and manufacture of microelectronic packages. The goal of this research was to determine the viscoelastic characteristics of the MP7100 molding compound, and to develop a methodology for the characterization of these types of materials. These characteristics were determined through the use of stress-relaxation testing and constant strain-rate testing.

Stress-relaxation tests were conducted at various strain levels and temperatures to determine the relaxation modulus of the material. It was found that MP7100 is a thermorheologically simple material which exhibits nonlinear viscoelastic behavior. For each strain level investigated, stress-relaxation master curves were formed through horizontal shifting alone. The error in these shift factors was investigated and it was found that the error becomes larger for temperatures further away from the glass-transition temperature. Because MP7100 exhibits non-linear viscoelastic behavior, the shape of the stress-relaxation curve and magnitude of the relaxation modulus was dependent on the strain level. The time dependence of the relaxation modulus for each strain level was modeled using a Prony series.

Constant strain-rate testing was used to examine the effects of load-rate on the material. Tests were conducted at various temperatures and
strain-rates. From the data, families of curves were developed to illustrate the effects of both temperature and strain rate. It was found that the elastic modulus of MP7100 is highly dependent on temperature while strain-rate has minimal effects. This is illustrated in both the Figures of Chapter III and in Table 6.

Also, a master curve relating the secant modulus (@ 0.2% strain) and the strain-rate was produced to investigate the validity of the use of the time-temperature superposition principle. Using the horizontal shift factors obtained from the stress-relaxation master curves and using the limited experimental data available, a coherent secant modulus master curve was produced.

Using the Prony series fits to the stress-relaxation master curves, the constant strain-rate behavior was predicted. A linear viscoelastic constitutive relation was assumed for the predictions. These predictions all underestimated the modulus of the material initially, while at larger strains the predicted behavior overestimated the actual response. These discrepancies can be attributed to using a linear constitutive relation to predict the nonlinear viscoelastic response of the material. Because a constitutive relation assuming linear viscoelastic behavior was used, the best prediction of initial response was found using the lowest strain level master curve data. A quasi-non-linear method of predicting the response was investigated. It was found that this method produced relatively accurate prediction of stress-strain response even for larger strain levels than seen in the predictions. Theses quasi-non-linear predictions were most useful for temperatures above 100°C.
APPENDIX A

RELAXATION DATA FOR NITTO-DENKO MP7100
(AT INITIAL STRAINS OF 0.25%, 0.5%, AND 1.0%)
Figure 26: Log E versus Log t for $\varepsilon_0 = 0.25\%$ Strain
$T = 24^\circ C$
Figure 27  Log E versus Log t
for $\varepsilon_o = 0.25\%$ Strain
$T = 50^\circ$C
Figure 28  
Log E versus Log t  
for $\varepsilon_0 = 0.25\%$ Strain  
$T = 50^\circ$C (replicate test)
Figure 29  Log E versus Log t
for $\varepsilon_0 = 0.25\%$ Strain
$T = 75^\circ$C
Figure 30  
Log $E$ versus Log $t$  
for $\varepsilon_0 = 0.25\%$ Strain  
$T = 100^\circ C$
Figure 31  
Log E versus Log t  
for $\varepsilon_0 = 0.25\%$ Strain  
$T = 110^{\circ}C$
Figure 32  Log E versus Log t
for $\varepsilon_0 = 0.25\%$ Strain
T = 120°C
Figure 33  Log E versus Log t
for $\varepsilon_0 = 0.25\%$ Strain
$T = 135^\circ C$
Figure 34  Log E versus Log t
for $\varepsilon_0 = 0.25\%$ Strain
T = 150°C
Figure 35  Log E versus Log t  
for $\varepsilon_0 = 0.5\%$ Strain  
$T = 24^\circ C$
Figure 36  
Log E versus Log t  
for $\varepsilon_0 = 0.5\%$ Strain  
$T = 50^\circ C$
Figure 37  \(\log E\) versus \(\log t\) for \(\varepsilon_0 = 0.5\%\) Strain

\(T = 75^\circ C\)
Figure 38
Log E versus Log t
for ε₀ = 0.5% Strain
T = 75°C (replicate test)
Figure 39: Log E versus Log t
for $\varepsilon_0 = 0.5\%$ Strain
$T = 87^\circ C$
Figure 40  
Log E versus Log t  
for $\varepsilon_o = 0.5\%$ Strain  
$T = 100^\circ$C
Figure 41  
Log E versus Log t  
for $\epsilon_0 = 0.5\%$ Strain  
$T = 112^\circ C$
Figure 42  Log E versus Log t
for $\varepsilon_0 = 0.5\%$ Strain
$T = 125^\circ C$
Figure 43 Log E versus Log t for $\varepsilon_0 = 0.5\%$ Strain
$T = 137^\circ C$
Figure 44: Log E versus Log t for $\varepsilon_o = 0.5\%$ Strain
$T = 150^\circ C$
Figure 45  Log E versus Log t
for $\epsilon_0 = 1.0\%$ Strain
$T = 100^\circ$C
Figure 46
Log E versus Log t
for ε₀ = 1.0% Strain
T = 112°C
Figure 47 Log E versus Log t
for $\varepsilon_o = 1.0\%$ Strain
$T = 125^\circ C$
Figure 48  
Log E versus Log t  
for $\varepsilon_0 = 1.0\%$ Strain  
$T = 125^\circ\text{C}$ (replicate test)
Figure 49  
Log E versus Log t  
for ε₀ = 1.0% Strain  
T = 137°C
Figure 50
Log E versus Log t
for $\varepsilon_0 = 1.0\%$ Strain
$T = 150^\circ$C
APPENDIX B

CONSTANT STRAIN-RATE DATA FOR NITTO-DENKO MP7100

(AT STRAIN-RATES OF $10^{-4}$ s$^{-1}$, $10^{-5}$ s$^{-1}$, AND $10^{6}$ s$^{-1}$)
Figure 51  Stress versus Strain for Strain-Rate = $10^{-4}$s$^{-1}$
$T = 24^\circ$C
Figure 52  Stress versus Strain
for Strain-Rate = 10^{-4}s^{-1}
T = 50^\circ\text{C}
Figure 53  Stress versus Strain
for Strain-Rate = 10^{-4}s^{-1}
T = 75°C
Figure 54 Stress versus Strain
for Strain-Rate = $10^{-4}$ s$^{-1}$
$T = 100^\circ$C
Figure 55  Stress versus Strain for Strain-Rate = 10^{-4} s^{-1}  
T = 125°C
Figure 56  Stress versus Strain
for Strain-Rate = 10^{-4}s^{-1}
T = 125^°C (replicate test)
Figure 57  
Stress versus Strain  
for Strain-Rate = 10^{-4}s^{-1}  
T = 150°C
Figure 58  Stress versus Strain
for Strain-Rate = $10^{-5}$s$^{-1}$
$T = 24^\circ$C
Figure 59  
Stress versus Strain  
for Strain-Rate = $10^{-5}$s$^{-1}$  
T = 50$^\circ$C
Figure 60  Stress versus Strain
for Strain-Rate = 10^{-5}s^{-1}
T = 75°C
Figure 61  Stress versus Strain
for Strain-Rate = 10^{-5}s^{-1}
T = 75^\circ C (replicate test)
Figure 62  Stress versus Strain
for Strain-Rate = 10^{-5}s^{-1}
T = 100°C
Figure 63  Stress versus Strain
for Strain-Rate = 10^{-5}s^{-1}
T = 100°C (replicate test)
Figure 64  Stress versus Strain for Strain-Rate = $10^{-5}\text{s}^{-1}$
$T = 125^\circ\text{C}$
Figure 65 Stress versus Strain for Strain-Rate = 10^{-5}s^{-1} T = 150°C
Figure 66  
Stress versus Strain  
for Strain-Rate = 10^{-6}s^{-1}  
T = 24°C
Figure 67  Stress versus Strain
for Strain-Rate = 10^{-6} s^{-1}
T = 50^\circ C
Figure 68  Stress versus Strain
for Strain-Rate = 10^{-6}s^{-1}
T = 75°C
Figure 69 Stress versus Strain for Strain-Rate $= 10^{-6}\text{s}^{-1}$
$T = 100^\circ\text{C}$
Figure 70  Stress versus Strain for Strain-Rate = 10^{-6}s^{-1}  
T = 125°C
Figure 71  Stress versus Strain for Strain-Rate = 10^{-6}s^{-1}
            T = 150^\circ C
LIST OF REFERENCES


