To the Graduate Council.

I am submitting herewith a thesis written by Ryan Lee Karkkainen entitled "Empirical Modeling of In-Cure Volume Changes and Elasticity Development of Thermoset Polymers." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Mechanical Engineering

Madhu S. Madhukar

Madhu S. Madhukar, Major Professor

We have read this thesis
and recommend its acceptance.

Accepted for the Council

EMPIRICAL MODELING OF IN-CURE VOLUME CHANGES AND ELASTICITY DEVELOPMENT OF THERMOSET POLYMERS

A Thesis
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ABSTRACT

In the interest of evaluating the cure-induced residual stresses that develop during manufacturing of a thermoset polymer composite, a course of research has been carried out to determine the nature of volume changes that occur during a cure cycle These volume changes are known to be from two different sources thermal expansion and cure shrinkage A well-characterized aerospace material, Hercules 3501-6 Epoxy, has been used to develop a model for the cure shrinkage and thermal expansion during cure The developed methods are also applied to RS-3 and EX-1515 resins The primary equipment used includes a volumetric dilatometer, which monitors total sample volume change during cure, a differential scanning calorimeter (DSC), which is used to evaluate sample degree of cure, and a cure induced stress test (CIST) which monitors the cure induced stresses that are developed in embedded fibers Cure shrinkage was isolated by monitoring isothermal cure processes, in which case there are no thermal volume changes to account for. Cure shrinkage was shown to be linear with respect to degree of cure Thermal volumetric effects were determined by investigating cure cycles of constant heat rate. The thermal expansion coefficient was shown to be constant over a wide range of temperature and degree of cure Based upon experimental data, a model has been developed to predict total volume changes for an arbitrary cure cycle As a follow-on study, the volume change data has been combined with analysis of the polymer stress state to develop an investigation of in-cure development of elastic modulus The development of elasticity was shown to mimic the progression of degree of cure.

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LIST OF SYMBOLS

α	degree of cure
K	cure shrinkage constant of linearity
ΔV_{SH}	volumetric cure shrinkage
ΔV_{TH}	thermal volume change
ΔV_{TOT}	total volume change
Θ	volumetric thermal expansion coefficient
T	temperature
H_R	total heat of reaction
H	cumulative heat of reaction
$^{dH}/_{dt}$	rate of heat generation
E	modulus of elasticity
ΔF	change in fiber tension
ε_{VOL}	volumetric strain
ε	linear strain
Δv	change in specific volume
v_0	initial specific volume

1. INTRODUCTION

A study of volume changes during cure is essential in the investigation of manufacturing of polymer composite materials The dual-component nature of composite materials can cause internal stresses to develop due to volume changes during processing. Generally, polymer matrices will see considerable volume changes during a typical cure cycle due to thermal expansion/contraction and due to cure shrinkage caused by polymer chain cross-linking Conversely, the volume change in typical fiber materials, such as carbon or glass, during a cure cycle is comparatively insignificant. This incongruity in volume change behavior between fiber and matrix can cause considerable buildup of internal stresses, which can diminish the mechanical properties and dimensional stability of a processed composite material. This can lead to a degradation of aerodynamic performance, poor fit-up of linked components, microcracking, delamination of a layered composite part, or premature failure.

Identification and characterization of cure shrinkage and thermal expansion as the mechanisms of volume change during cure have been seen distinctly in several previous studies (1-4) Shrinkage due to cross-linking, dependent upon the chemical composition and polymerization reaction taking place, was seen to reach up 10 or 20% (5, 6) The effect of cure cycle on volume changes has been investigated qualitatively to examine the relative effects of cure shrinkage and thermal expansion (7) This work was done

primarily to explore the potential modification of cure cycles for the relaxation of internal stresses rather than actual modeling of volume changes

Coupling between volume change and cure-induced stresses has been shown extensively through investigations of in-cure internal stresses (8,9) The predominant mechanism for development of internal stresses is "effective" volume change, which may occur during processing or during cooldown. The "effective" volume changes occur for an appreciably cured specimen for which stresses are not readily relaxed. Much work has been done to develop the effect of cure cycle on residual stresses (10), in which development of volume change, viscosity, and stress are investigated for various cure cycles. These cure cycles can be optimized so that volume changes occur primarily during periods of the cure cycle for which stresses are readily relaxed.

Previous research dedicated to quantitative modeling of volume change behavior is limited Various cure shrinkage models exist for which shrinkage is shown to behave according to quadratic or power law models involving material parameters (11,12) Most work lacks extensive experimental verification.

In this study, Hercules 3501-6 epoxy has been used to develop a model of in-cure volume changes. This is a well-characterized aerospace resin that has been a subject of study for many years. A well-known cure kinetics model (13) has been developed for this material, which greatly facilitates the investigation of degree of cure dependent behavior as well as

the development of a volume change model which must calculate the degree of cure for an arbitrary input cure cycle.

An effective model of in-cure volume change can be developed by isolating and then superposing the effects of cure shrinkage and thermal expansion. Cure shrinkage may be isolated by investigation of isothermal cure cycles, for which there are no thermal effects to account for Once an accurate cure shrinkage model has been formulated, thermal expansion behavior can be isolated by investigation of a cure cycle for which temperature changes occur. In this case, thermal volume changes account for the remainder of total volume change not produced by cure shrinkage.

2. EXPERIMENTAL METHODS

2.1 In-Cure Volume Change Measurement

Total volume changes were measured directly using a volumetric dilatometer The volumetric dilatometer used was the Gnomix Research PVT Apparatus as shown in Figure 1 (all figures are located in the appendix) This instrument yields measurements of total sample volume change during a given cure cycle. The specific volume of polymers can be accurately determined in the 30-400°C temperature range and the 0-200 MPa pressure range.

Samples of 0 2 to 0.6 grams were enclosed in a piezometer cell, a stainless steel container closed off with flexible metal bellows and filled with mercury The mercury containing fluid assures smooth translation of sample volume changes to the deflectable metal bellows The piezometer cell was placed in a pressure vessel and charged with silicon oil until equilibrium of hydrostatic pressure in the vessel with pressure in the cell was achieved Pressure was maintained at 10 MPa to assure no evaporation of the containing fluid, which would cause a false reading of sample volume change. The volume change in the polymer was determined through the deflection of the bellows, given a known cross-sectional area of the bellows. A linear variable differential transducer (LVDT) measured the deflection of the bellows.

Vessel pressure was measured with a high-precision Bourdon gauge. Temperature was measured with a K-type thermocouple. Temperature was controlled via an Omega Solid State Relay controller output to an 1800-Watt electrical heater. Sample temperature and LVDT voltage were read by a DASCON-1 data acquisition board interfaced with a PC.

2.2 In-Cure Stress Testing

The cure induced stress test (CIST) developed at The University of Tennessee was used to measure internal stresses developed during cure of a polymer composite due to volume changes For this test, the polymer is cured around a portion of pretensioned fiber Once the polymer develops sufficient stiffness, polymer expansions and contractions cause changes in the fiber tension, which is measured by a load cell

Figure 2 shows a schematic of the CIST The fiber is glued to a rigid support at one end, the other end is attached to a load cell. The fiber passes through a flexible silicon mold which contains the polymer that is to be cured. A ceramic shield is used to form a cure chamber around the mold A thermocouple is located next to the mold to monitor temperature.

3. MODELING APPROACH

3.1 Volumetric Effects

Volume changes are known to be of two different sources thermal expansion and contraction due to heating and cooling, and cure shrinkage due to polymer chain cross-linking The total volume change results from a superposition of these two effects A well-known material, 3501-6 epoxy, has been used to develop a model for the cure shrinkage and thermal expansion during cure

A plausible assumption is to assume linear cure shrinkage with respect to degree of cure This is the starting point for the current work, cure shrinkage is approximated as a linear function of degree of cure (α) of the form

$$\Delta V_{SH} = K\Delta\alpha \qquad \textbf{Equation 1}$$

The constant K has been determined by measuring volume change for several isothermal cure cycles. In this case it is known that all volume changes can be attributed to cure shrinkage, since no temperature changes occur

Once a model of cure shrinkage volumetric effects was established, thermal volumetric effects were then evaluated This was accomplished by determining the thermal expansion coefficient as a function of temperature and degree of cure The total thermal

expansion was found experimentally as the difference of measured total volume change minus the calculated cure shrinkage (cure shrinkage having been determined by the above linear expression):

$$\Delta V_{TH} = \Delta V_{TOT} - \Delta V_{SH} \qquad \textbf{Equation 2}$$

The volumetric thermal expansion coefficient (Θ) is then.

$$\Theta = \frac{\Delta V_{TH}}{\Delta T} \qquad \textbf{Equation 3}$$

Using these expressions, thermal volume change behavior has been determined from the results of several constant heating rate cure cycles In the case of these constant heat rate cure cycles, there are continuous thermal volume changes to account for, in addition to concurrent cure shrinkage The thermal and cure shrinkage volume change effects were then superposed to form a final model

3.2 Cure Kinetics Modeling

In order to evaluate cure shrinkage according to Equation 1, it was necessary to evaluate the degree of cure as a function of time and temperature. This was accomplished using a well-known cure kinetics model proposed by Springer, Lee, and Loos (13). In their study, differential scanning calorimetry (DSC) techniques were used to develop

expressions for correlating rate of degree of cure with degree of cure. From this, degree of cure as a function of time and temperature can be extracted.

The degree of cure is defined as the quotient of amount of heat (heat of reaction) released to a certain point in time and total heat released during a complete reaction Rate of heat generation (dQ/dt) is measured directly by DSC measurement Either total or cumulative heat of reaction (H_R and H respectively) can then be determined by integrating this measurement with respect to time. The degree of cure as it has been defined is then

$$\alpha = H/H_R \qquad \textbf{Equation 4}$$

The rate of degree of cure is calculated by

$$d\alpha/dt = \left(dH/dt\right)/H_R \qquad \textbf{Equation 5}$$

From which rate of heat generation (dQ/dt) is a direct DSC measurement, and total heat of reaction (H_R) is found by a cumulative DSC measurement for a completely reacted sample

The degree of cure and rate of degree of cure being so determined, an attempt was made to fit α vs $d\alpha/dt$ to an Arrhenius type equation based on the results of isothermal DSC measurements The following were found to yield accurate fits:

$$d\alpha/dt = (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \qquad \alpha \leq 0.3$$

$$d\alpha/dt = K_3(1-\alpha) \qquad \alpha > 0\ 3 \qquad \textbf{Equation 6}$$

where

$$K_1 = A_1 \exp(-\Delta E_1 / RT)$$

$$K_2 = A_2 \exp(-\Delta E_2 / RT) \qquad \textbf{Equation 7}$$

$$K_3 = A_3 \exp(-\Delta E_3 / RT)$$

The data can not be correlated by a single equation. Results of DSC measurements show two "humps" in the heat rate data, indicating two different dominant reactions that occur during cure of the 3501-6 resin. Therefore two equations are required to model the complete range of cure; one is used for degree of cure less than 0.3, after which the second equation applies.

The ΔE terms are activation energies, R is the universal gas constant, T is the absolute temperature, A's are pre-exponential factors, and B is a temperature independent constant. The constants K_1, K_2, and B were found by using non-linear least squares curve fits to the $d\alpha/dt$ vs α data using the Levenberg-Marquardt algorithm K_3 was found by a linear least squares curve fit to the $d\alpha/dt$ vs α data for $\alpha > 0\ 3$ The Arrhenius expressions for the K constants were determined by linear fitting of K_1, K_2, and K_3 versus 1/T data (data taken from several isothermal experiments) to determine A and ΔE terms

In order to develop an expression appropriate for assessing degree of cure from an expression involving rate of degree of cure, it was necessary to modify the $d\alpha/dt$ model to obtain the degree of cure as a function of time and temperature (for an arbitrary input cure cycle) Direct solution proves to be prohibitively difficult, therefore the 4th order Runge-Kutta numerical method was applied [In brief, the Runge-Kutta technique approximates the $d\alpha/dt$ differential equation as a summation of small linear segments Degree of cure is calculated by summation of the product of values of the $d\alpha/dt$ function with values of incremental time ($\alpha = \sum {}^{d\alpha}/_{dt}\ \Delta t$).]

4. RESULTS

4.1 Cure Shrinkage Modeling

Four isothermal cure cycles (with 4 °C/minute heatup ramps to the isothermal plateau temperature) were investigated using the volumetric dilatometer. 169, 159, 136, and 126 °C. These were used to evaluate the cure shrinkage constant of linearity

A typical chart of volume change behavior for 169°C isotherm is shown in Figure 3. Initially, volume increases due to thermal expansion. After approximately 20 minutes, the rate of this thermal expansion begins to be counteracted by cure shrinkage, as evidenced by a decrease in the slope of the volume change curve Once the temperature reaches a constant level, all volume change is due to cure shrinkage, as governed by Equation 1. Eventually, the volume change curve approaches a plateau as rate of degree of cure decreases

To determine the accuracy of the assumption of Equation 1, the nature of the relationship between cure shrinkage and degree of cure was evaluated through use of the experimental data in tandem with the Springer, Lee, and Loos kinetics model. Application of the Runge-Kutta numerical technique to these equations yields the time-varying values of degree of cure for this cure cycle. This was then correlated to the time-varying experimental output of specific volume change These results are shown in Figure 4 The relationship between cure shrinkage (ΔV) and theoretical degree of cure (α) appears

to be quite linear during the constant temperature plateau, for which there are no thermal expansion effects. This confirms the assumption of linearity of cure shrinkage as stated by Equation 1.

The other isothermal cure cycles showed similar behavior, in which cure shrinkage is linear with respect to degree of cure. There was, however, a noticeable trend in the magnitude of this constant for the various isothermal plateau temperatures, as shown by Figure 5

Although cure shrinkage has been shown to be linear with respect to degree of cure for a given temperature, there appears to be a decrease in this constant when extracted from lower isothermal hold temperatures (see Figure 5). A possible explanation for this fact is the limitation of the Springer kinetics model (described in section 3 2) for long isothermal cycles The model does not account for the fact that the cure reaction may "stall" at a given isothermal temperature and require further temperature increase to resume reaction It is assumed that the degree of cure will assymptotically approach complete cure, regardless of the vagaries of the cure cycle. This disparity would cause the Springer model to overstate the degree of cure towards the end of a relatively low-temperature isotherm, thus understating the calculated value of cure shrinkage constant (which is dependent upon degree of cure as per equation 1) at lower plateau temperatures This

overstatement of degree of cure could in fact account for the trend illustrated in Figure 5 since, according to Equation 1, a lower $\Delta\alpha$ will increase the K value.

However, such an overstatement of degree of cure should also disrupt the linearity of cure shrinkage, since the model would be accurate early on in the cure cycle, then less accurate through the progression of the isotherm. This was not seen to be the case. Furthermore, the final model showed a slight improvement in accuracy (with respect to experimental data) by incorporating the trend of Figure 5. Thus, it seems that the trend is an actual phenomenon and should be incorporated into the overall volume change model

4.2 Thermal Expansion Modeling

Given the known cure shrinkage behavior, the thermal expansion of the 3501-6 was the next effect to be isolated. Using an average value of cure shrinkage constant in association with Equation 2, the thermal expansion was extracted for constant heat rate cure cycles.

Some characteristic dilatometer data of total volume change is shown in Figure 6 for a ½ °C/minute cure cycle. Initially, thermal expansion dominates as cure shrinkage is limited by low temperatures and low curing times Cure shrinkage then gradually overcomes this thermal expansion as higher degrees of cure are achieved. The final upward trend, past 275 minutes, indicates the reassertion of thermal expansion as cure is nearly complete and the effects of cure shrinkage are minimized

The volume change due to thermal expansion was then extracted from the total volume change data, as per Equation 2, and the overall results are illustrated in Figure 7 and Figure 8, which plot thermal volume change (as well as cure shrinkage and total volume change measurements) as a function of degree of cure and temperature, respectively The cure shrinkage is calculated using an average value of cure shrinkage constant of linearity (K). The thermal expansion is shown by Figure 8 to be linear with respect to temperature, even over this complete range of degree of cure. This implies a constant coefficient of thermal expansion, as calculated according to Equation 3. Intuitively, it seems likely that as the phase changes signifigantly during cure, the thermal expansion coefficient should change as well. In some cases, slight changes in the thermal expansion coefficient were seen, but the change was still small enough that the average thermal expansion coefficient was sufficiently representative of material behavior. Initially it was assumed that thermal expansion would be a function of degree of cure and temperature, but several constant heat rate experiments showed that the thermal expansion coefficient did not significantly change during the entire cure cycle over a complete range of degree of cure and temperature The results of the various constant heat rate cure cycles are summarized in Table One

Table 1: Thermal Volumetric Behavior

Heating Rate (°C/min)	Thermal Expansion Coefficient, Θ (cm^3/g °C)
4	3.26×10^{-4}
4	4.24×10^{-4}
2	3.59×10^{-4}
¾	5.74×10^{-4}
½	5.39×10^{-4}
½	4.94×10^{-4}

There is considerable variability in this data (approximately 20% standard deviation). This is attributable to variability in experimental processes and results, both of which are difficult to accomplish with complete consistency. The qualitative trends and linearity are consistent. This deviation of the thermal expansion coefficient is thought to be the root cause of some of the deviations betwen the final volume change model and the experimental data as will be illustrated later.

5. MODEL FORMULATION AND VALIDATION

The model of total volume change of 3501-6 superposes the effects of cure shrinkage and thermal expansion according to the following equation.

$$\Delta V = K(\Delta\alpha) + \Theta(\Delta T) \qquad \textbf{Equation 8}$$

where ΔV is the total resin volume change, K is the experimentally determined cure shrinkage constant, $\Delta\alpha$ is the theoretically calculated change in degree of cure, Θ is the experimentally determined volumetric coefficient of thermal expansion, and ΔT is the change in resin temperature dictated by the given cure cycle. Calculations were performed for one-minute time intervals to match the data sampling rate of all the dilatometer experiments

As discussed earlier, the value of K was shown to experience some variation between the various isothermal experiments used to determine the constant of linearity (see Figure 5) This variation has been incorporated into the total in-cure volume change model and has been shown to noticeably improve the agreement between the model and experimental volume change data

The charts shown in Figure 9 through Figure 14 show comparisons of the experimental dilatometer volume change data compared with the calculated values yielded by the model of Equation 8

For any given data set, it is possible to select values for K and Θ that very closely model the experimental volume change The bulk of the model inaccuracies that occur can be attributed to the experimental variation in thermal expansion behavior, or in other words, due to problems selecting one value of thermal expansion coefficient to model data that was seen to have significant scatter. The values of thermal expansion coefficient taken from the various cycles illustrate this point (see Table One) Significant variation was seen, even for the same cure cycle. Given this, there is not always one value that will reconcile two varying sets of experimental data. The charts comparing model to theory for two of the isothermal cycles (Figure 11 and Figure 12) further illustrate the point There is no one value of the thermal expansion coefficient that will yield values of volume change after the 4C/min heatup that will agree with experimental values They exhibited significantly different values of thermal expansion coefficient during heat-up, despite the fact that the heat-up cycles are largely the same This is an experimental variation more so than a modeling inaccuracy. The cure shrinkage behavior agrees closely, and the downward trend of the theoretical and experimental volume change stays "parallel" through the remainder of the cure cycle. The assumptions of linear cure shrinkage and constant coefficient of thermal expansion are still shown to be valid It is felt that the data of Figure 11 is more an experimental anomaly than a model inaccuracy

6. EX-1515 AND RS-3 RESULTS

The same methods developed with 3501-6 were used for similar investigations of EX-1515 and RS-3 resins These resins differ from 3501-6 epoxy in that they are cyanate esters. Analysis of these resins was useful in providing insight into the generality of modeling procedures developed with the 3501-6 epoxy

Kinetics modeling and calculation of degree of cure for these resins was accomplished using proprietary computer models provided by The Boeing Company.

6.1 Cure Shrinkage Modeling

For each resin, two isothermal cure cycles (each being repeated to evaluate consistency of results) were investigated using the volumetric dilatometer The cycles were designed using results of the kinetics modeling to assure cure cycles of reasonable times with a complete range of degree of cure. Typical results of the dilatometer experiments are very similar in character to what was seen in the study of 3501-6

The nature of the relationship between cure shrinkage and degree of cure was evaluated through use of the experimental data in tandem with the Boeing kinetics models As was the case for 3501-6, the relationship between cure shrinkage (ΔV) and theoretical degree of cure (α) appears to be quite linear during the constant temperature plateaus, for which there are no thermal expansion effects These results are shown in Figures 15 through 18

There is significant scatter seen in the RS-3 dilatometer data This is the direct cause for the scatter in the cure shrinkage linearity relationship, but the linear trend still seems evident The results of all isothermal runs for these resins are summarized below in Table Two

Table 2: Results of Isothermal Testing of RS-3 and EX-1515 Resins

RS-3	
Isothermal Temperature (C)	Cure Shrinkage Constant of Linearity
206	0.0901
206	0.0678
175	0 0550
EX-1515	
Isothermal Temperature (C)	Cure Shrinkage Constant of Linearity
121	0 0422
121	0.0421
174	0 0783
174	0 0796

The results above for the EX-1515 resin show good consistency and, as was the case for 3501-6, show a trend of an increasing constant of proportionality between cure shrinkage and degree of cure at higher plateau temperatures The magnitude of this trend is similar to what was seen for 3501-6, the difference being almost 50%. The data for RS-3 also shows this same type of trend in cure shrinakge constant, but the magnitude is difficult to characterize given the inconsistency in data sets.

6.2 Thermal Volume Change Modeling

Given known cure shrinkage behavior, thermal volume changes have been isolated from total volume change measurements during constant heat rate cure cycles. This analysis has been performed for RS-3 and EX-1515 resins according to the same procedure used for 3501-6. As was the case for the 3501-6 resin, the thermal expansion appears to be largely constant, regardless of degree of cure (Figures 19-24). There is consistently a deviation from linearity shown around 160° C, but again the deviation was not enough to significantly affect the accuracy of using a constant value of thermal expansion coefficient.

The results of the above figures are summarized in Table 3 below

Table 3: Thermal Expansion Coefficients for Various Constant Heat Rate Cure Cycles

RS-3	
Heating Rate (C/min)	Thermal Expansion Coefficient ($cm^3/g°C$)
4	5.96×10^{-4}
2	5.83×10^{-4}
2	5.71×10^{-4}
EX-1515	
Heating Rate (C/min)	Thermal Expansion Coefficient ($cm^3/g°C$)
0.5	5.83×10^{-4}
1	6.05×10^{-4}
1	6.38×10^{-4}

6.3 Model Validation for RS-3 and EX-1515

As was done previously for the 3501-6 model, the theoretically calculated volume change has been compared to experimental values for an arbitrary two-tier cure cycle which includes constant heating rate ramps and isotherms over a complete range of degree of cure Figure 25 and Figure 26 show comparisons of the experimental dilatometer volume change data compared with the calculated values yielded by the model of the form of Equation 8 The agreement is very close, so the methods developed with 3501-6 epoxy seem to apply well to these cyanate esters.

7. DEVELOPMENT OF ELASTIC MODULUS OF 3501-6

7.1 Introduction

Polymer volume change behavior during various cure cycles has been modeled as detailed in the previous sections. This second part of the research characterizes the effect of this polymer volume change on the elasticity of the polymer. As the polymer cross-linking progresses during cure, its stiffness changes from a very low magnitude to that of a fully cured polymer. Low stiffness implies that the change in polymer volume will not produce any significant stress in the embedded fibers Whereas, the volumetric changes of the fully cured polymer could induce significant stresses in the embedded fibers Using the fiber tension data from the Cure Induced Stress Test (CIST- see section 2 2) and the volume change data from the volumetric dilatometer, a correlation between stiffness (E) development as a function of temperature and the degree of cure can be established.

$$E = E(T, \alpha)$$ **Equation 9**

During the first phase of this research, an attempt was made to characterize the behavior of the polymer stiffness change during cure cycles The second phase was aimed at quantifying this behavior

The procedure to determine the qualitative behavior of stiffness during a given cure cycle involves both the results of volume change modeling and the results of CIST testing. First, the polymer volume change is measured during a given isothermal cure cycle During an isotherm, there are no varying temperature effects on the polymer stiffness, furthermore, volume change is due only to cure shrinkage. Secondly, the CIST is performed using the same isotherm. The fiber tension will change as a result of the cure shrinkage. The magnitude of fiber tension change will depend on the current average stiffness of the polymer. Since the fiber stiffness does not vary much during a typical cure cycle, the ratio of fiber tension change (ΔF) and polymer volume change (ΔV) can be assumed to be proportional to the polymer stiffness. These ratios were determined by taking the derivatives (dF/dV) of the equation describing the change in fiber tension as a function of change in polymer volume, as will be further described in section 7.3.

7.2 Correlation between Fiber Tension and Volume Change

Figure 27 through 30 show the volume change and fiber tension change curves during four different isothermal cure cycles Note that fiber tension values in these figures are indicated in millivolts output by the load cell (40 mV = 1 gram) The volume and tension data are taken from the volumetric dilatometer and the CIST respectively.

During the CIST, polymer volume changes have a direct effect on the tension of an embedded fiber As the resin contracts due to cure shrinkage, compressive stresses are applied to the fiber through the interface due to adhesion between the two phases. The

fiber is fixed at both ends and of constant length, so compression at the fiber-matrix interface causes an increase in fiber tension that is measured by the CIST load cell. The relative effect of polymer volume changes on fiber tension changes is directly related to the elasticity of the polymer, which changes during cure both due to advancement of degree of cure and stress relaxation over time.

During the isothermal cure cycles, the only volume change is that due to the advancement of the degree of cure As the degree of cure increases, the polymer stiffness should increase Therefore, the polymer volume change occurring toward the later part of the cure cycle should produce a larger change in fiber tension, since stresses are not readily relaxed in a more fully cured polymer

The linear strain was deduced from the total volume change data using the following equations

$$\varepsilon_{vol} = \frac{\Delta v}{v_o}$$ **Equation 10**

$$\varepsilon = (1 + \varepsilon_{vol})^{1/3} - 1$$ **Equation 11**

where Δv is change in specific volume, v_o is original specific volume (room temperature, pre-cure), ε_{vol} is volumetric strain, and ε is linear strain

Figures 31 through 32 show the relationship between fiber tension and matrix volume changes for isothermal cure cycles of 126, 136, and 159 °C. The charts show fiber load vs. strain data, analogous to a stress-strain curve. In each case, the data have also been approximated with an appropriate curve fit It is important to note that time actually progresses from right to left in these figures since the strain is compressive. Towards the beginning of cure, the elasticity of the polymer is comparatively low in its gel-like uncured state The strains applied by cure shrinkage do little to increase the stresses in the polymer As cure begins to progress, the sample hardens Applied strains begin to show more and more effect on increasing the stress level, due to the fact that the sample is curing to a hardened state and stress relaxation times continue to increase.

The derivative of the curve fit to the load-strain curve then calculates the slope at each discrete time point, which qualitatively indicates the development of elastic modulus during cure This was done to generate Figures 33-35, which indicate the development of the elastic modulus during cure, as calculated from the instantaneous slope of each of the load-strain curves. The character of the curves seems intuitively reasonable. As the rate of degree of cure begins to decrease upon approaching final degree of cure, so does the development of the elastic modulus begin to decrease, asymptotically approaching the fully cured state The results shown are also consistent in that the values of final elastic modulus developed for each cure cycle are similar. Some of the elasticity curves show an initial negative value for elastic modulus. This is an idiosyncrasy of an imperfect curve fit and can be disregarded; initial curvature of the load-strain curves is seen to be virtually

zero (see Figures 31-33), which makes sense given that the initial elasticity of the uncured gel-like resin is negligible compared to the polymer elasticity as the epoxy cures. This implies initial modulus of the resin should be virtually zero, and its behavior is most likely controlled by viscous-like relaxation. Curve fits were selected for their accuracy in modeling the load-strain data after the aforementioned initial region of zero curvature

The actual values indicated as elasticity (final value generally around 2.2) are qualitative only, in a sense As detailed earlier, the values are calculated as the slope of a load-strain curve, so the units are not congruent with those of elasticity Furthermore, the elasticity value indicated is an "apparent elasticity" since it includes the effects of continually relaxing stresses What is important is the trend illustrated by this curve To quantify this curve with more meaningful units, the trend can be scaled to fit actual values of elasticity, given the known value of the elastic modulus of fully cured 3501-6 at room temperature (0.6 MPsi). This has been done to generate Figure 37, which shows room temperature elastic modulus values for samples cured (assumed completely) at various isothermal temperatures

8. CONCLUSIONS

1. Cure shrinkage of 3501-6 epoxy, RS-3 cyanate ester, and EX-1515 cyanate ester is linear with respect to degree of cure for a given isothermal cure cycle
2. Some localized variation in the constant of linearity of cure shrinkage for isothermal temperatures in the regime of the cure temperature has been shown for these resins This may be a result of limitations in cure kinetics modeling rather than a true material response.
3. Thermal expansion coefficient remains constant during cure, independent of degree of cure or cure temperature.
4. An empirical model superposing effects of cure shrinkage and thermal expansion can effectively model in-cure volume changes of 3501-6, RS-3, and EX-1515
5. Use of a volume change model in tandem with information about the internal stress state can yield an analysis of the in-cure elasticity development of 3501-6 epoxy
6. The development of the elastic modulus during cure of 3501-6 mimics the progression of degree of cure.

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APPENDIX

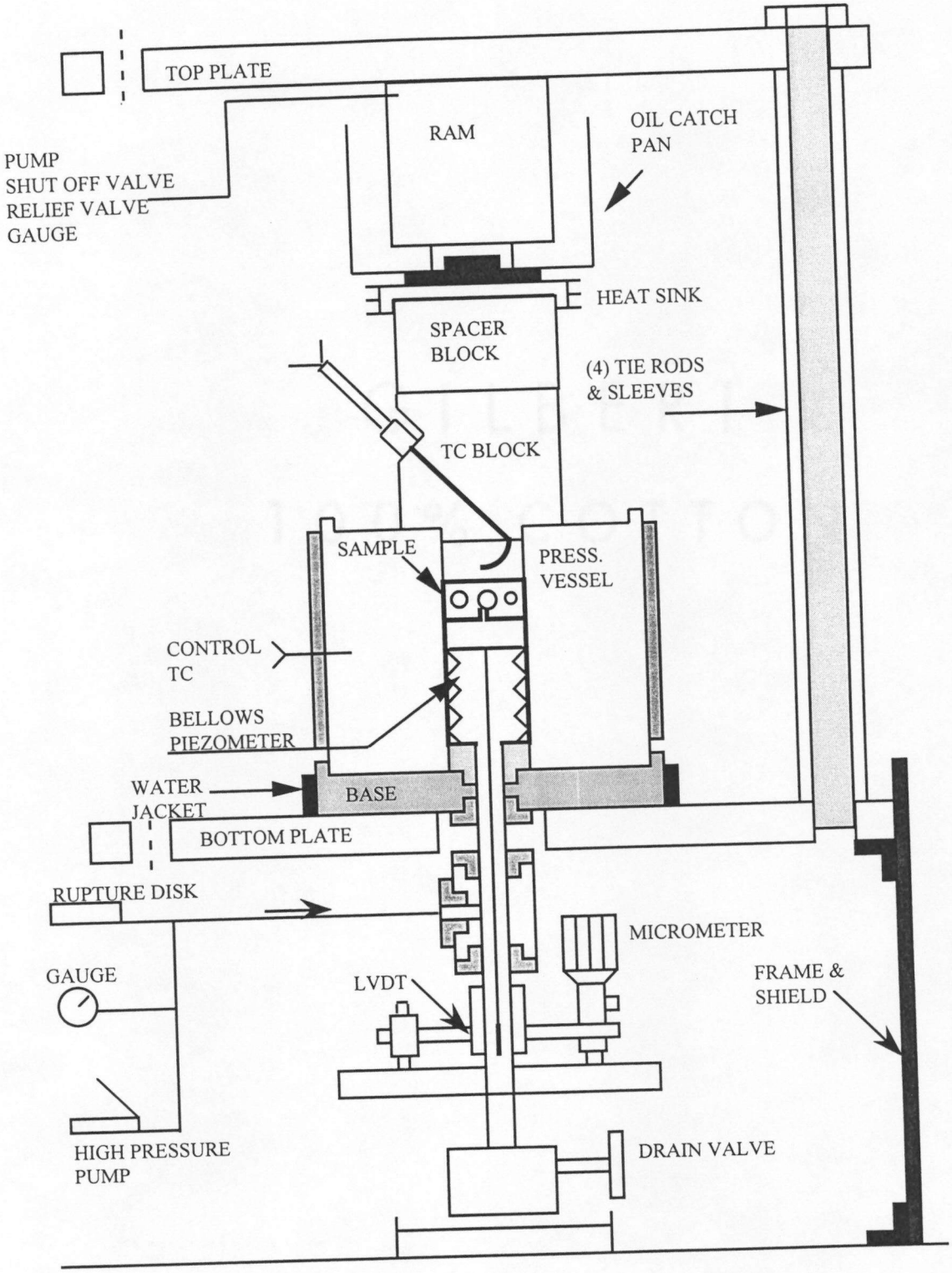

Figure 1: PVT Dilatometer Schematic

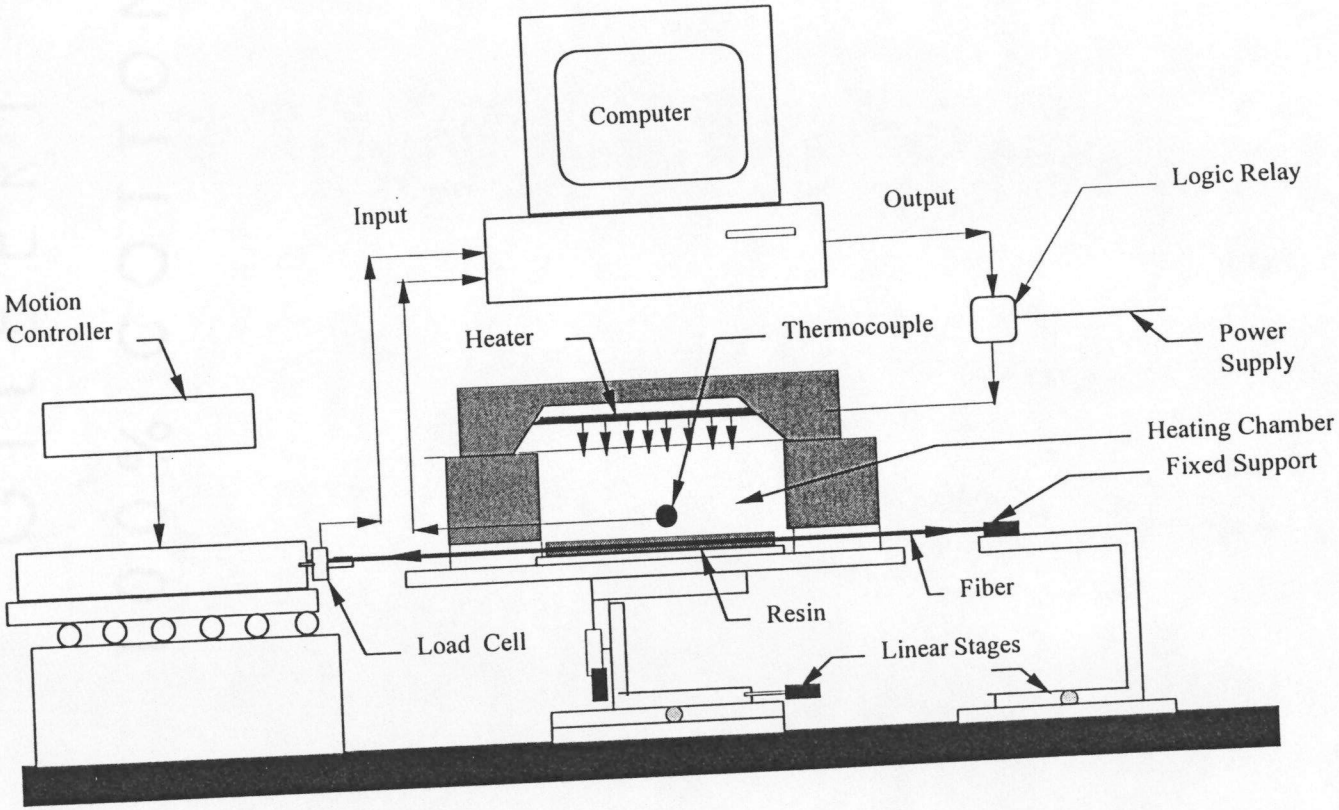

Figure 2: Schematic of CIST Apparatus

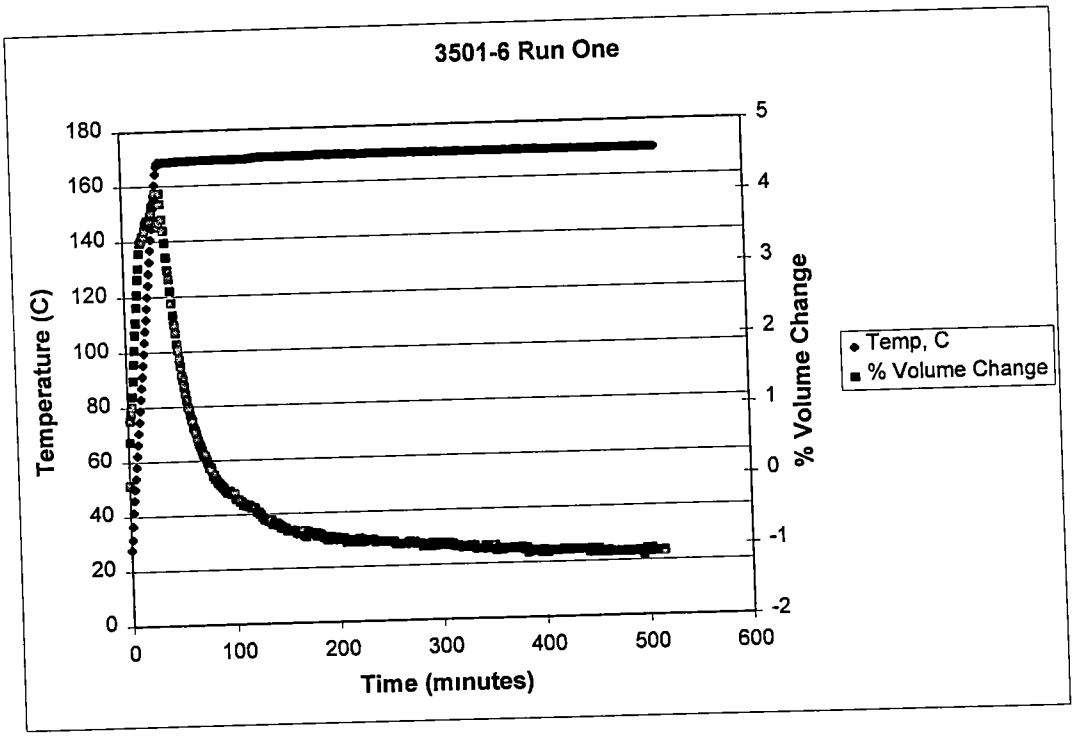

Figure 3· Typical dilatometer output for an isothermal (169°C) cure cycle Thermal expansion during heatup is followed by isothermal cure shrinkage

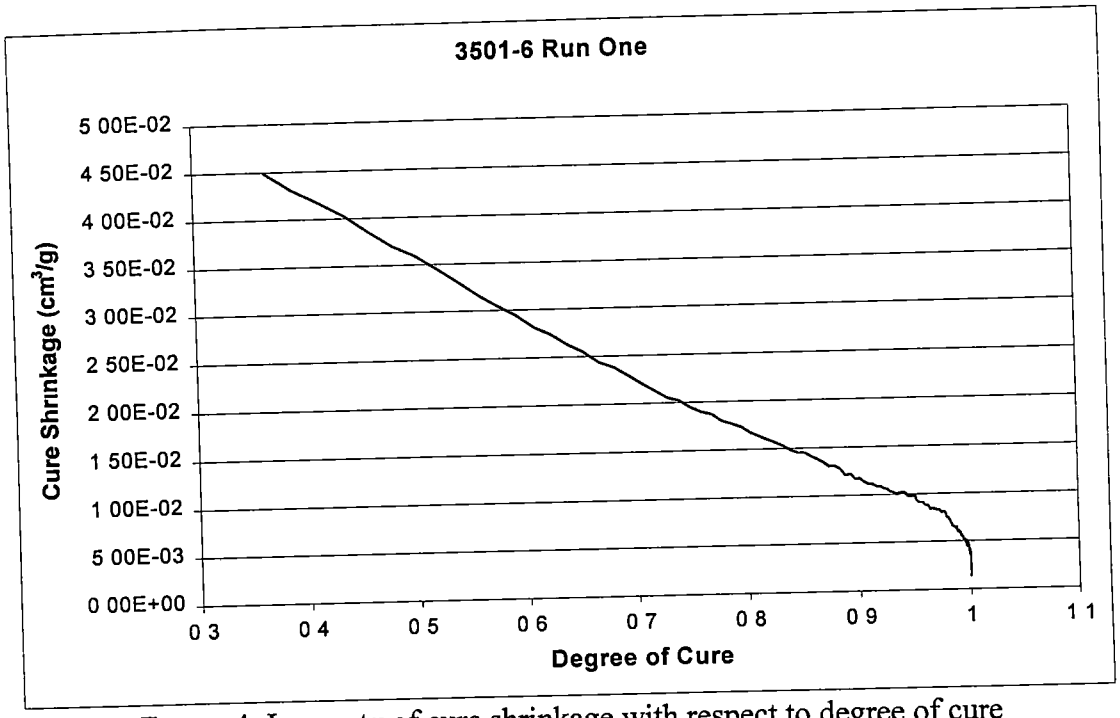

Figure 4· Linearity of cure shrinkage with respect to degree of cure

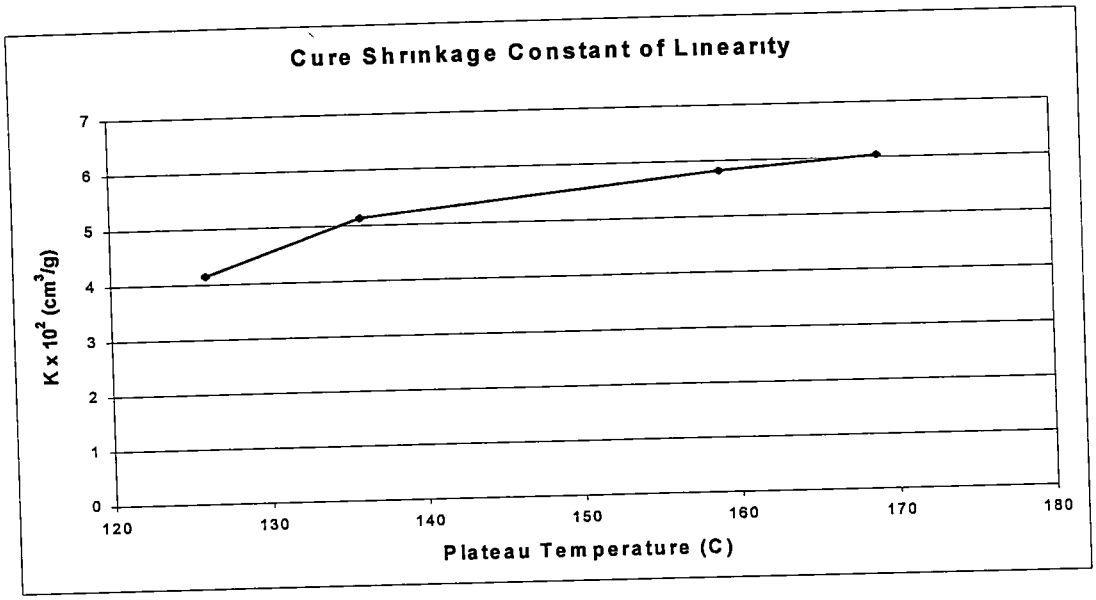

Figure 5: Trend in cure shrinkage constant of linearity A lower temperature isothermal cure cycle will exhibit a lower constant over this temperature range.

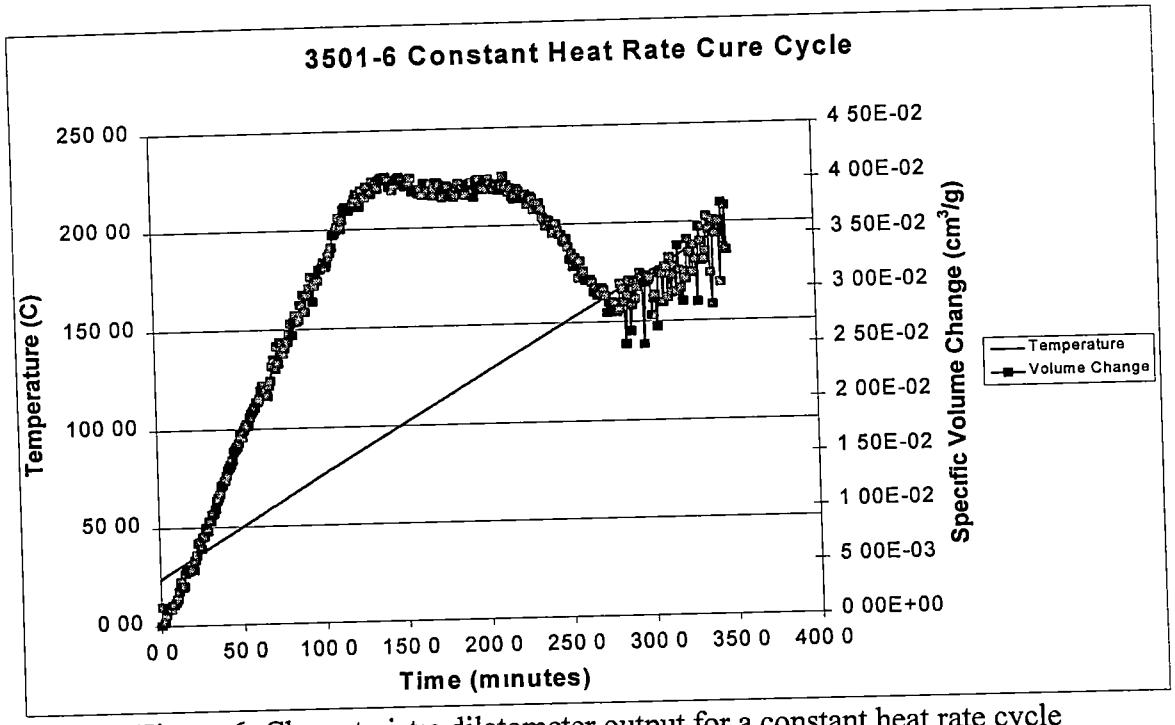

Figure 6 Characteristic dilatometer output for a constant heat rate cycle

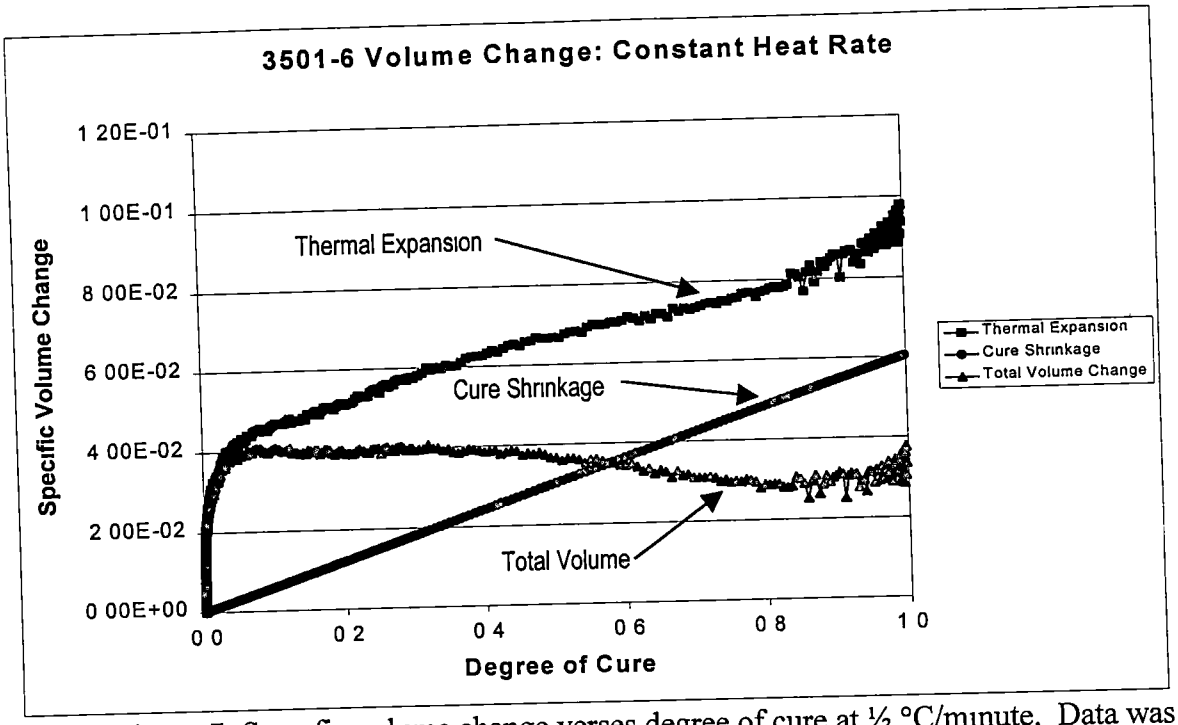

Figure 7· Specific volume change verses degree of cure at ½ °C/minute. Data was taken from room temperature to 200°C

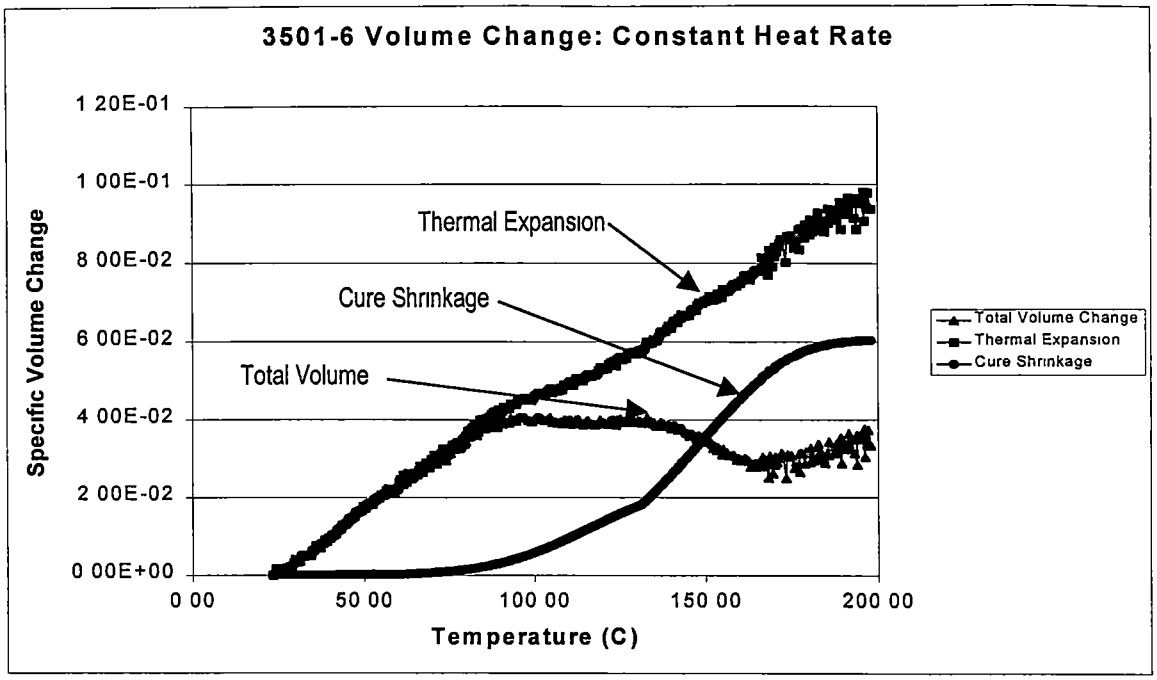

Figure 8 Specific volume change verses temperature at ½ °C/minute. The linear change in thermal volume change with temperature suggests a constant thermal expansion coefficient.

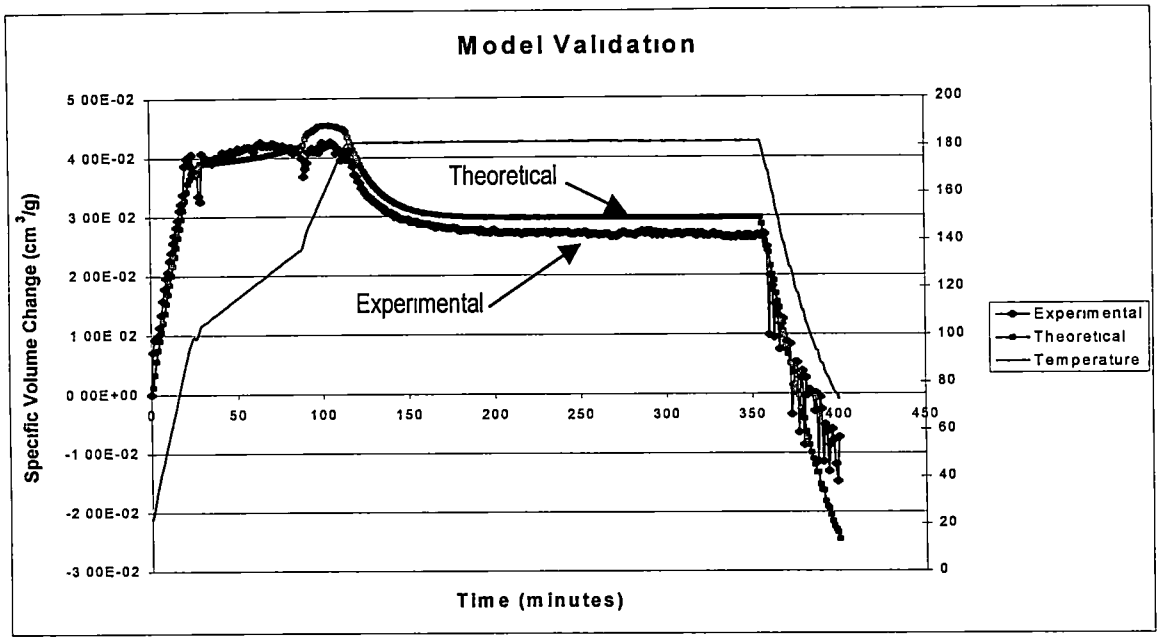

Figure 9: 3501-6 model comparison with experimental data for the total volume change measured during a cure cycle with three heat ramps to temperature hold. The predicted volume change agrees well with the measured data

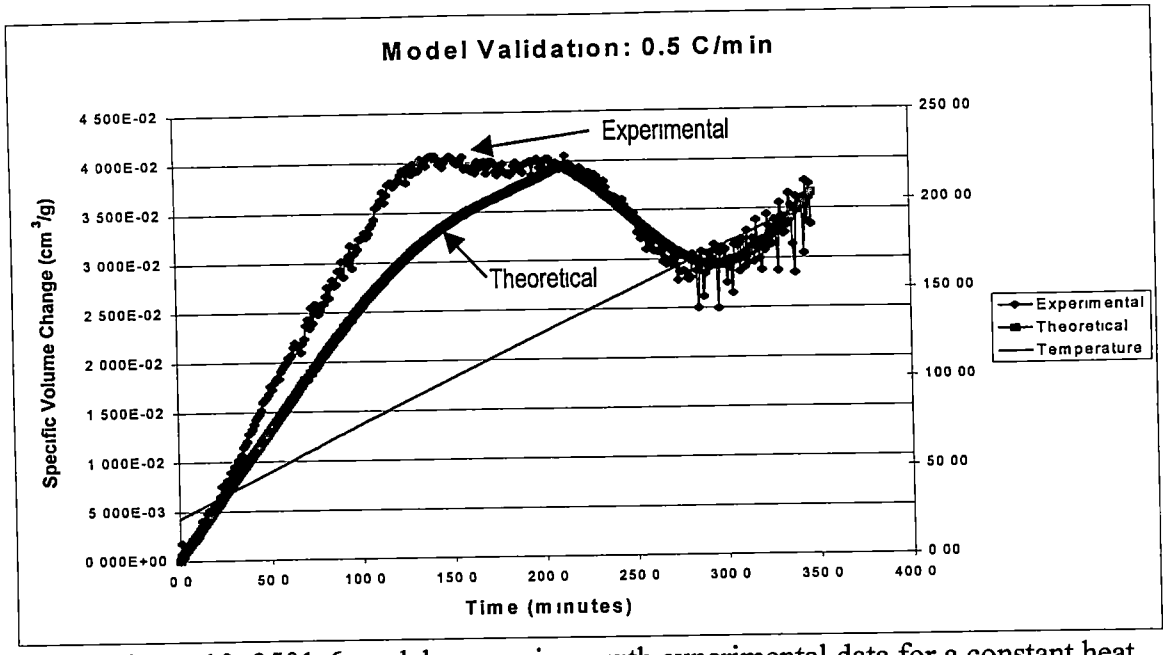

Figure 10· 3501-6 model comparison with experimental data for a constant heat rate cure cycle There is slight overprediction from 50 to 200 minutes

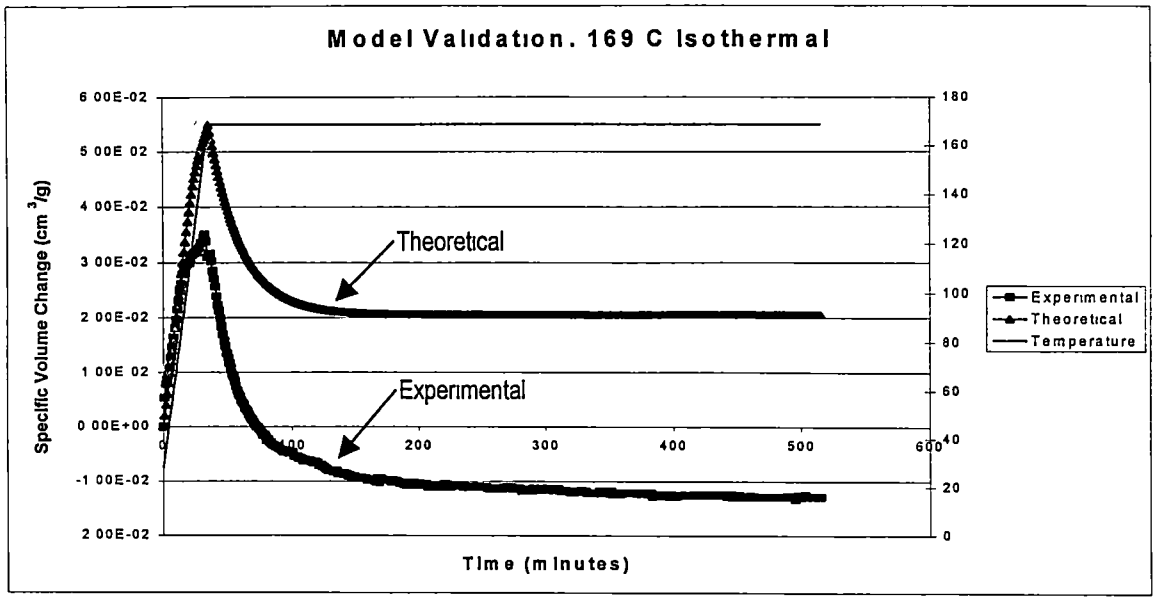

Figure 11: 3501-6 model comparison with experimental data for an isothermal cure cycle While the model predicts the cure shrinkage trend accurately, the predicted values of the specific volume change are larger This behavior is attributed to the overprediction of the thermal expansion during the initial heat ramp.

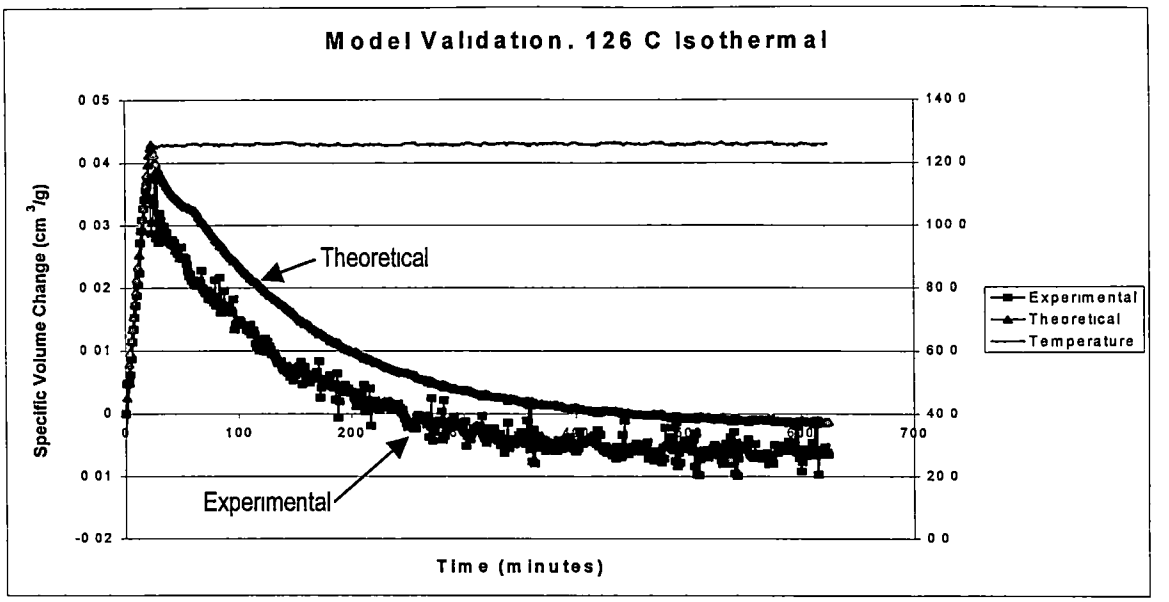

Figure 12 3501-6 model comparison with experimental data for an isothermal cure cycle. Initial thermal expansion is slightly overstated, followed by close agreement in cure shrinkage behavior during the isotherm

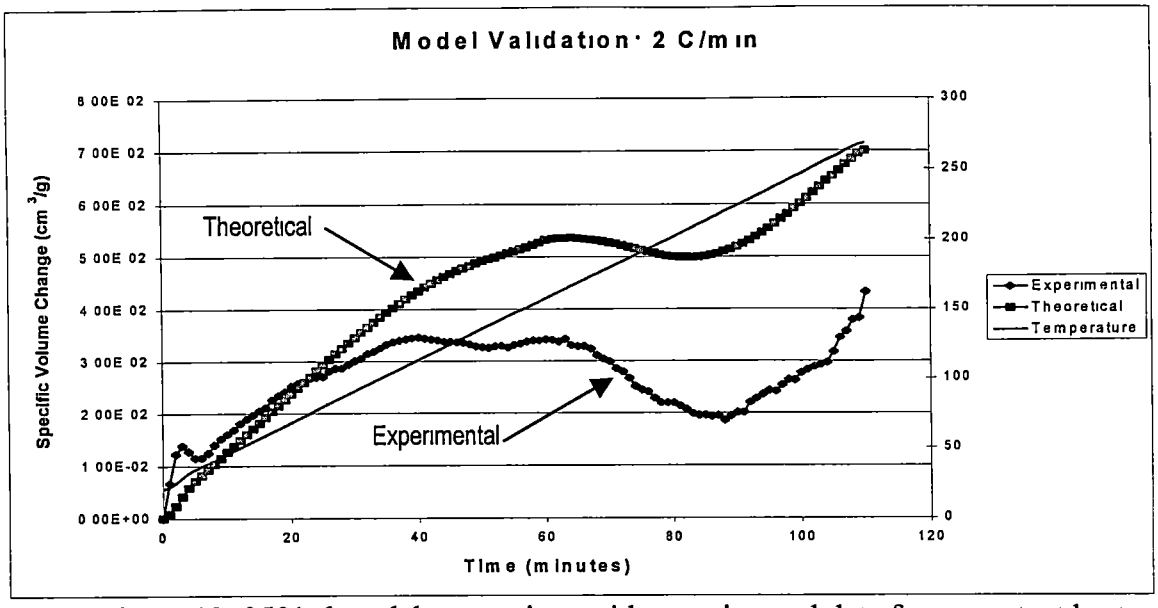

Figure 13· 3501-6 model comparison with experimental data for a constant heat rate cure cycle The higher values of the volume change calculated from the model are attributed to the overprediction of the thermal volume change.

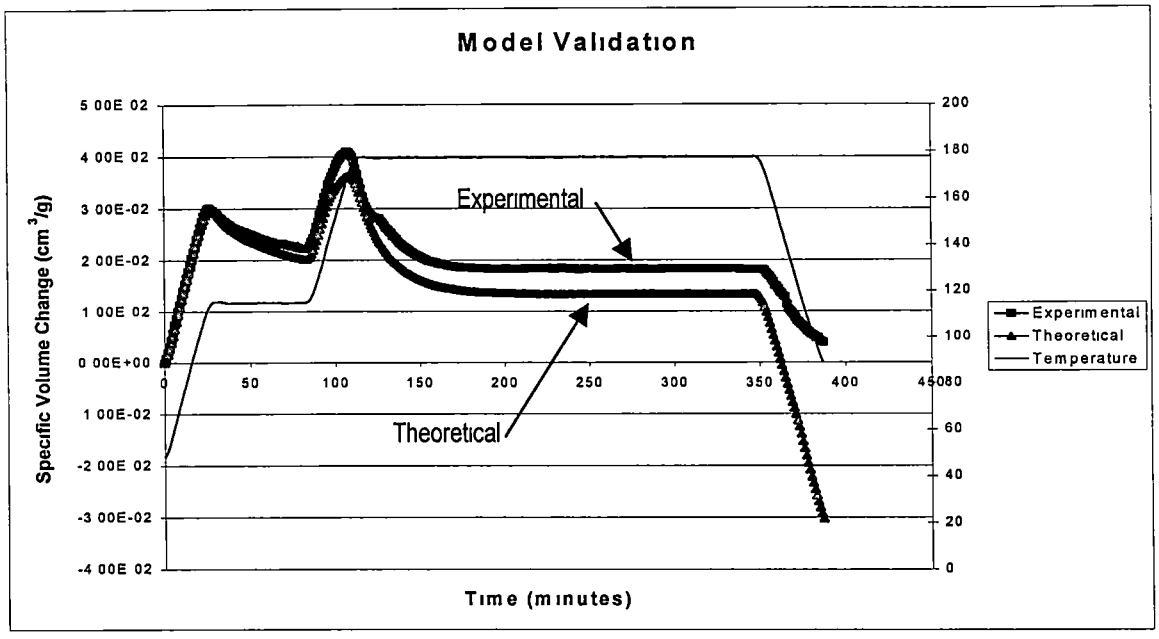

Figure 14 3501-6 model comparison with experimental data for a typical two-tier cure cycle. Agreement between theory and experimental values is close.

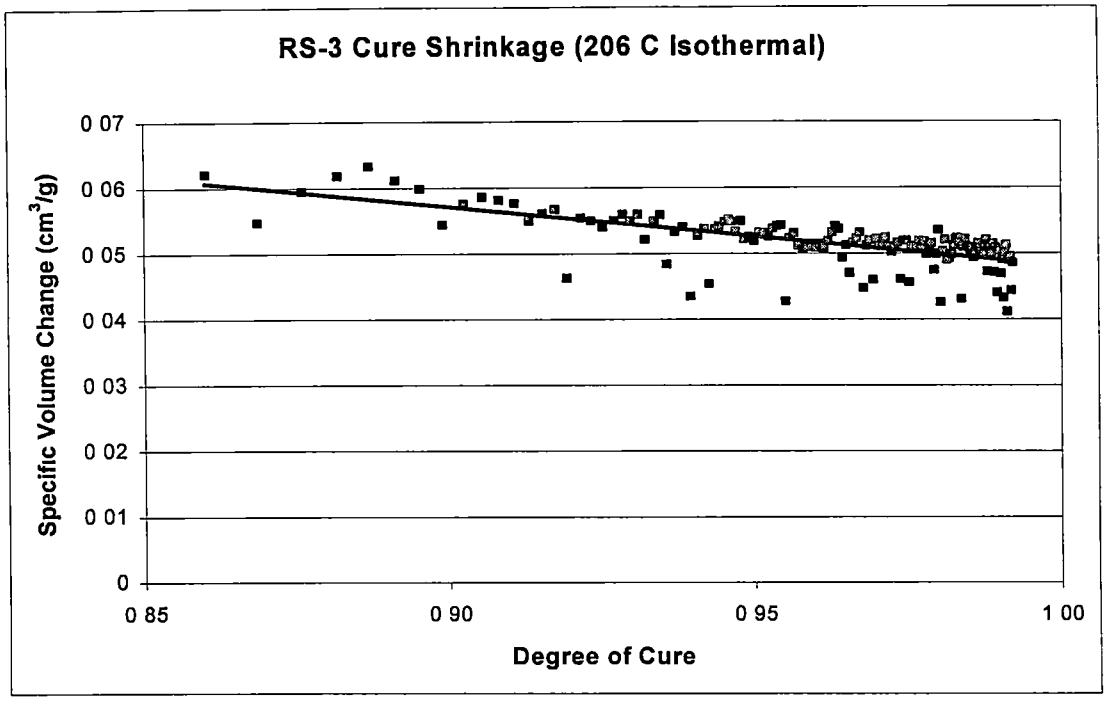

Figure 15: Cure shrinkage versus degree of cure during an isothermal cure cycle of RS-3 showing a linear relationship between the shrinkage and the degree of cure. The straight line indicates the linear curve fit

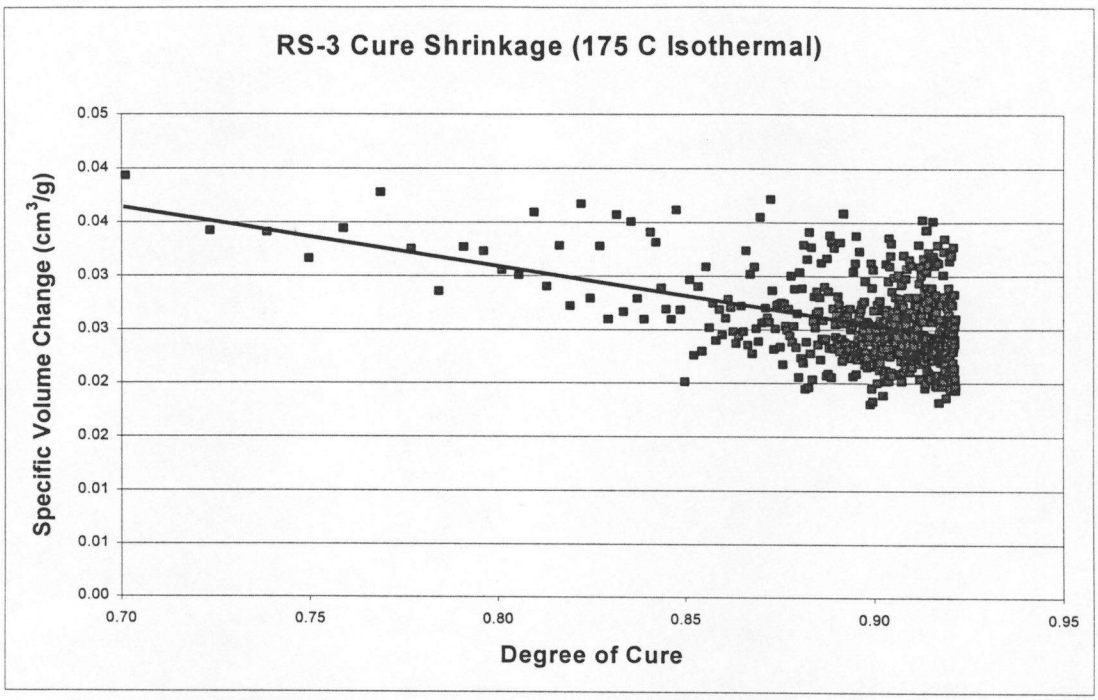

Figure 16: Cure shrinkage versus degree of cure during an isothermal cure cycle of RS-3 showing a linear relationship between the shrinkage and the degree of cure. The straight line indicates the linear curve fit.

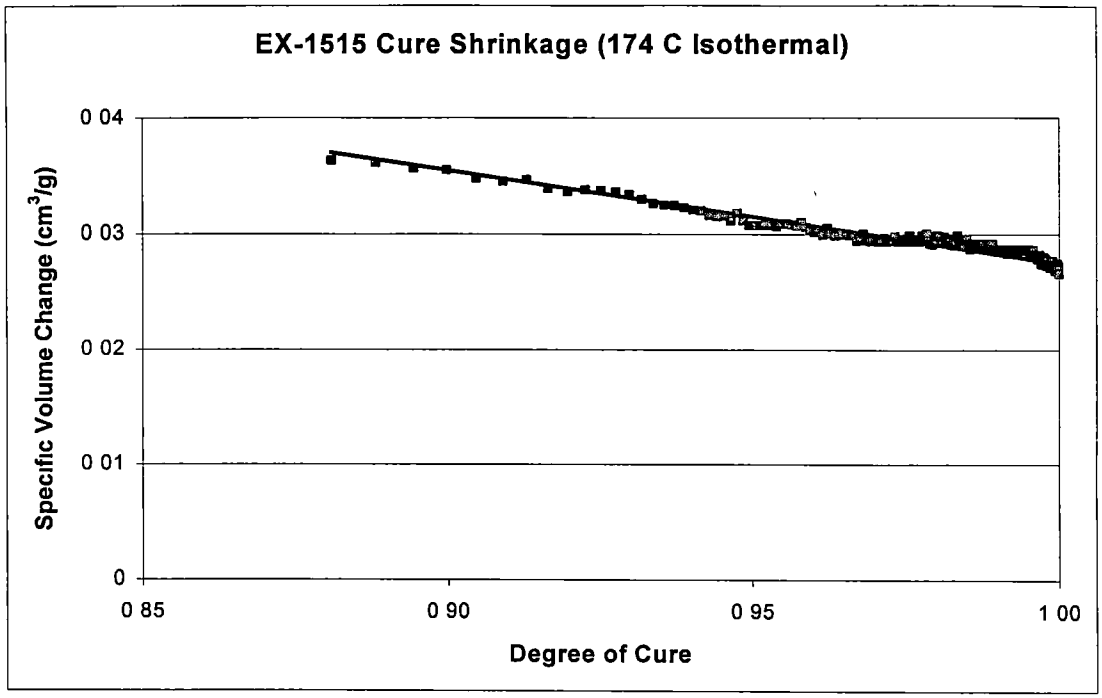

Figure 17: Cure shrinkage versus degree of cure during an isothermal cure cycle of EX-1515 showing a linear relationship between the shrinkage and the degree of cure. A straight line indicates the linear curve fit.

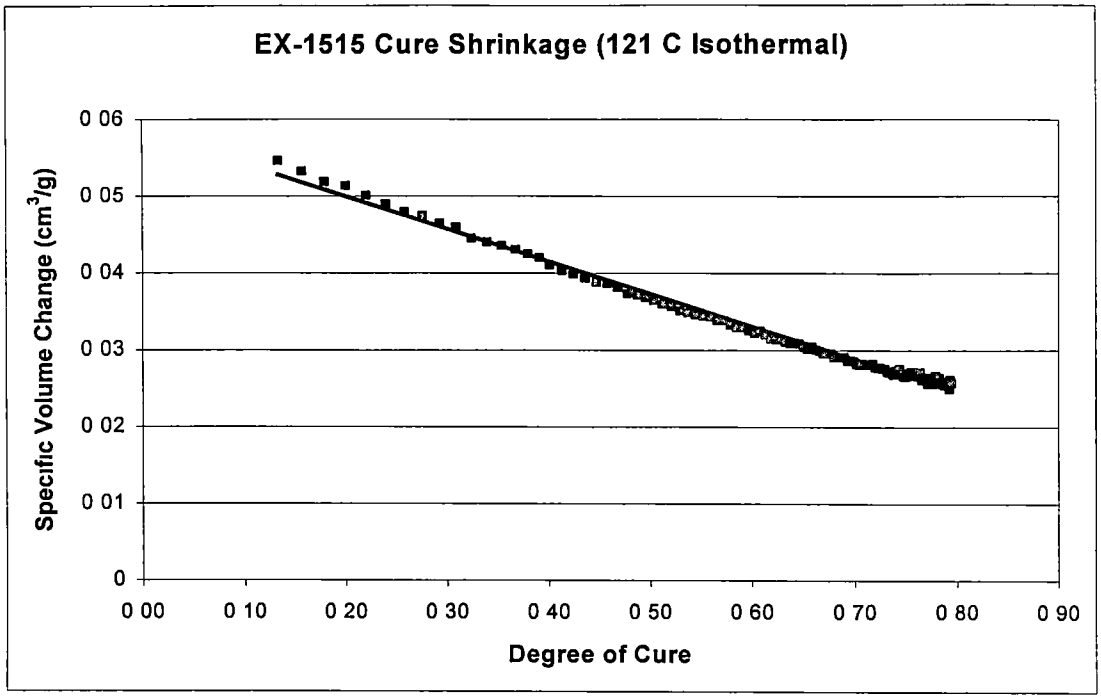

Figure 18: Cure shrinkage versus degree of cure during an isothermal cure cycle of EX-1515 showing a linear relationship between the shrinkage and the degree of cure A straight line indicates the linear curve fit.

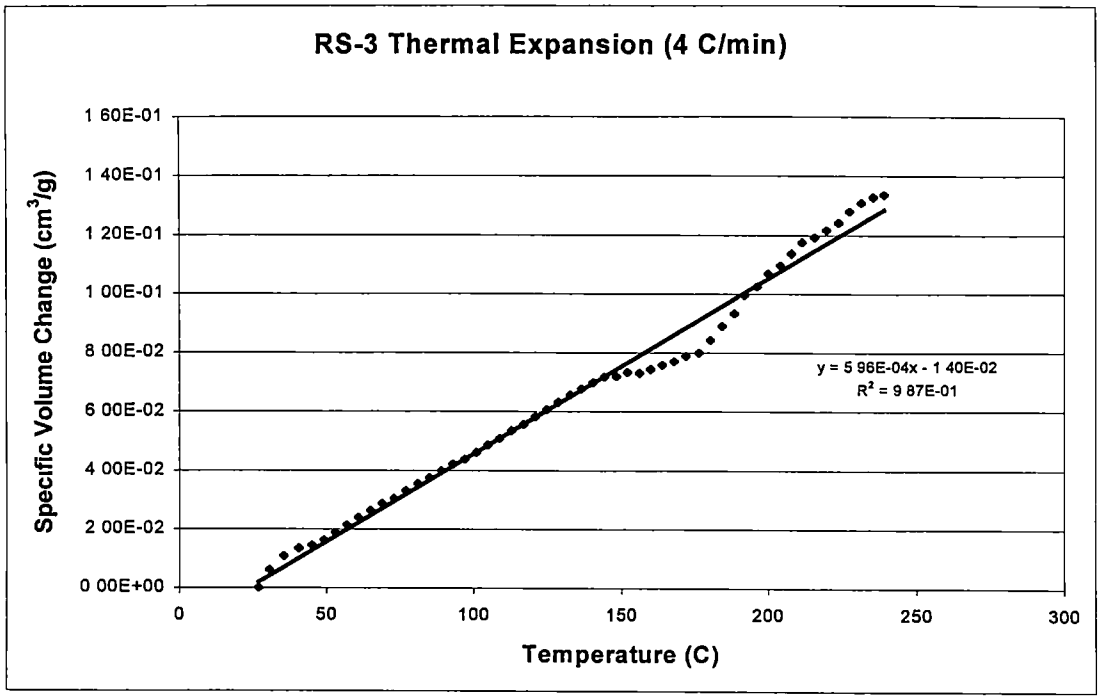

Figure 19 A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate A straight line indicates the linear curve fit.

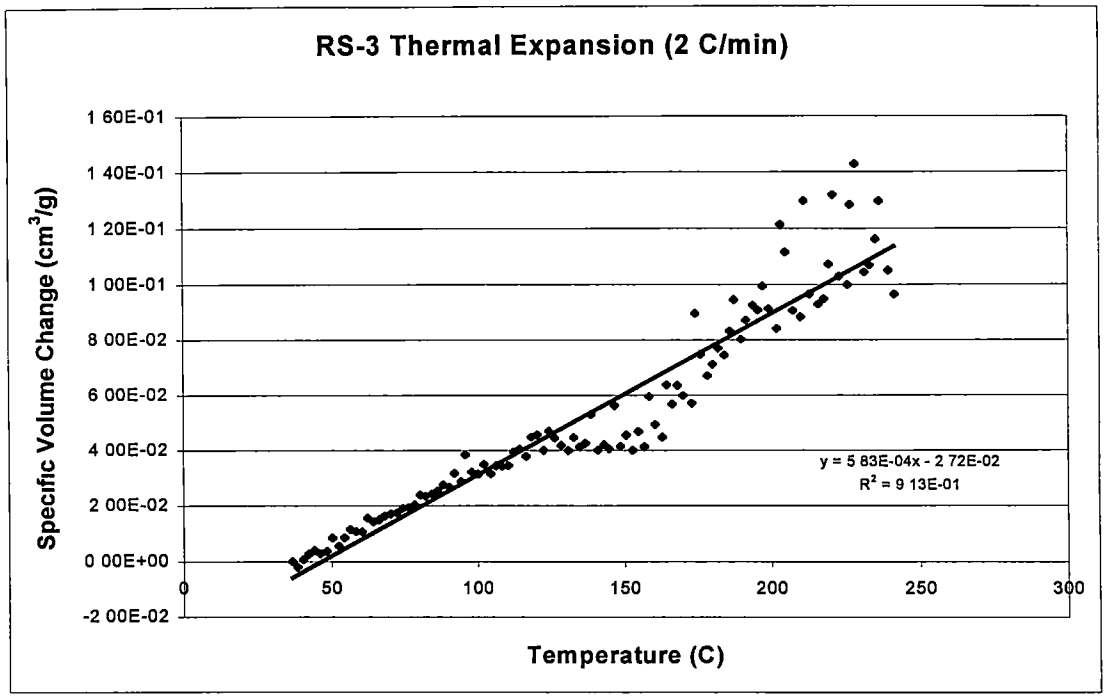

Figure 20 A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate. A straight line indicates the linear curve fit

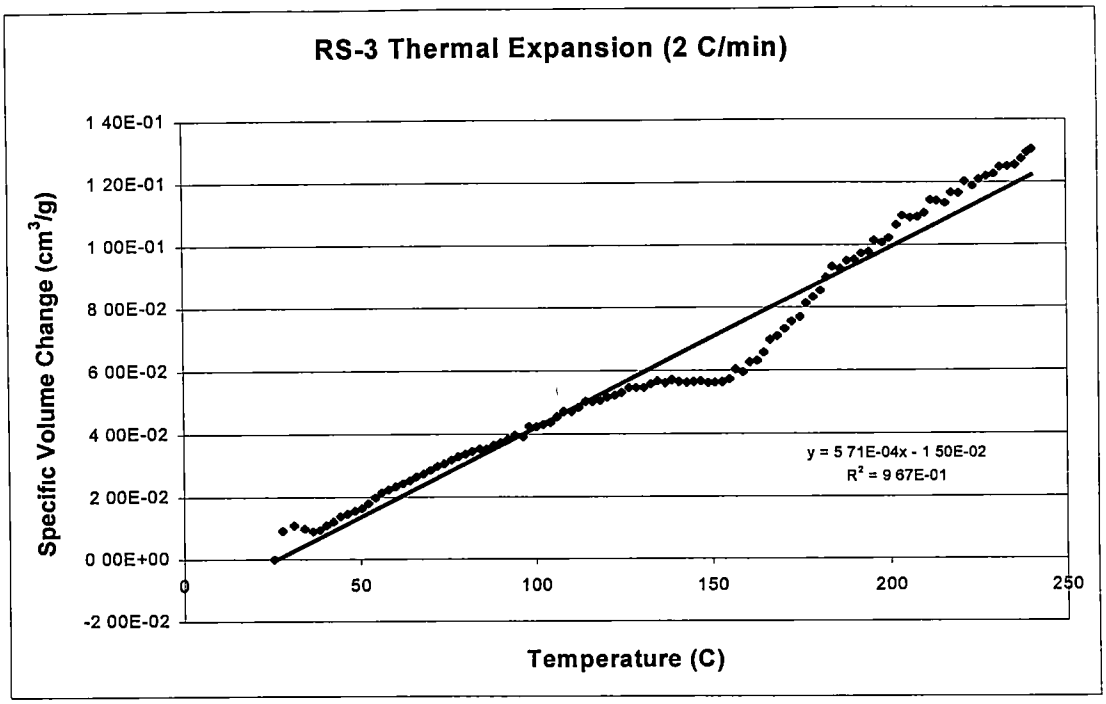

Figure 21· A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate A straight line indicates the linear curve fit

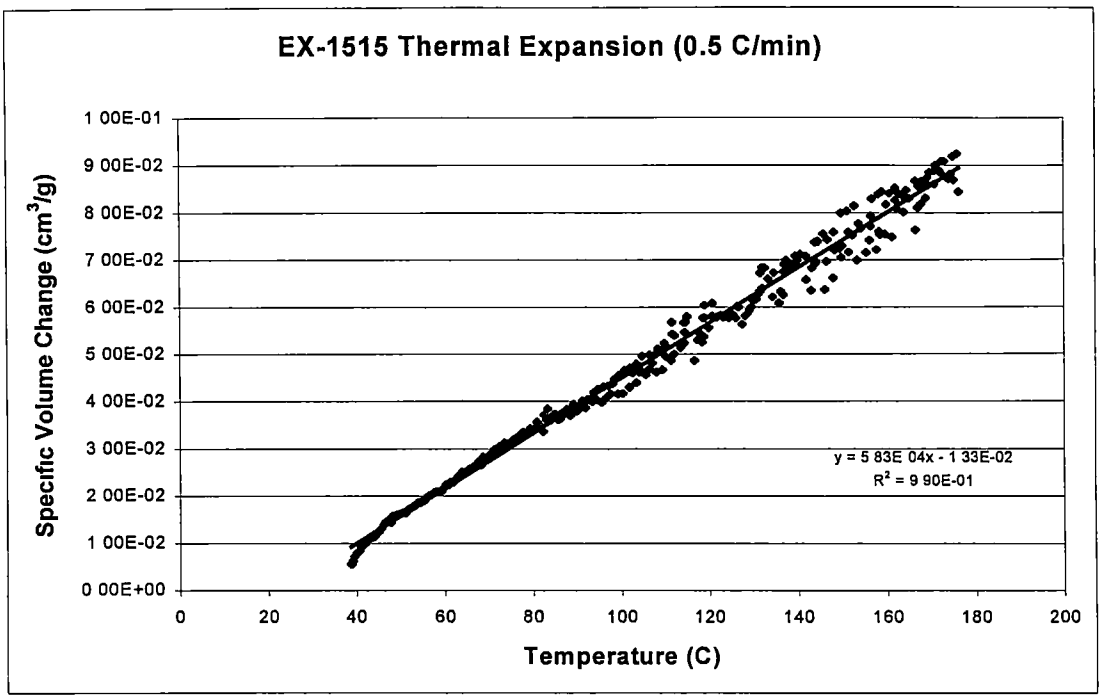

Figure 22 A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate A straight line indicates the linear curve fit.

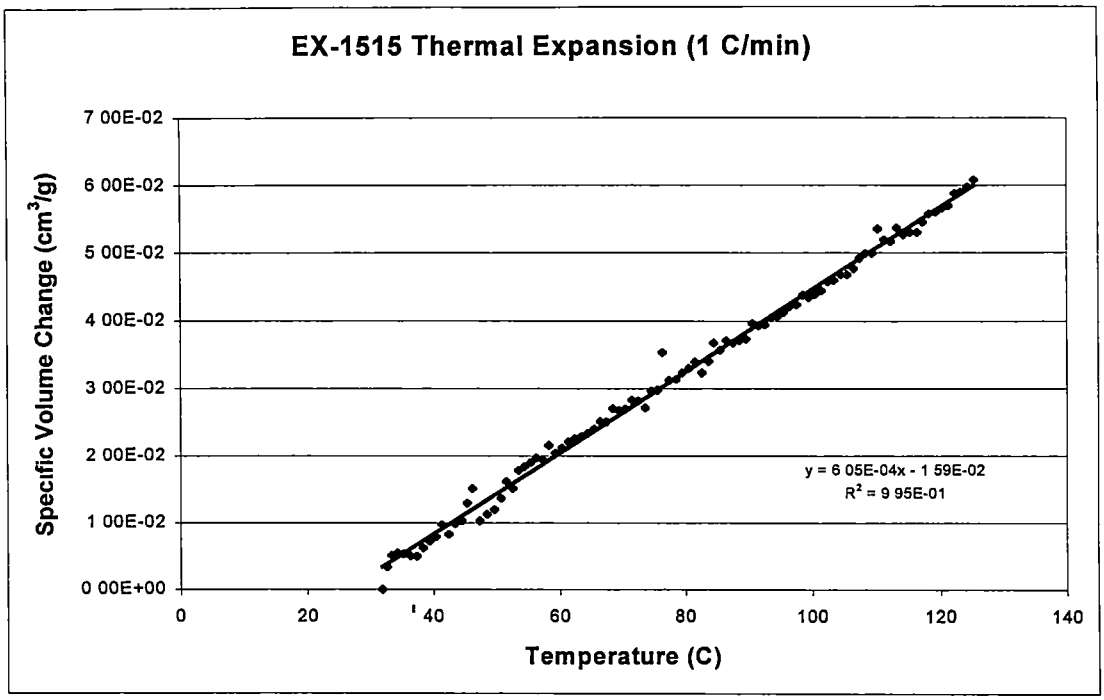

Figure 23 A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate. A straight line indicates the linear curve fit

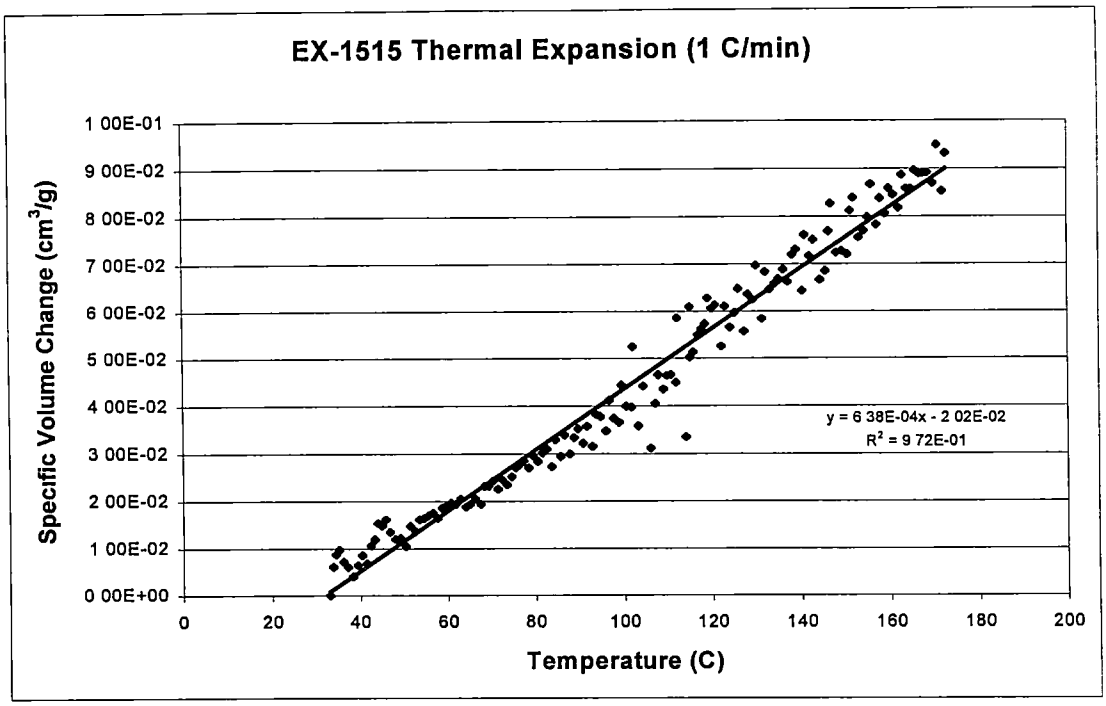

Figure 24 A linear increase in the thermal volume change with temperature suggests a constant thermal expansion coefficient for the given heat rate. A straight line indicates the linear curve fit.

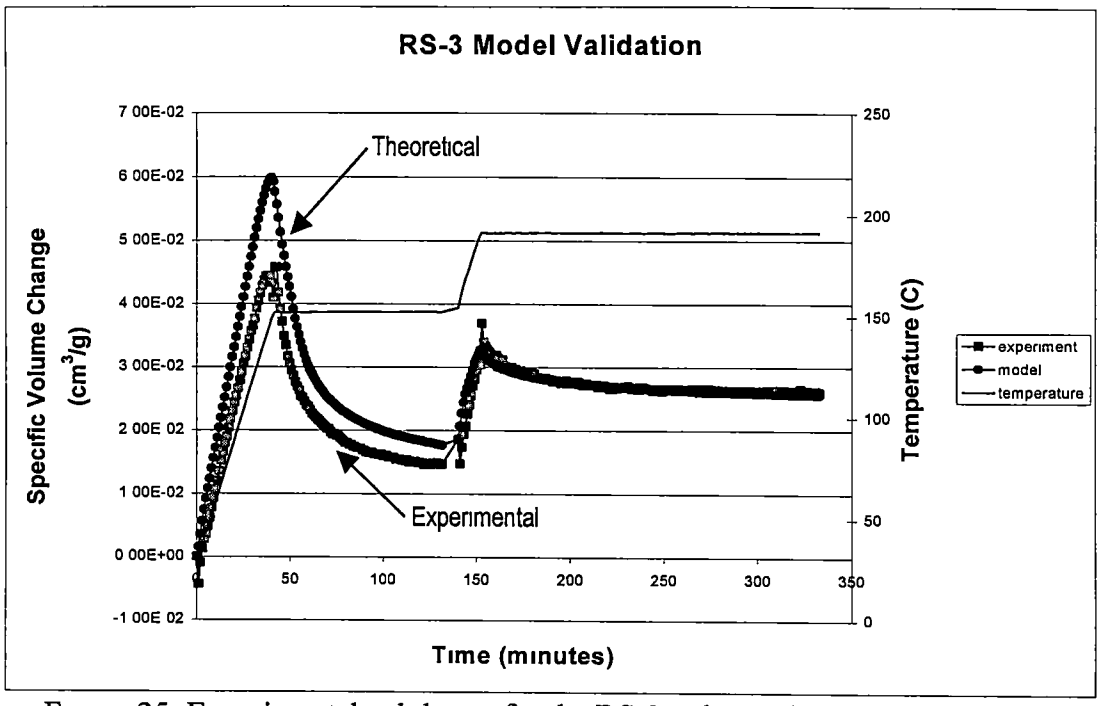

Figure 25 Experimental validation for the RS-3 volume change model for a typical two-tier cure cycle. The predictions agree well with the experimental data

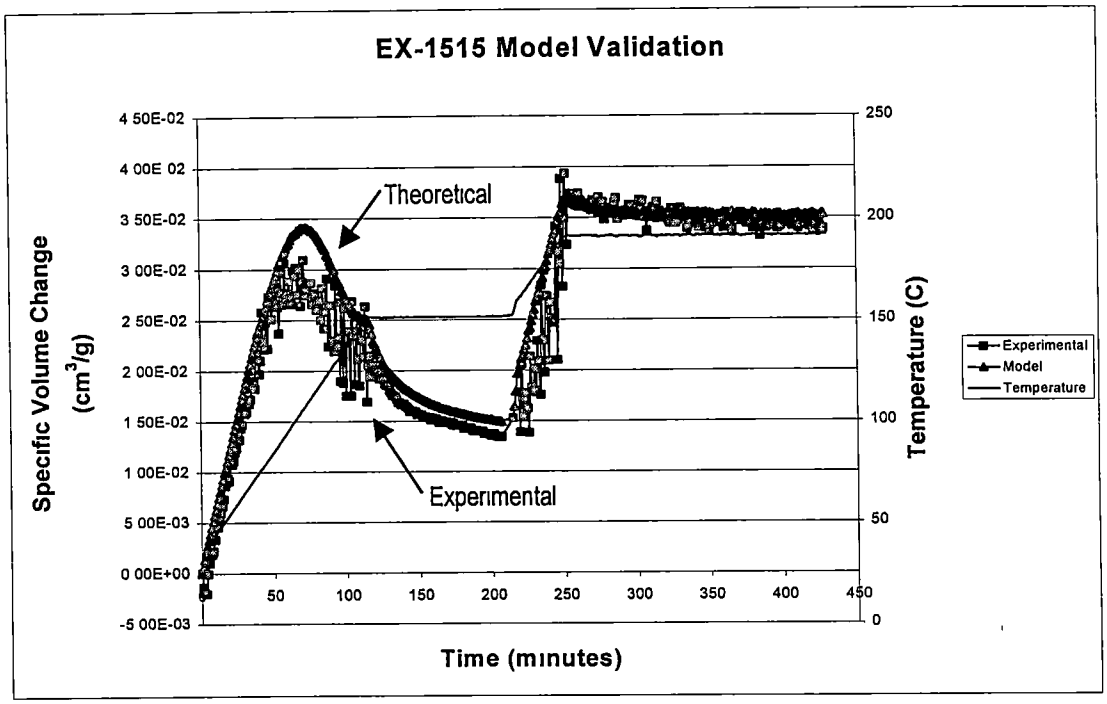

Figure 26 Experimental validation for the EX-1515 volume change model for a typical two-tier cure cycle. The predictions agree well with the experimental data

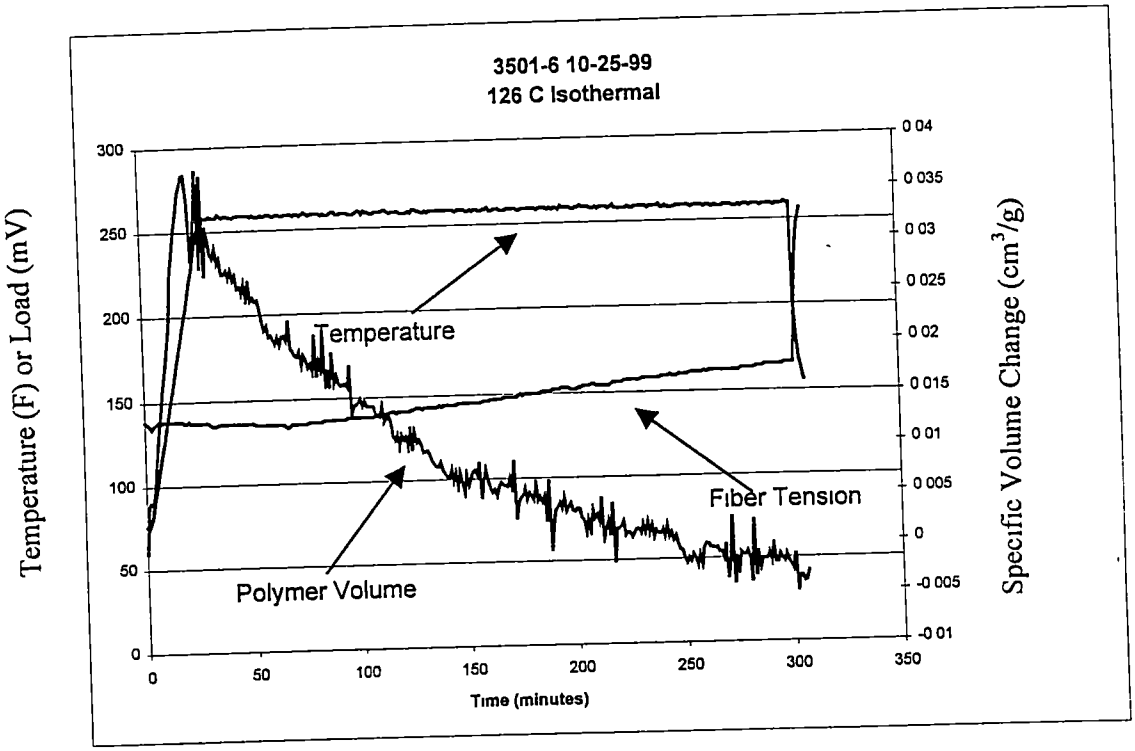

Figure 27: Correlating fiber tension with polymer volume changes Effect of volume change on induced stresses is greater at higher degrees of cure (40mV=1gram)

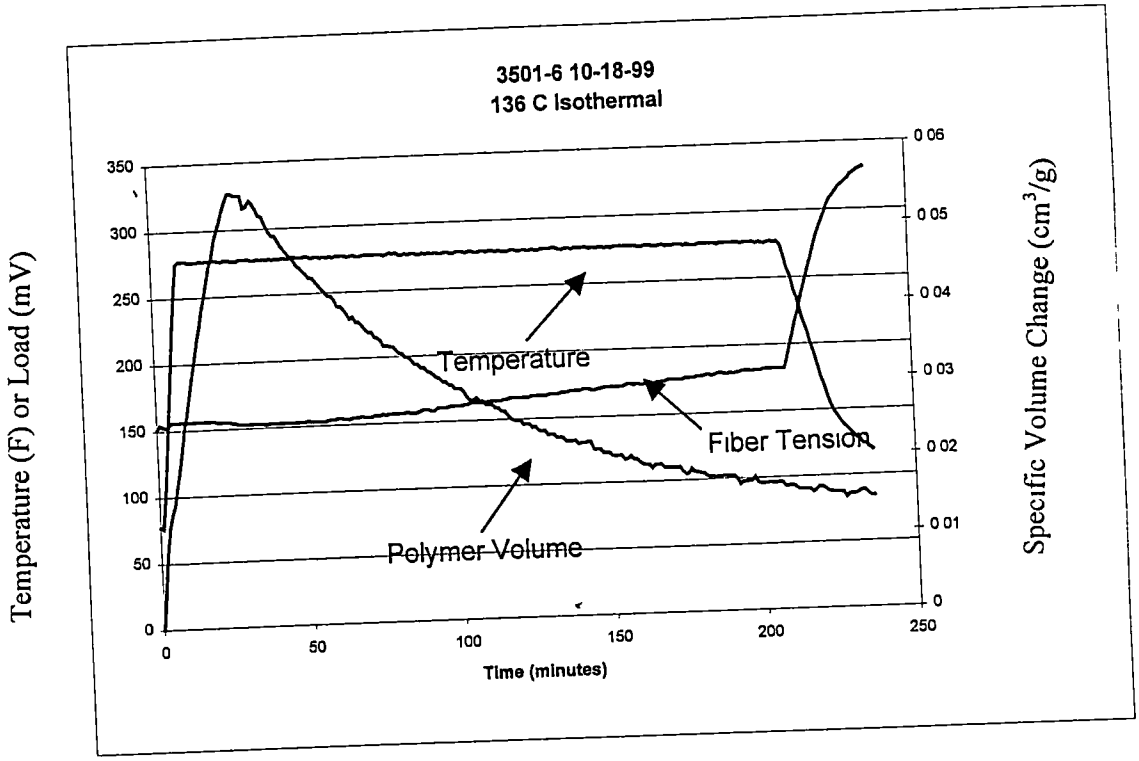

Figure 28: Correlating fiber tension with polymer volume changes Effect of volume change on induced stresses is greater at higher degrees of cure (40mV=1gram)

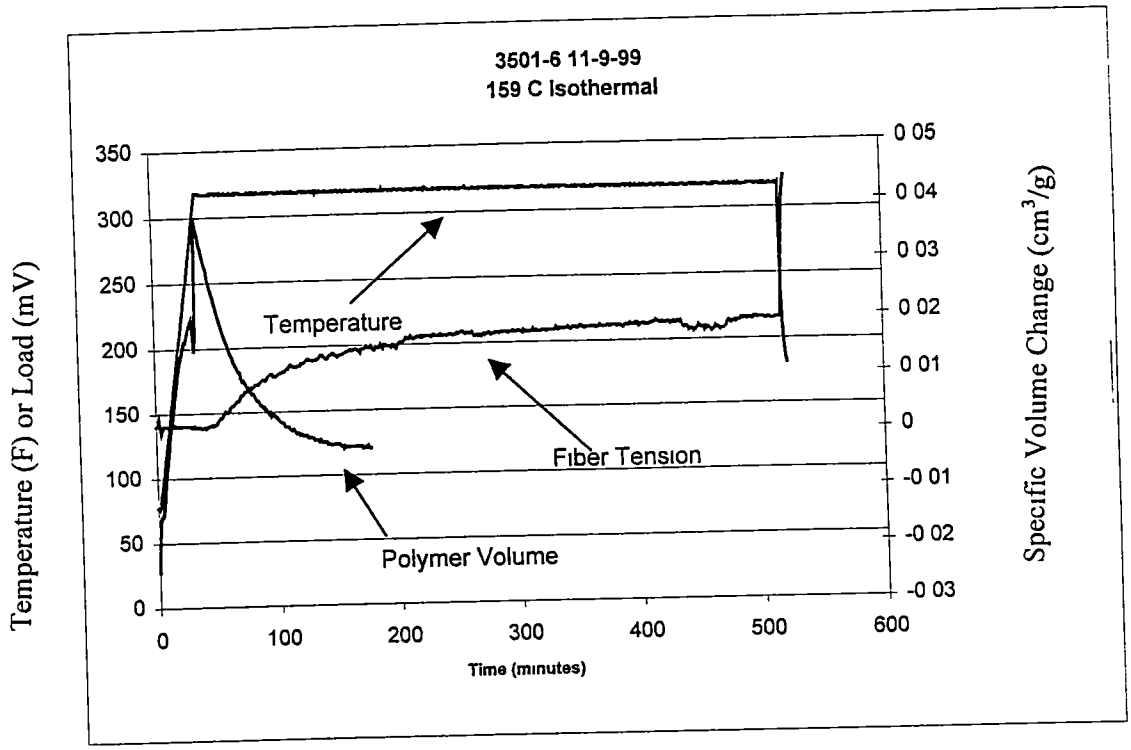

Figure 29 Correlating fiber tension with polymer volume changes Effect of volume change on induced stresses is greater at higher degrees of cure. (40mV=1gram)

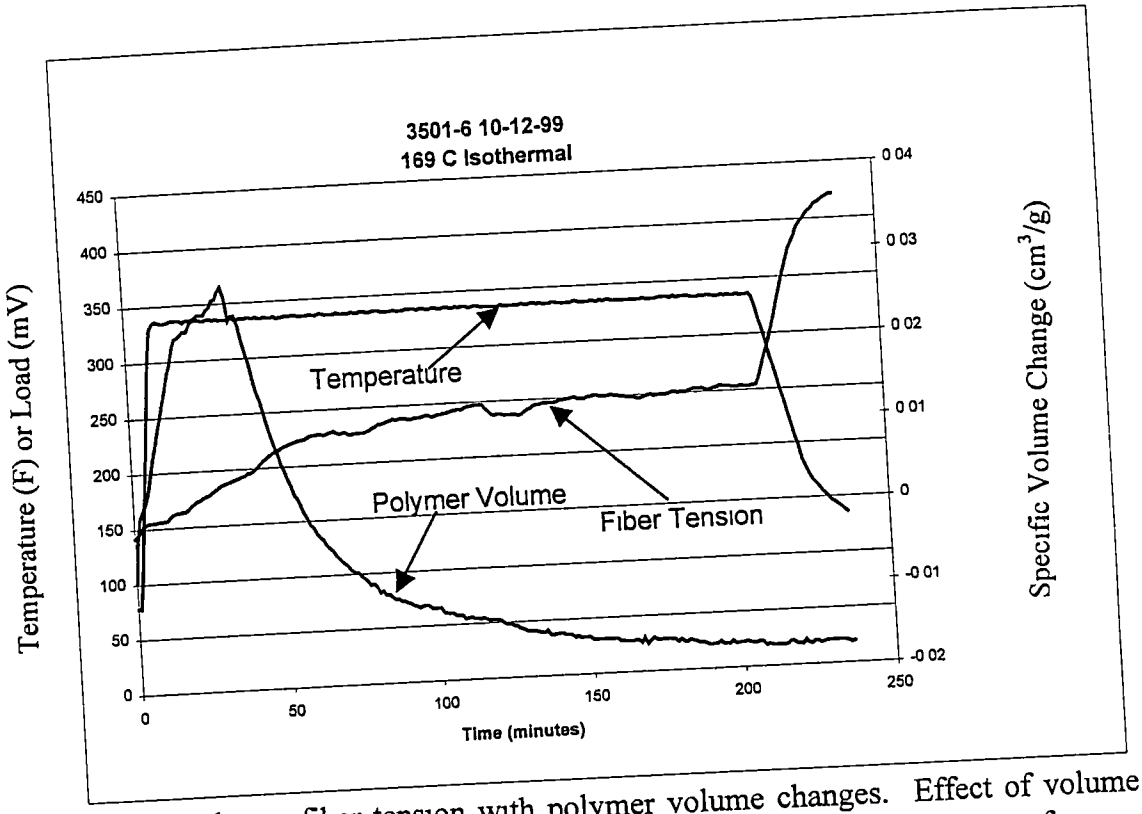

Figure 30: Correlating fiber tension with polymer volume changes. Effect of volume change on induced stresses is greater at higher degrees of cure (40mV=1gram)

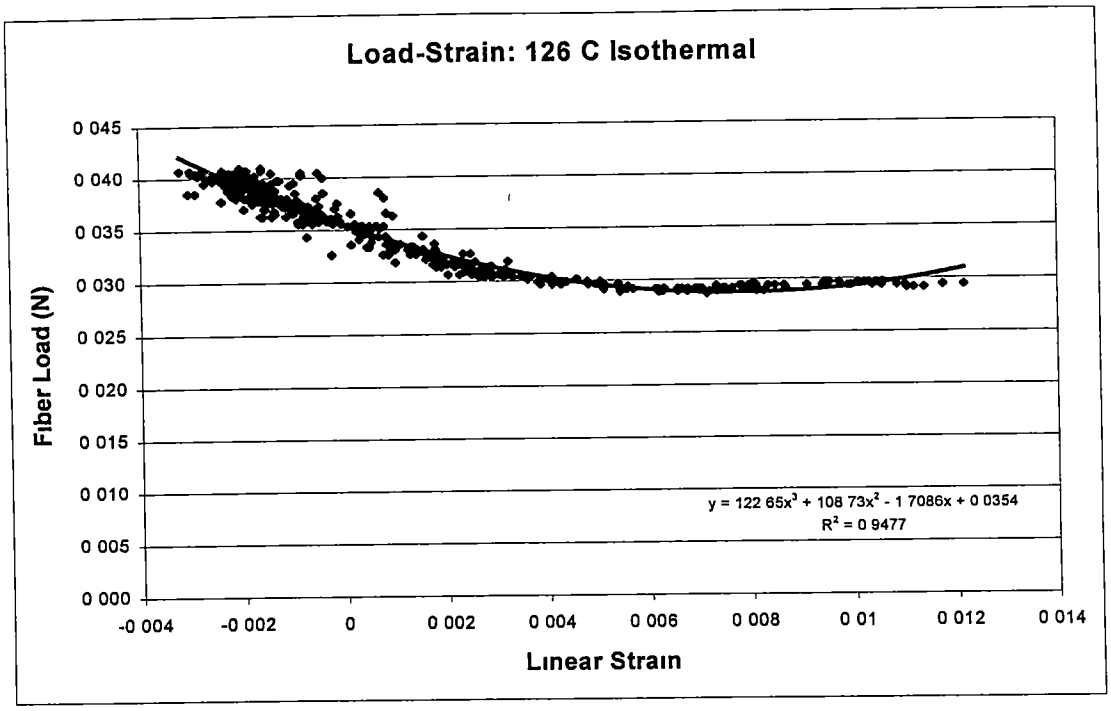

Figure 31· Fiber load-strain curve of 3501-6 for a 126 °C isotherm The slope of fiber tension versus strain is proportional to the polymer elasticity A solid line indicates the curve fit.

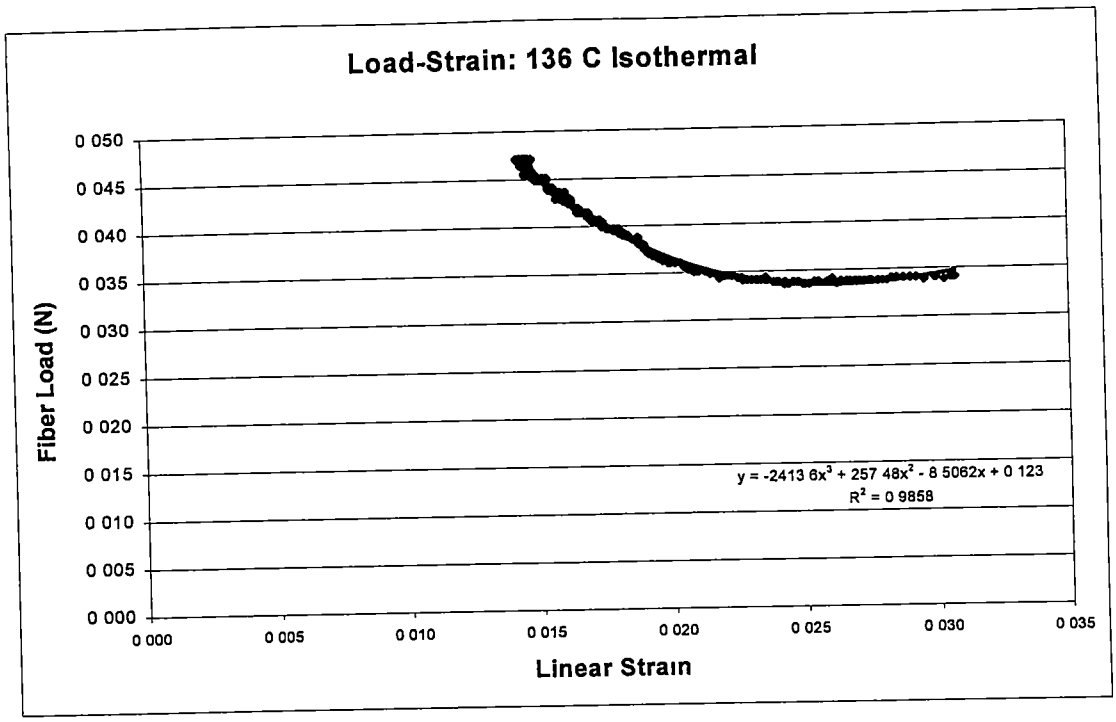

Figure 32: Fiber load-strain curve of 3501-6 for a 136 °C isotherm The slope of fiber tension versus strain is proportional to the polymer elasticity. A solid line indicates the curve fit.

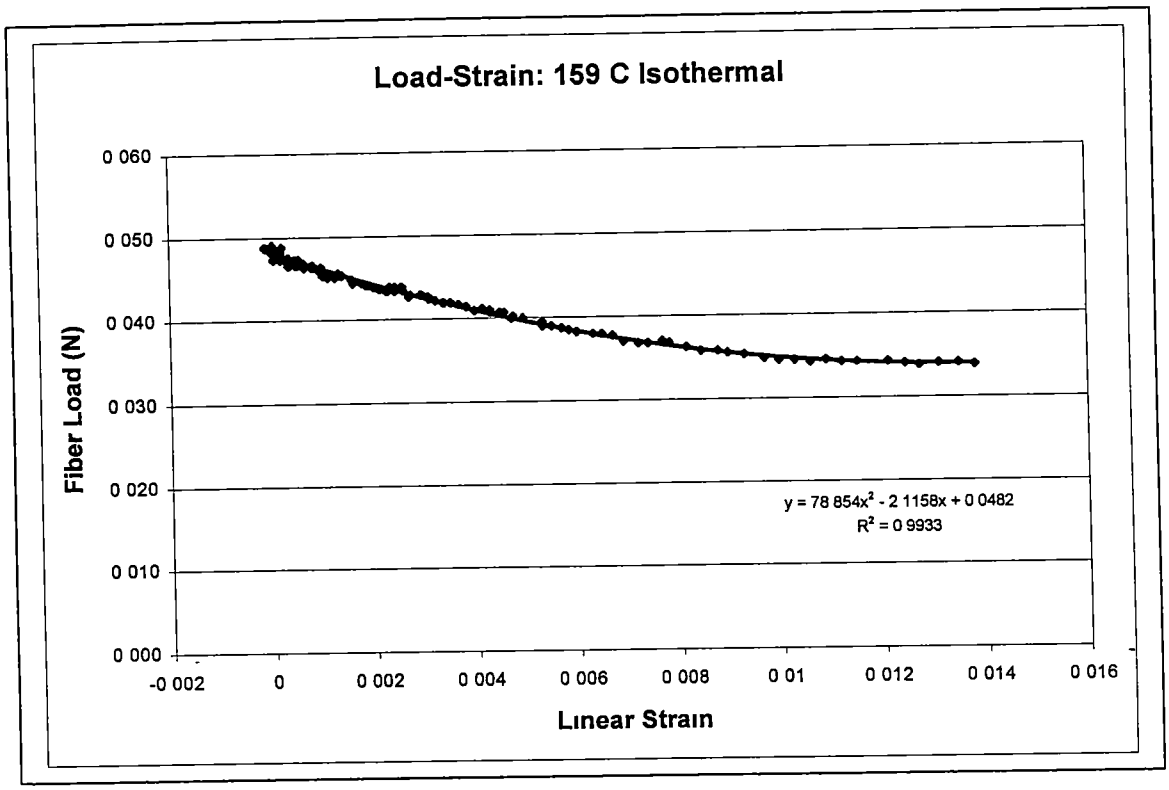

Figure 33. Fiber load-strain curve of 3501-6 for a 159 °C isotherm. The slope of fiber tension versus strain is proportional to the polymer elasticity A solid line indicates the curve fit

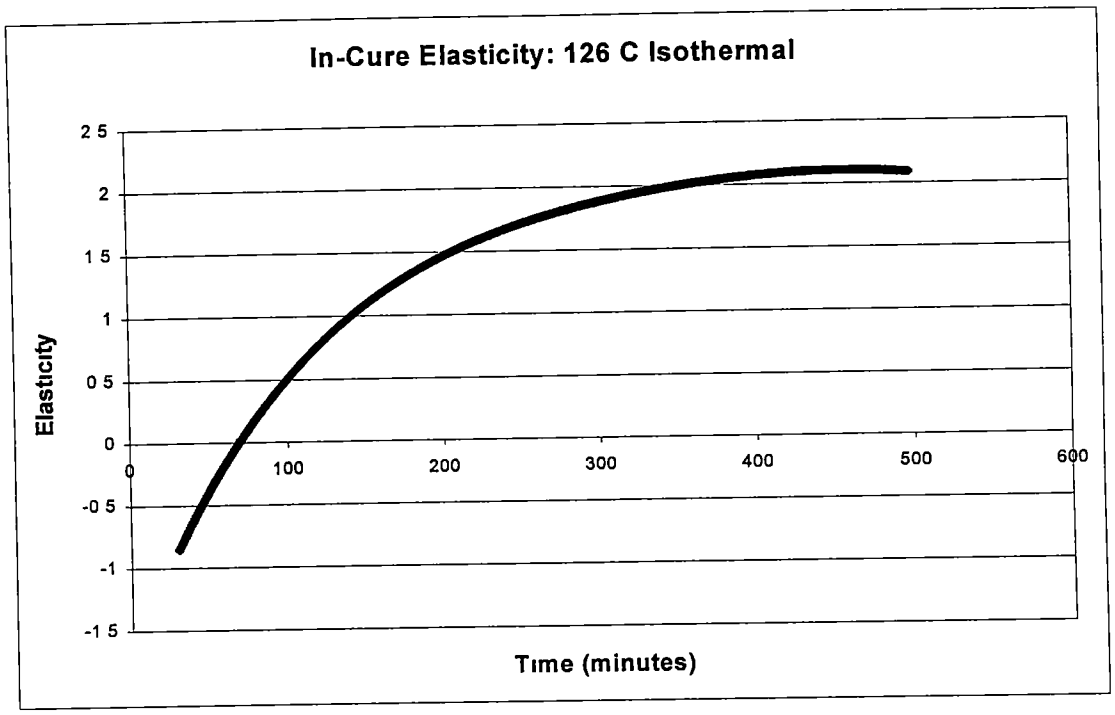

Figure 34: Development of elastic modulus during 126 °C isothermal cure for 3501-6. The development is seen to mimic progression of degree of cure.

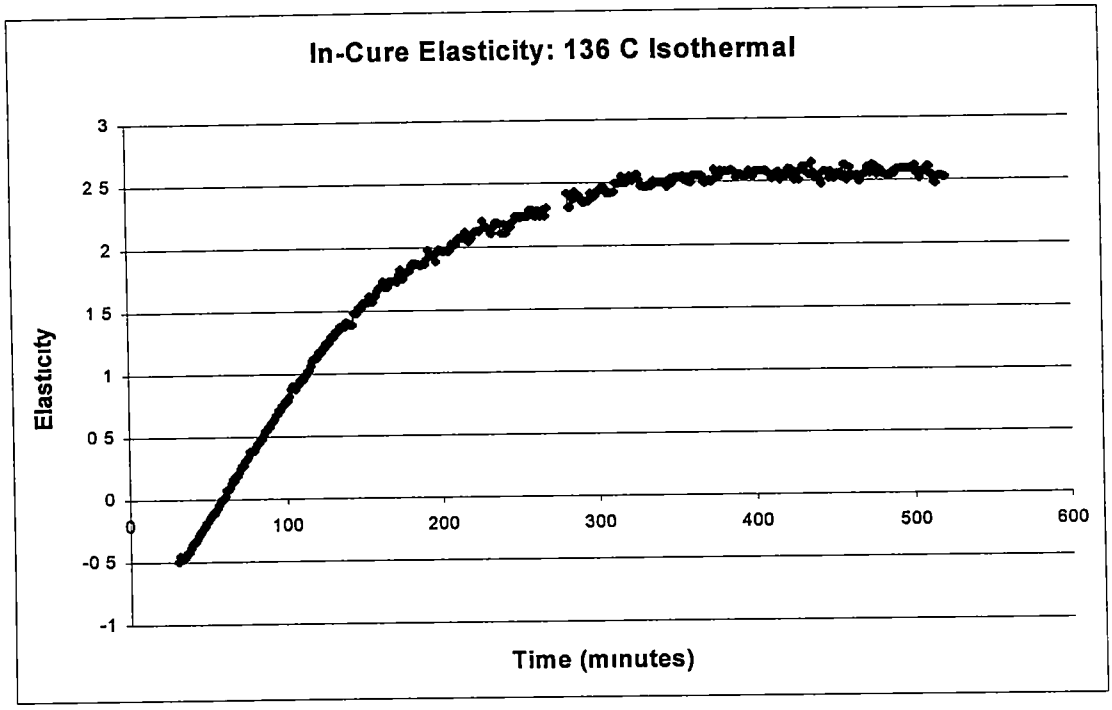

Figure 35: Development of elastic modulus during 136 °C isothermal cure for 3501-6 The development is seen to mimic progression of degree of cure

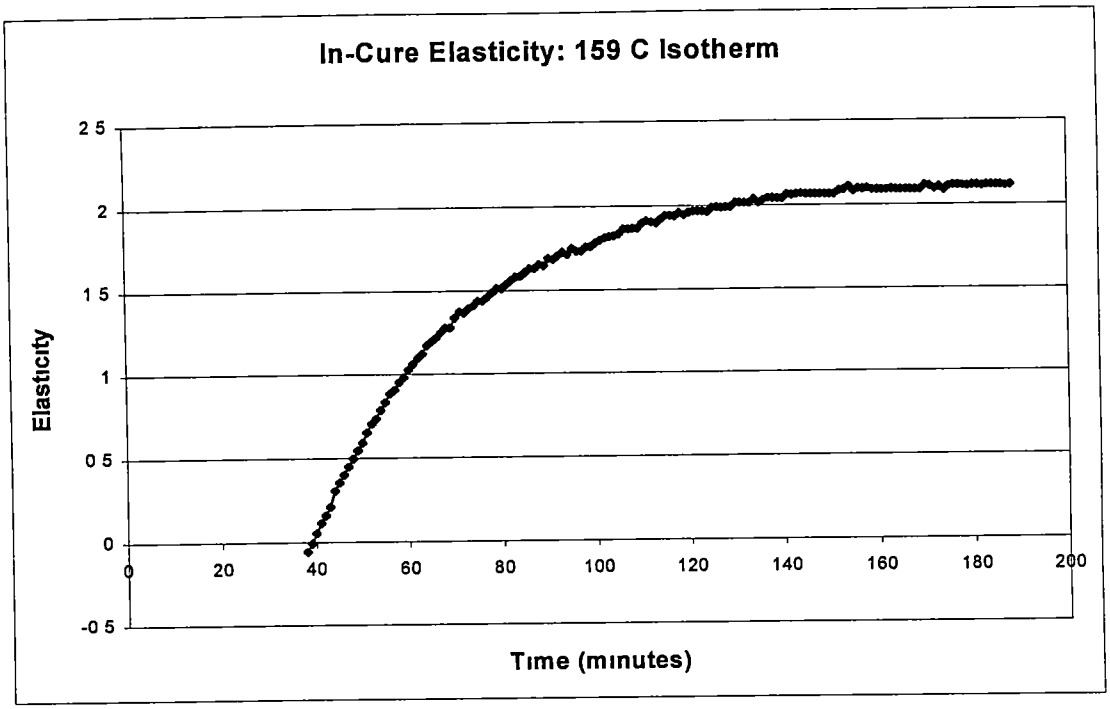

Figure 36: Development of elastic modulus during 159 °C isothermal cure for 3501-6 The development is seen to mimic progression of degree of cure

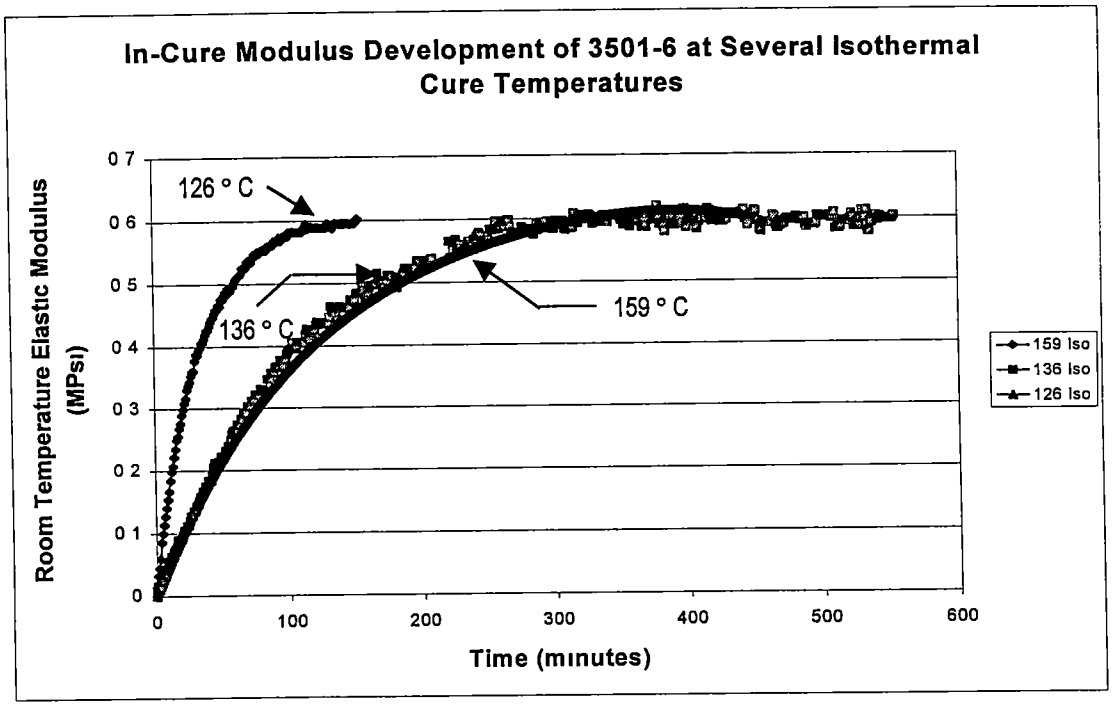

Figure 37: Scaled values of elastic modulus during cure of 3501-6 for three isothermal cure cycles The development is seen to mimic progression of degree of cure

VITA

Ryan Lee Karkkainen was born in Pensacola, Florida on February 19, 1975 His early childhood was spent in Germantown, Tennessee, and he later moved to Baton Rouge, Louisiana in 1987. He obtained his high school diploma from Baton Rouge High School in 1993 From 1993 to 1998, Ryan worked successfully towards completion of a B S in mechanical engineering from Louisiana State University in Baton Rouge After receiving his B S degree, he enrolled at The University of Tennessee in order to begin his current work in the composite mechanics area in fulfillment of requirements of an M.S in mechanical engineering.

Ryan will begin work at Ford Motor Company in Dearborne, Michigan in the summer of 2000. He will work as an engineer in the Body Engineering group, in the areas of research, design, and manufacturing of automotive structural mechanics.