

# A THERMO-VISCOELASTIC MODEL FOR THE MODULUS OF EPOXY DURING CURE

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## Abstract

The cure kinetics for a commercial epoxy have been established and the influence of the degree of cure on the glass transition determined. Time-temperature and time-conversion superposition principles have been built into a model that successfully predicts the development of the viscoelastic properties of the epoxy during isothermal cure from gelation to vitrification.

## Introduction

Understanding the cure of thermosetting materials is important to their application in the automotive, aerospace, and electronic industries. The isothermal time-temperature-transformation (TTT) cure diagram of Gillham [1,2] provided an intellectual framework for understanding the behavior of these systems during cure, particularly the effects of gelation and vitrification on the cure kinetics and properties. Although the kinetics of the cure reaction(s) in crosslinking systems are well understood, quantitative descriptions of the evolution of mechanical properties during cure are not well-developed. Here we propose a methodology using the principles of time-temperature superposition and time-crosslink density (degree of conversion) superposition to model the evolution of the viscoelastic properties during isothermal cure.

The principle of time-temperature superposition is based on the fact that the mechanical response at short times (or high frequencies) is analogous to the response at low temperatures, and vice versa. The general validity of the concept is demonstrated by the ability to satisfactorily reduce creep or stress relaxation data to form master curves [3,4]. The temperature dependence of the shift factors used to reduce viscoelastic data can normally be described with the Williams-Landel-Ferry (WLF) [5] equation or the equivalent Vogel [6] equation. In addition, polymer networks have been

found to follow time-crosslink superposition [7,8]. Here we combine the two concepts of time-temperature superposition and time-crosslink (taken as degree of conversion) to model the evolution of the viscoelastic modulus of a commercial epoxy resin during isothermal cure.

## Thermo-Viscoelastic Model

### Viscoelastic Response

The viscoelastic response was modeled using classical methods of linear viscoelasticity. In this case storage and loss moduli are represented as sums of Maxwell elements [4]:

$$G'(\omega) = G_r + [G_g - G_r] \sum_{i=1}^n g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad (1)$$

$$G''(\omega) = [G_g - G_r] \sum_{i=1}^n g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (2)$$

where  $G_g$  is the glassy modulus (not a strong function of T),  $G_r$  is the rubbery modulus which is a function of both T and degree of cure (crosslink density),  $t$  is time and  $\omega$  is the radian frequency. The  $\tau_i$  are relaxation times and the  $g_i$  are weighting factors such that  $\sum g_i = 1$ . The relaxation times are functions of temperature and conversion through appropriate shift factors.

## Effects of Temperature and Conversion on $G_r$

Network and rubber elasticity theories provide the means of modeling the effects of temperature and conversion on  $G_r$ :

$$G_r(T, x) = A \nu RT = \frac{G_{r,ref} T \nu}{T_{ref} \nu_{ref}} \quad (3)$$

where  $x$  is conversion,  $A$  is a prefactor,  $\nu$  is the effective concentration of network chains, and  $G_{r,ref}$  refers to the value of the rubbery modulus at the reference conditions,  $T_{ref}$  and  $\nu_{ref}$ . The effective concentration of network chains can be related to conversion using a recursive approach of Miller and Macosko [9]. For a difunctional epoxy and a tetrafunctional crosslinker,  $\nu$  is given by:

$$\nu = (1-P)^4 + \frac{1}{2} P(1-P)^3 \quad (4)$$

$P$  is the probability that a given arm of the crosslinker is not connected to the infinite network:

$$P = \left( \frac{1}{r x^2} - \frac{3}{4} \right)^{\frac{1}{2}} - \frac{1}{2} \quad (5)$$

where  $r$  is the stoichiometric ratio of reactants and  $x$  is the conversion.

## Temperature and Conversion Shift Factors

The effects of temperature and conversion on the relaxation time are accounted for by applying the principles of time-temperature [3-6] and time-crosslink density [7,8] superposition. The temperature shift factor  $a_T$  is defined as

$$a_T = \frac{\tau(T)}{\tau(T')} \quad (6)$$

and the crosslink (or conversion) shift factor  $a_x$  is defined as:

$$a_x = \frac{\tau(T_g(x))}{\tau(T(x))} \quad (7)$$

where the subscripts *ref* refer to reference temperature in equation 6 and reference degree of conversion in

equation 7. We expect  $a_T$  to follow the general Vogel [6] equation:

$$\log a_T = \frac{B}{T - T_\infty} - \frac{B}{T_{ref} - T_\infty} \quad (8)$$

where  $T_\infty$  (Vogel temperature) and  $B$  are material parameters.

We postulate that the crosslink (conversion) shift factor has a similar form based on the work of Suzuki and Migano [10]:

$$\log a_T = \frac{B}{T_g(x) - T_\infty} - \frac{B}{T_g(x_{ref}) - T_\infty} \quad (9)$$

The total shift factor  $a_{T,x} = a_T a_x$  and we note that  $T_{ref}$  and  $T_g(x_{ref})$  need not be the same.  $T_{ref}$  is the reference temperature for the viscoelastic master curve, whereas  $T_g(x_{ref})$  is the glass temperature of the material at the reference degree of conversion  $x_{ref}$  (=1.0 in this study).

In order to describe the shift factors in terms of conversion and temperature rather than in terms of  $T_g$  and temperature, we need to relate  $T_g$  to conversion. For many thermosetting systems, there is a relationship between  $T_g$  and conversion [11-13] which is given by the empirical DeBenedetto [14] equation:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad (10)$$

where  $T_{g0}$  is the  $T_g$  of the monomer,  $T_{g\infty}$  is the  $T_g$  of the fully cured material ( $x=1$ ) and  $\lambda$  is a material constant. By combining Equations 1-10 one can calculate the evolution of the viscoelastic properties for a given cure history providing that the history of  $x$  and  $T$  are known.

## Experimental [15]

### Material

The material investigated here was a toughened epoxy resin (Hecel 8551-7) provided by Hexcel Corporation. The cure kinetics and  $T_g$  vs  $x$  behavior of this material have been studied [16]. Cure kinetics were found to be first order in epoxy concentration:

$$\frac{dx}{dt} = -k_0 e^{-\left(\frac{E}{RT}\right)} (1-x) \left(\frac{1}{r} - x\right) (b+x) \quad (11)$$

where  $r$  is the stoichiometric ratio of the limiting reagent to the excess reagent and  $b$  accounts for impurities that catalyze the reaction initially. Table 1 presents the parameters found to fit the cure kinetics [16].

The  $T_g$  conversion behavior was found to follow equation 10 based on DSC results. Since the dynamic mechanical  $T_{g\omega}$  are approximately thirty degrees higher than DSC  $T_{g\omega}$ , we use these higher values to model the viscoelastic material. The parameters values used are given in Table 2

## Viscoelastic Measurements

The fully cured epoxy resin was obtained by curing at 180 °C for 5 h in a test tube approximately 1 cm in diameter and 10 cm in length. The sample was cooled to ambient in two hours, the test tube broken, and the epoxy removed. Test samples were obtained by machining the diameter and length to final dimensions of  $d=6.5$  mm and  $l=30$  mm. Loss and storage moduli were obtained using a Rheometrics ARES instrument with solid rod fixtures and tested at temperatures ranging from 140 °C to 180 °C. Prior to making measurements, the sample was heated to 170 °C, which is above  $T_{g\omega}$ , for 1 h. The sample was then cooled to the testing temperature and aged for 3960 s prior to testing.  $G'$  and  $G''$  were obtained for frequencies between 1 and 10 rad/s. The magnitude of the shear strain was 0.0002 to assure linear viscoelastic response.

The properties during cure were obtained with the Rheometrics ARES instrument in a parallel plate geometry at 1 Hz. The disposable platen fixtures were used with a platen diameter of 8 mm. The gap between platens was between 2 and 4 mm, depending on test. Samples were loaded at room temperature and heated at a rate of 5 °C/min to the desired cure temperature (between 145 °C and 180 °C) and measurements were made as a function of time as the material cured.

## Results

Figures 1 and 2 show the storage and loss moduli  $G'(\omega)$ ,  $G''(\omega)$  and the resulting time-temperature reduced master curves referenced to 160 °C for the fully-cured material. Experimental data were obtained every 2.5 °C but only some of the temperatures are shown for purposes of clarity. At the lowest temperatures, the storage modulus shows glassy behavior with a modulus of 810 MPa. As the testing temperature is increased through the glass transition temperature, the storage modulus drops and the loss modulus goes through a maximum. At the highest temperatures, the rubbery modulus is found to be 4.7 MPa. No vertical shifts were

needed in the construction of the master curves. The master curves were fit to equations 1 and 2 using a distribution of relaxation times found from a least squares regression of the combined loss modulus and storage modulus data.

The shift factors used to reduce the data in Figures 1 and 2 are found to follow an Arrhenius-like behavior ( $T_\infty=0$  in equation 8). The shift factors are shown in Figure 3.

Knowing the cure kinetics and the  $T_g$  versus conversion from other work [15], we can model the evolution of the dynamic mechanical properties during cure. By taking the cure kinetic parameters of Table 1 into account, we converted the cure time into a degree of conversion and then obtained the appropriate shift factors for  $a_{T,x}$  from equations 8 and 9 and the data of Figures 1-3. Figures 4 and 5 shows the isothermal cure data at 145 °C and 180 °C as  $G'$  vs  $x$ . Also shown are the curves predicted from the model calculations. Fits at 160 °C and 170 °C are comparable. Clearly, the model describes well the evolution of the dynamic storage and loss moduli during isothermal cure. Importantly, the model parameters were based only on the experimental master curves of the fully-cured material, the temperature dependence of the shift factors for the fully-cured material, and the  $T_g$ -conversion relationship.

## Conclusions

A thermo-viscoelastic model has been successfully developed that can describe the evolution of the linear viscoelastic properties,  $G'(\omega)$ , and  $G''(\omega)$  of a commercial epoxy resin during cure. The model is based on the assumption that time-temperature and time-crosslink (degree of conversion) superposition principles can be applied to the curing epoxy material.

The viscoelastic response of the fully cured epoxy was measured over a range of temperature and frequency and master curves constructed. These data, combined with previously obtained data for the cure kinetics and  $T_g$  vs conversion for the epoxy of interest, were used to obtain the parameters required in the model. Values of  $G'$  and  $G''$  were obtained during isothermal cure at four temperatures that spanned the ultimate glass transition of the epoxy and the results were compared with model predictions. The cure model agrees well with the measurements.

## Acknowledgements

Part of this work was supported by General Electric Company. O. Sindt is grateful to NIST for making

available a position as a visiting researcher.

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**Table 1.** Cure kinetics parameters.

$k_0$ ( $s^{-1}$ )	$1.2 \times 10^5$
E/R (K)	$5.8 \times 10^3$
r	1.12
b	0.16

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**Table 2.** Parameters for  $T_g$  vs conversion.

$T_{g0}$ ( $^{\circ}C$ )	25
$T_{g\infty}$ ( $^{\circ}C$ )	186
$\lambda$	0.45

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Figure 1: Storage Modulus Data and Master Curve

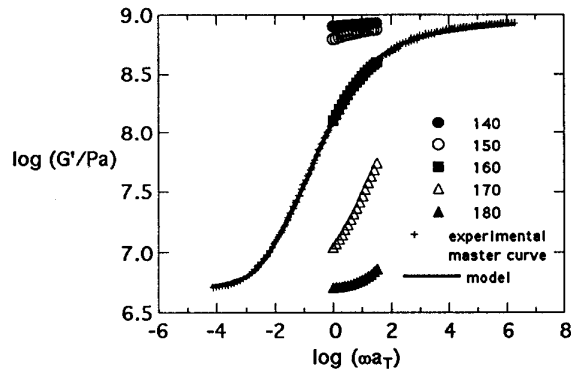


Figure 5: Evolution of  $G'$  at 180°C

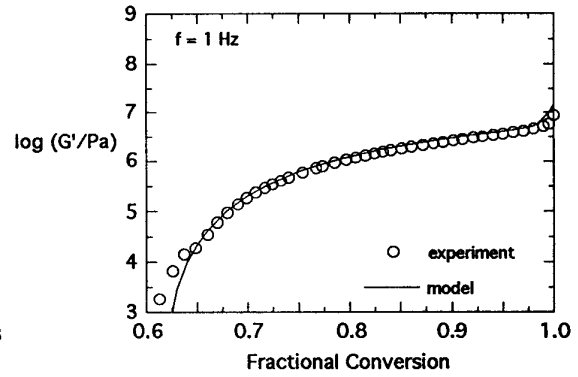


Figure 2: Loss Modulus Data and Master Curve

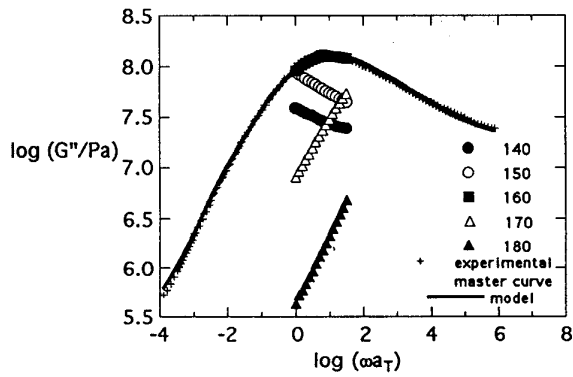


Figure 4: Evolution of  $G'$  at 145°C

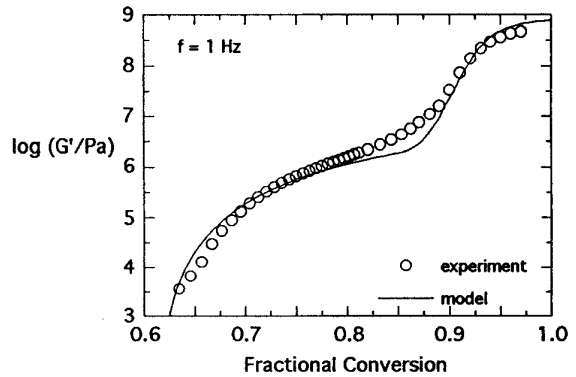


Figure 3: Temperature Shift Factors

