

Viscoelastic Behavior of Cytec FM73 Adhesive During Cure

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ABSTRACT: In this work, the viscoelastic properties of Cytec FM73 structural film adhesive were characterized. Several resin plates were cured using various process cycles to achieve a range of final cure states. Specimens cut from these plates were tested using a dynamic mechanical analyzer (DMA) and the glass-transition temperature at each degree of cure was determined. Stress relaxation tests at different temperatures were then performed using DMA in stress relaxation mode and time-temperature superposition was used to generate master stress relaxation curves and associated shift functions for each degree of cure. Several different constitutive models were examined for their ability to describe relaxation modulus development during cure. A simple three-parameter model consisting of a stretched exponential with cure-dependent terms was found to provide

the best results. The results indicate that of the parameters used in the model, relaxation time strongly depends on cure state. The empirical DiBenedetto equation was used to obtain an expression for glass-transition temperature as a function of degree of cure. This expression was in turn used to derive a new relation to describe stress relaxation time as a function of degree of cure. The shift function was modeled using a simplified form of the Vogel equation with cure-dependent coefficients. Good correlation between measured relaxation modulus and model predictions was observed.

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Key words: viscoelastic properties; relaxation; adhesives; curing of polymers; glass transition

INTRODUCTION

An increasingly important technology for life extension of aging aircraft is the use of bonded polymer composite patches for repair and local strengthening of primary and, more commonly, secondary aircraft structures.^{1,2} To ensure maximum patch mechanical performance and durability, an important concern is reduction of patch and bond-line residual stresses.³ New analytical tools are required to assist in determination of improved cure cycles that minimize residual stresses, while ensuring full cure of the composite and adhesive resins using a short processing time. Development of these analytical tools requires data on such parameters as the cure kinetics and viscoelastic behavior of both the composite patch and the patch adhesive. The focus of this article is on modeling of the evolution of mechanical properties of a common structural adhesive resin during cure.

During curing, a low molecular weight liquid epoxy resin is transformed through a series of chemical reactions into a crosslinked solid polymer. It has been

shown that, at a given curing temperature, the viscoelastic properties of resin change considerably with increasing conversion.^{4–8} It is also well known that polymer mechanical properties are time- and temperature-dependent.^{9,12} Therefore, to accurately model the development of mechanical properties of resins, the time, temperature, and degree of cure must be accounted for in the development of the constitutive equation.

There are two “superposition” principles that are important in the theory of viscoelasticity. The first of these is the Boltzmann superposition principle,⁹ which describes the response of a material to different loading histories. The second is the time-temperature superposition principle, which describes the effect of temperature on the time scale of the response, and has been widely used to describe the viscoelastic behavior of materials.^{9–16} This principle is based on the hypothesis that the mechanical response at long times (or low frequencies) is analogous to the response at high temperature and vice versa. Creep or stress relaxation curves developed at different temperatures have been shown to be superposable by horizontal shifts along a logarithmic time scale to give a single curve, known as the “master curve,” which covers an extensive range of times. Master curves made by superposition using a convenient “reference” temperature can cover time scales well beyond the range easily accessible by prac-

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TABLE I
Degree of Cure and Glass-Transition Temperature of Different Plates

Specimen	Cure cycle	H_R (J/g)	H_U (J/g)	α_f	T_g (°C)
Plate 1	60 min @ 120°C	2.2	—	0.99	98.12
Plate 2	240 min @ 80°C	9.2	—	0.95	74.5
Plate 3	210 min @ 80°C	23.79	—	0.87	69.1
Plate 4	180 min @ 80°C	47.28	—	0.74	46.3
Uncured adhesive	—	—	184.2	0	7.5

tical experiments.^{9,12} The shift factors used to shift the experimental data often follow the Williams-Landel-Ferry (WLF) equation or the equivalent Vogel equation.^{8,9,12}

Cytec Fiberite FM73 is a high-performance structural adhesive widely used for composite patch repair in aerospace applications. The linear and nonlinear viscoelastic properties of completely cured FM73 were studied previously.^{17–21} However, no constitutive model is currently available for FM73 adhesive that can predict its mechanical property development during cure.³ In this work, an equation for stress relaxation modulus is derived that accounts for time, temperature, and degree of cure.

Stress relaxation testing was performed using a dynamic mechanical analyzer in stress relaxation mode. Normally characterization of stress relaxation response is performed by conversion of either dynamic mechanical data in the frequency domain, or creep data in the Laplace domain.^{9,12} Because direct testing of stress relaxation in the time domain is possible using the present setup, no error arising from the conversion calculation is introduced into the data.

Several plates of neat FM73 adhesive were cured using various cure cycles to produce different desired final cure states. Specimens were cut and tested using a dynamic mechanical analyzer (DMA) in stress relaxation mode. Master curves and shift functions for each degree of cure case were obtained using time-temperature superposition. Adhesive stress relaxation response was modeled in a chemo-thermorheologically complex manner. A simple three-parameter model consisting of a “stretched” exponential with cure-dependent terms was used to describe the development of relaxation modulus. The empirical DiBenedetto equation was used to obtain an expression for glass-transition temperature as a function of degree of cure. Based on this expression, a new equation was proposed to describe the stress relaxation time as a function of degree of cure. Shift function was modeled using a simplified form of the Vogel equation with cure-dependent coefficients. Good correlation between measured data and model prediction was observed.

EXPERIMENTAL

Specimen preparation

The material used in this work was FM73M adhesive from Cytec Fiberite, a toughened epoxy widely used in the aerospace industry for bonding metals and many structural composite systems. The first step in characterization of adhesive response was fabrication of plates of neat resin. To do this, the adhesive film was first precut to square shapes (20 × 20 cm) and stored in a freezer. The material was later removed from the freezer and allowed to slowly equilibrate to room temperature. Ten layers of adhesive film were placed inside an aluminum mold. A layer of release film was placed between the mold and the adhesive film to prevent sticking. Two sheets of perforated release and layers of breather were then placed on top of the stack followed by an aluminum caul plate. A small hole was drilled at the middle of the caul plate as an additional vacuum access point, thereby reducing the sample void content. The whole assembly was finally covered with two layers of breather and placed inside a vacuum bag. After 1 h of debulking under vacuum pressure, the mold was transferred to an autoclave for curing.

Several different cure cycles were chosen to achieve different final cure states (see Table I). The first cure cycle used was that recommended by the resin manufacturer. The temperature ramp during heating was about 1.7°C/min. Vacuum was applied during the cure. After processing each plate, the adhesive degree of cure was determined using a TA differential scanning calorimeter (DSC; TA Instruments, New Castle, DE) to measure its residual heat of reaction. In these tests, specimens massing 6 to 12 mg, were heated from room temperature to 250°C at 5°C/min in a nitrogen atmosphere. The total heat of reaction of uncured adhesive was also measured to provide a baseline. The final degree of cure for each specimen was determined from

$$\alpha_f = 1 - \frac{H_R}{H_U} \quad (1)$$

where H_U is the total heat of reaction, H_R is the residual heat of reaction, and α_f is the final degree of cure.

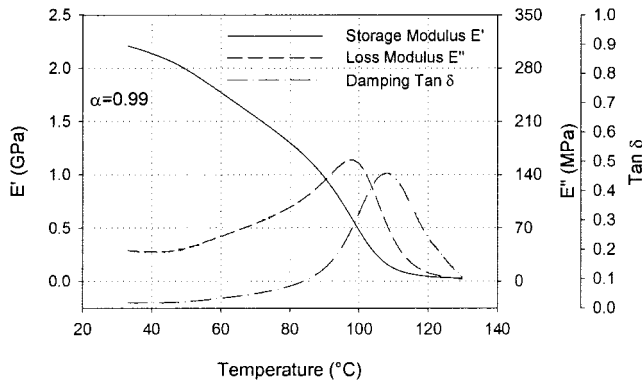


Figure 1 DMA results at a frequency of 1 Hz for degree of cure $\alpha = 0.99$.

Four different resin plates with final degree of cures 0.74, 0.87, 0.95, and 0.99 were obtained (Table I).

Upon curing, the plates were cut into strips about 13 mm wide and 60 mm long using diamond and band saws. Sample surfaces were found to be quite rough and significant thickness variations were observed, and thus sandpaper (320 grit) was then used to obtain uniform thickness and to make surfaces smooth and parallel.

The glass-transition temperature (T_g) was measured for specimens at each degree of cure using a TA Instruments DMA 983. The beam specimens were installed between the parallel arms of a DMA and were mechanically cycled at 1 Hz to obtain the storage and loss moduli as the temperature increased from room temperature to 120°C at the rate of 2°C/min. The T_g was defined as the temperature at the peak of the loss modulus curve (see Fig. 1). The results are presented in Table I. As shown, this resin system has a low glass-transition temperature at low degree of cure (i.e., $T_g = 46^\circ\text{C}$ at $\alpha = 0.74$).

Stress relaxation testing

After their dimensions were measured, the specimens were clamped to the parallel arms of the DMA. The tests were performed in stress relaxation mode at several different temperatures. The length-to-thickness ratio for all the samples was greater than 16 : 1, resulting in a mode of deformation that was almost pure flexure.²² The initial displacement was chosen to be 0.1 mm for partially cured adhesive and 0.2 mm for completely cured adhesive. The strains generated inside the samples were calculated from the sample dimensions, DMA geometrical values, and initial displacements. The maximum strains were about 0.01 and 0.02% for partially and completely cured adhesives, respectively.²² The linear limit for strain is reported to be about 1% for fully cured adhesive in the tempera-

ture range of -55 to 82°C .²³ Therefore, the imposed strains in the samples remained in the linear region.

After clamping, the specimens were equilibrated for 15 min at 30°C . They were then deformed for 30 min and stress relaxation data were recorded. Then the load was removed and specimens were held for another 30 min at the same temperature to recover. The specimen temperature was then increased by 5–15°C (depending on the degree of cure) and the procedure was repeated. Temperature was increased in uniform increments until the specimen was found to fully relax at the end of the test. Figure 2 shows the raw data for the $\alpha = 0.99$ case. For each degree of cure the maximum temperature tested was less than the glass-transition temperature so as to prevent the specimen from curing during the experiment. After test, relaxation modulus was calculated using

$$E(t) = 2(1 + \nu)G(t) \quad (2)$$

Here, ν is Poisson's ratio and $G(t)$ is the sample shear relaxation modulus, obtained in the experiment. Although many investigators studied the variation of the Poisson's ratio during cure and its effect on their models,³ no significant effect was ever reported. Although there might be minor variation of the Poisson's ratio with degree of cure, it was assumed that the Poisson's ratio of FM73 adhesive remained constant at 0.4 during cure.^{21,24}

Figure 3(a) shows the measured relaxation modulus versus logarithmic time for degree of cure $\alpha = 0.99$. Experimental results indicate that at room temperature, the resin modulus for low cure levels is lower than that at higher degree of cure, attributed to the low glass-transition temperature at the low degree of cure. However, it should be mentioned that the glassy modulus (modulus at $T \ll T_g$) can still remain fairly constant during cure.⁶

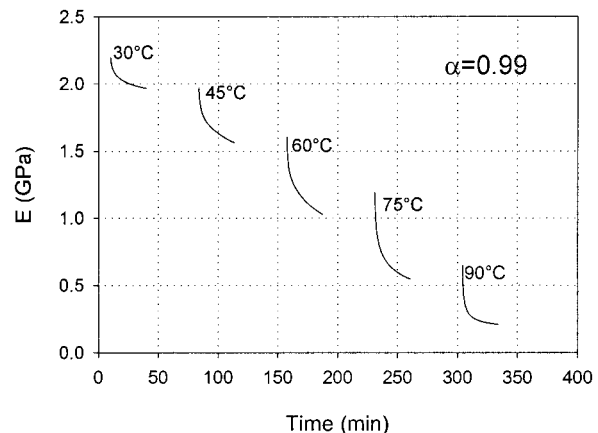


Figure 2 Raw data of a stress relaxation test for $\alpha = 0.99$.

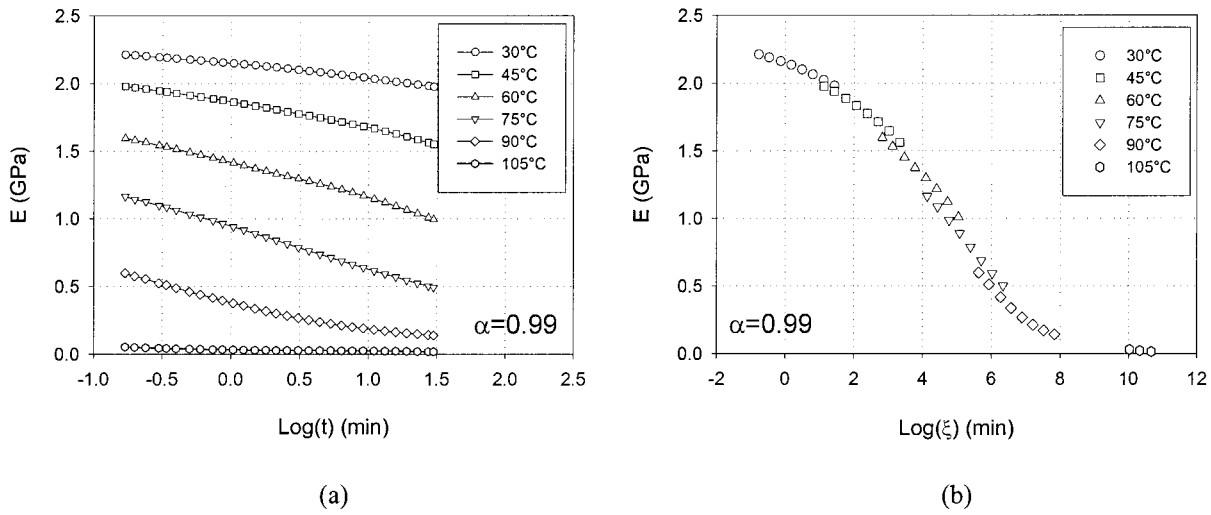


Figure 3 (a) 30-min stress relaxation profiles at various temperatures for degree of cure $\alpha = 0.99$. (b) Relaxation modulus master curves for degree of cure $\alpha = 0.99$.

The reference temperature T_{ref} for all curves was chosen to be 30°C. The data at each temperature were shifted to obtain the master curve by employing time-temperature superposition. This means that the modulus E at the T_{ref} at any time t can be defined relative to the modulus at any other temperature T as

$$E\left(T_{ref}, \frac{t}{a_T}\right) = E(T, t) \quad (3)$$

where a_T is the shift function. A “reduced time” ξ can be defined by noting that all relaxation mechanisms in time increment dt at temperature T are a factor of a_T slower or faster than those in a time increment $d\xi$ at T_{ref} .²⁶ It can be shown that^{9,26}

$$\xi = \int_0^t \frac{1}{a_T} dt \quad (4)$$

If the temperature is constant, a_T is also constant and therefore $\xi = t/a_T$. The power of the concept of reduced time becomes apparent when the stress relaxation has to be determined while the temperature changes. Figure 3(b) shows the master curves for degree of cure $\alpha = 0.99$ after superposition. The shift functions used to obtain the master curves are shown in Figure 4. It is clear from this figure that the cure state has a significant effect on relaxation behavior.

VISCOELASTIC CONSTITUTIVE MODEL

Stress relaxation modulus

A Maxwell model (a spring and dashpot in series) is often used to describe the stress relaxation behavior of

viscoelastic materials.¹² The relaxation modulus (E) for a single Maxwell element is given by¹²

$$E(\xi) = E^u \exp\left(-\frac{\xi}{\tau}\right) \quad (5)$$

where E^u is the unrelaxed modulus (glassy modulus), τ is the stress relaxation time, and ξ is the reduced time. The initial value of the modulus corresponds to the initial “instantaneous” elastic response (E at $t = 0^+$). It can be seen that the relaxation modulus decays over time and approaches a value near zero. Although for some materials (such as thermoplastics) the relaxation modulus decays almost to zero, for other materials (such as highly crosslinked polymers) it decays to a nonzero near-constant value designated as the material rubbery modulus E^∞ .^{4,9} A three-ele-

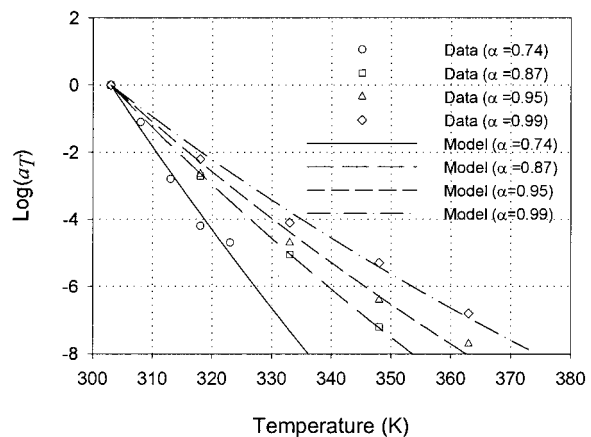


Figure 4 Shift functions used in time-temperature superposition to obtain master curves.

ment standard solid model (a Maxwell element with a spring in parallel) can be used to model a nonzero rubbery modulus. The relaxation modulus is then given as²⁵

$$E(\xi) = E^\infty + E^u \exp\left(-\frac{\xi}{\tau}\right) \quad (6)$$

Although the Maxwell model and the three-element solid model are simple to use, a single relaxation time is typically insufficient to represent a real polymeric material.^{9,12} In reality, different relaxation times are associated with different segments of the polymeric chains. To overcome this difficulty, two different approaches are often proposed. In one, a series of Maxwell elements connected in parallel is proposed as a mechanical analogy to the viscoelastic behavior of materials. Relaxation modulus then can be expressed by a Prony (exponential) series as²⁶

$$E(\xi) = E^\infty + \sum_{\omega=1}^N E_\omega \exp\left(-\frac{\xi}{\tau_\omega}\right) \quad (7)$$

A discrete exponential series is another form of this equation that has been used to model the stress relaxation behavior of epoxy. In this expression, the unrelaxed modulus can be more easily identified. Discrete exponential series can be expressed as⁵

$$E(\xi) = E^\infty + (E^u - E^\infty) \sum_{\omega=1}^N W_\omega \exp\left(-\frac{\xi}{\tau_\omega}\right) \quad (8)$$

where W_ω are weight factors and t_ω are discrete stress relaxation times. Determination of unknown parameters (W_ω and t_ω) is done through the use of curve-fitting techniques. The relaxation times are typically chosen to be evenly spaced in log time over the range of available data, then the weighting factors are used to fit the data. This approach was previously used to model the viscoelastic behavior of 3501-6 epoxy during cure.⁵ Because the master curves at different degree of cures cover different time scales, the weight factors are assumed constant in the whole range of cure and relaxation times are calculated from data at each degree of cure. Although the determination of parameters in the exponential series is difficult, there are some computational techniques that can benefit from the exponential series model.⁵

The simple exponential form for relaxation modulus [eq. (8)] requires a spectrum of relaxation times and hence a substantial number of parameters. To reduce the number of parameters, a simple three-parameter model consisting of a stretched exponential is proposed to describe the relaxation modulus as^{5,26}

TABLE II
Values of Different Parameters in Eq. (10) Obtained by Curve Fitting

Parameter	$\alpha = 0.99$	$\alpha = 0.95$	$\alpha = 0.87$	$\alpha = 0.74$
E^u (GPa)	2.41	2.69	2.63	2.61
b	0.19	0.18	0.19	0.2
τ (min)	1.103E+5	6.478E+3	1.557E+3	6.38

$$E(\xi) = E^u \exp\left[-\left(\frac{\xi}{\tau}\right)^b\right] \quad (9)$$

where b is a material constant, sometimes called the shape parameter. The shape parameter serves the purpose of ensuring a spectrum of relaxation times. This equation provides a good fit to much viscoelastic data and was used here to model the viscoelastic behavior of FM73 adhesive. To include the dependency of relaxation modulus on the degree of cure, eq. (9) can be expanded as

$$E(\xi, \alpha) = E^u(\alpha) \exp\left[-\left(\frac{\xi(\alpha, T)}{\tau(\alpha)}\right)^{b(\alpha)}\right] \quad (10)$$

This equation describes a thermorheologically complex material undergoing cure, given that the relaxation behavior can no longer be obtained by simple horizontal shifting along the time axis.

For each degree of cure, eq. (10) was fitted to the measured stress relaxation modulus versus reduced time using a least-squares technique and the Levenberg-Marquardt algorithm. The numerical values for different parameters are shown in Table II and model predictions are compared to experimental results in Figure 5. The fits shown are all made at a single degree of cure. To develop a single expression [eq. (10)] valid for all cure states, a correlation must be found between the different parameters (stress relaxation time τ , shift function a_T , unrelaxed modulus E^u , and exponent b) and the cure extent.

Stress relaxation time

To develop this correlation, let us first assume that the developments of T_g and stress relaxation time during cure are influenced by the same mechanisms.⁵ In this case, the normalized T_g can be used to describe the normalized stress relaxation time. To exploit this, a relationship between glass-transition temperature and extent of cure is required. In this work, resin T_g at a range of cure states was determined from the peak of the loss modulus measured by DMA. The results are shown in Table I.

For many thermosetting systems, the relationship between T_g and α can be described by the empirical DiBenedetto equation as⁸

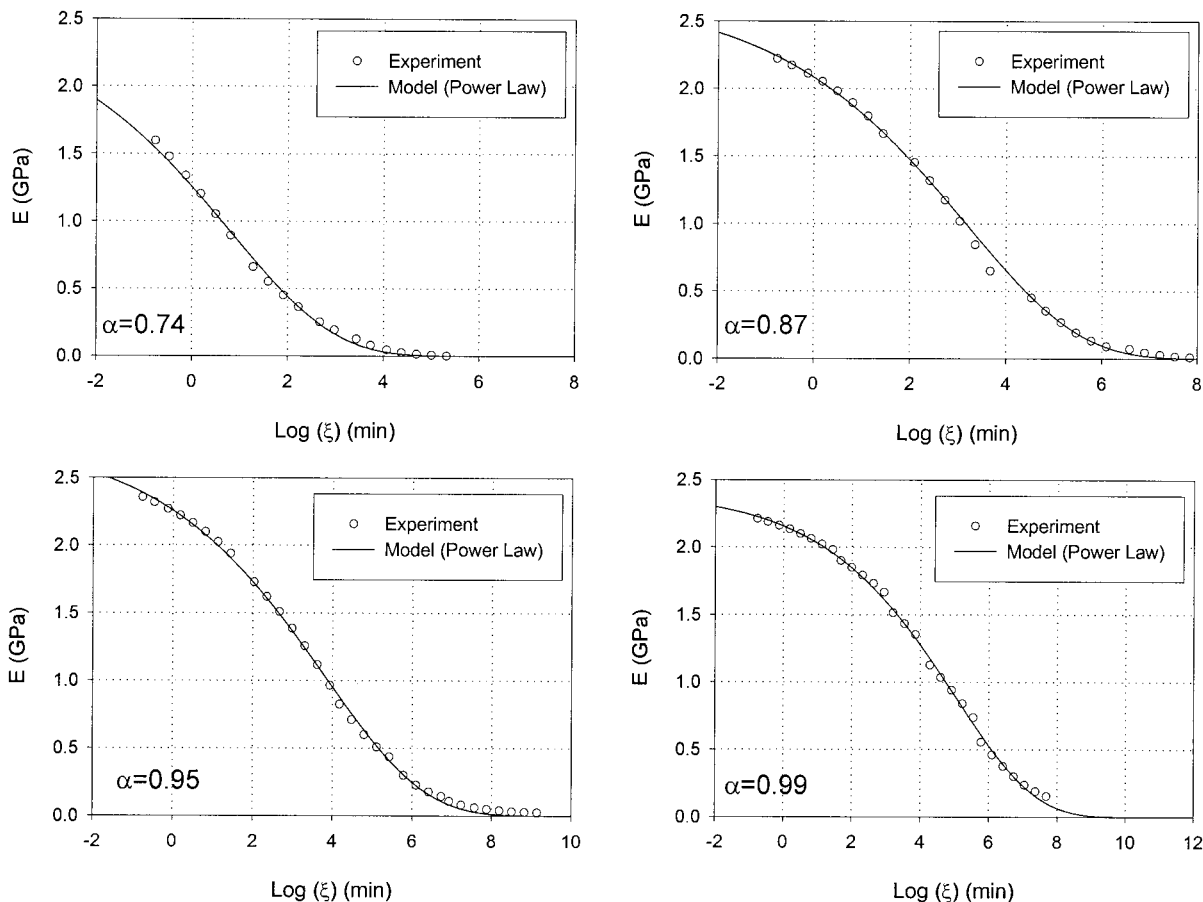


Figure 5 Relaxation modulus master curve model prediction obtained by curve fitting using eq. (10) and data.

$$\frac{T_g(\alpha) - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \tag{11}$$

where T_{g0} is the glass-transition temperature of the uncured resin, $T_{g\infty}$ is the glass-transition temperature of the fully cured material, and λ is a material constant. Equation (11) was fitted to the experimental data, with best fit provided by

$$\begin{aligned} T_{g0} &= 7.8^\circ\text{C} \\ T_{g\infty} &= 97.3^\circ\text{C} \\ \lambda &= 0.265 \end{aligned} \tag{12}$$

As shown in Figure 6(a), this relation shows a good fit to experimental T_g measurements.

The next step is to find an expression for the stress relaxation time. Kim and White⁵ used a second-order polynomial to show the relationship between the relaxation time and degree of cure. In this work, based on the DiBenedetto equation the following expression is proposed to describe the stress relaxation time:

$$\frac{\log[\tau(\alpha)] - \log(\tau_0)}{\log(\tau_\infty) - \log(\tau_0)} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \tag{13}$$

where τ_0 and τ_∞ are the relaxation times for uncured and fully cured resin, respectively. The parameter λ has already been calculated above, leaving $\log(\tau_0)$ and $\log(\tau_\infty)$ as the remaining unknowns. Given that no information was available regarding the stress relaxation time of uncured and fully cured resin, curve fitting was used to find the unknown parameters as

$$\begin{aligned} \log(\tau_0) &= -2.13 \\ \log(\tau_\infty) &= 5.32 \end{aligned} \tag{14}$$

Equation (13) can be used to describe the variation of stress relaxation time with degree of cure. The calculated stress relaxation times are shown in Figure 6(b) together with the experimental results. Although the model prediction at low degree of cure may not be accurate, a good correlation was obtained over the experimental range of degree of cure. It should be mentioned that because residual stresses develop primarily after the epoxy has gelled ($\alpha \cong 0.5$), inaccuracies in predictions before this point are not expected to result in substantial errors in prediction of processing-induced residual stress.

The good fit shown in Figure 6(b) supports the assumption that the same effective mechanisms that

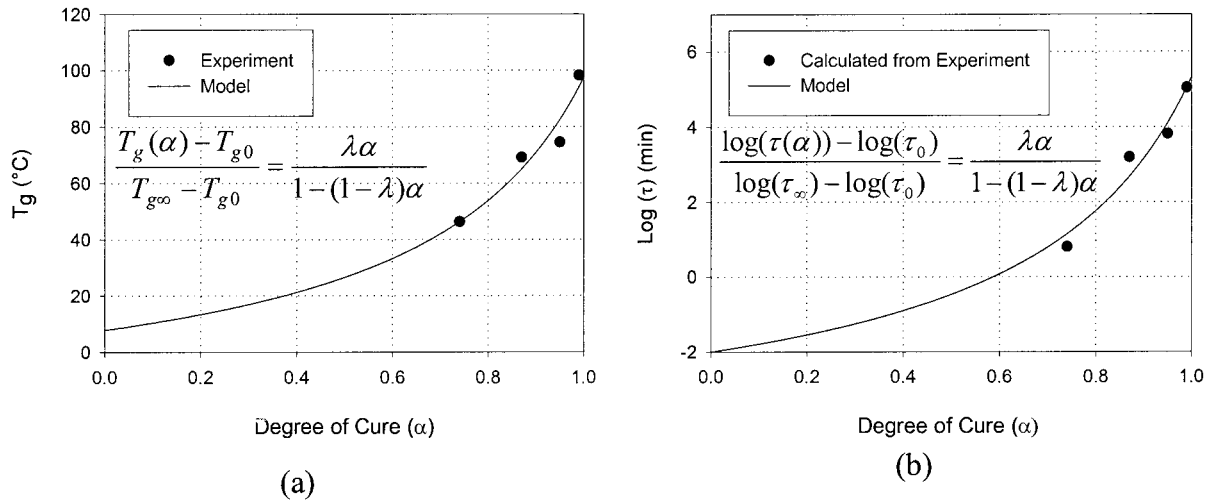


Figure 6 (a) Variation of glass-transition temperature with degree of cure. (b) Variation of stress relaxation time with degree of cure.

govern the development of T_g also describe the change in stress relaxation time during curing. The power of this technique becomes more evident if one wants to obtain the relaxation time for a new resin system. In this case, the development of glass-transition temperature with increasing degree of cure can be obtained from DMA measurements and using curve-fitting (DiBenedetto equation) techniques. The stress relaxation time for fully cured and uncured resins can then be calculated by experiment, time-temperature superposition, and curve fitting. The development of relaxation time during cure can then be predicted by eq. (13).

Shift function and reduced time

To use eq. (10) to model the development of relaxation modulus during cure, the shift function and its dependency on the degree of cure must be described as well. The temperature shift factor is expected to follow a generalized Vogel equation⁸:

$$\log(a_T) = \frac{C}{T - T_\infty} - \frac{C}{T_{ref} - T_\infty} \quad (15)$$

where C is a constant, T_{ref} is the reference temperature, and T_∞ is a constant temperature. The Vogel

equation is capable of describing both WLF behavior ($T_\infty = T_g - C_2$) and Arrhenius behavior ($T_\infty = 0$ K). Above T_g , the WLF equation is usually used for the temperature shift factor, whereas below T_g the Arrhenius equation should be used.²⁶ Assuming Arrhenius behavior for the shift factor and considering shift factor cure dependency, eq. (15) can be rewritten as

$$\log(a_T) = C_1(\alpha) + \frac{C_2(\alpha)}{T} \quad (16)$$

Because the value of the shift factor at the reference temperature should be unity, from eq. (16) it can be concluded that

$$C_2(\alpha) = -T_{ref}C_1(\alpha) \quad (17)$$

A curve fit to the experimental data using eq. (16) gives the values of $C_1(\alpha)$ and $C_2(\alpha)$ for different de-

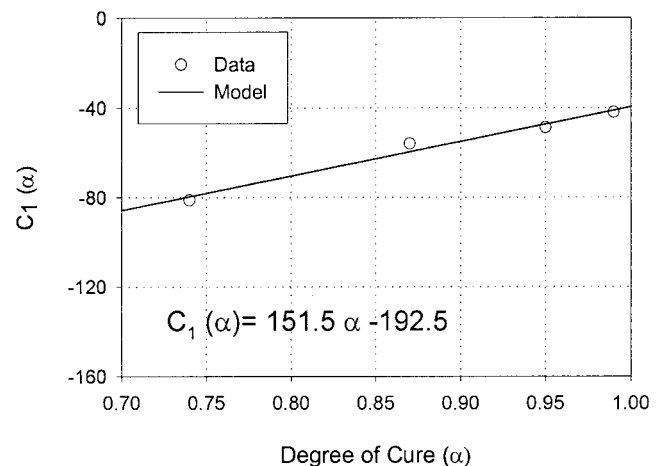


Figure 7 Variation of coefficient $C_1(\alpha)$ with degree of cure.

TABLE III
Values of $C_1(\alpha)$ and $C_2(\alpha)$ Obtained by Curve Fitting

α	$C_1(\alpha)$	$C_2(\alpha)$
0.74	-81.22	2.460×10^4
0.87	-55.94	1.695×10^4
0.95	-48.70	1.475×10^4
0.99	-41.97	1.272×10^4

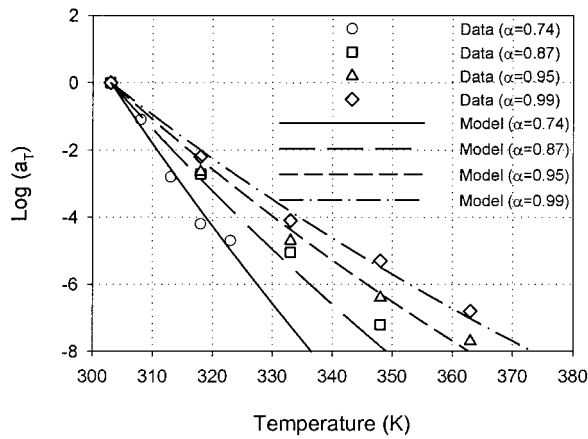


Figure 8 Shift functions predicted using eq. (16) compared with experimental data.

degrees of cure (see Table III). The next step is to find a correlation between C_1 and degree of cure. As a first approximation, C_1 is assumed to be linearly dependent on degree of cure:

$$C_1(\alpha) = a_1\alpha + a_2 \tag{18}$$

A least-squares fit of the data yields the constants $a_1 = 151.5$ and $a_2 = -192.5$. Figure 7 shows model predictions for $C_1(\alpha)$ together with the numerical data. $C_2(\alpha)$ is calculated from eq. (17) using the reference temperature $T_{ref} = 303$ K. Good agreement between this model and data was observed. The shift function model from eqs. (16), (17), and (18) is shown together with measured data in Figure 8.

Fully relaxed modulus and exponent b

As shown in Table II, E^u is relatively constant over the experimental range of degrees of cure range. The assumption of cure-independent initial modulus was previously proposed for polymers in the glassy state.⁶ Therefore, E^u is assumed to be constant, independent of degree of cure. The mean value is obtained from the results as

$$E^u = 2.59 \text{ GPa} \tag{19}$$

Exponent b is considered to be constant, with its value taken as the average of its calculated values at different degrees of cure (Table II), giving $b = 0.19$. Using constant values for E^u and b , eq. (10) can be reduced to a simpler form:

$$E(\xi, \alpha) = E^u \exp \left[- \left(\frac{\xi(\alpha, T)}{\tau(\alpha)} \right)^b \right] \tag{20}$$

Now the stress relaxation behavior at any degree of cure can be modeled using eqs. (4), (13), and (16)–(20). The model predictions and experimental data are shown in Figure 9. Overall, the correlation to the experimental data is quite good. The average initial unrelaxed modulus value is higher than that calculated for $\alpha = 0.99$, which causes the model to slightly overpredict the stress relaxation modulus at short time. With increasing time (reduced time), the model prediction starts to align more closely with the experimental data.

To verify model predictions, an additional resin plate was made and tested using the same process as described previously. For this plate, 12 layers of

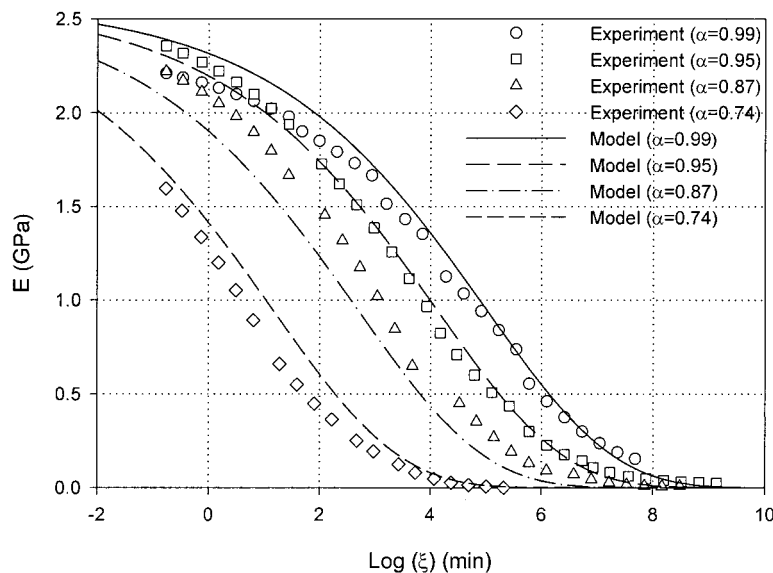


Figure 9 Relaxation modulus master curve model prediction.

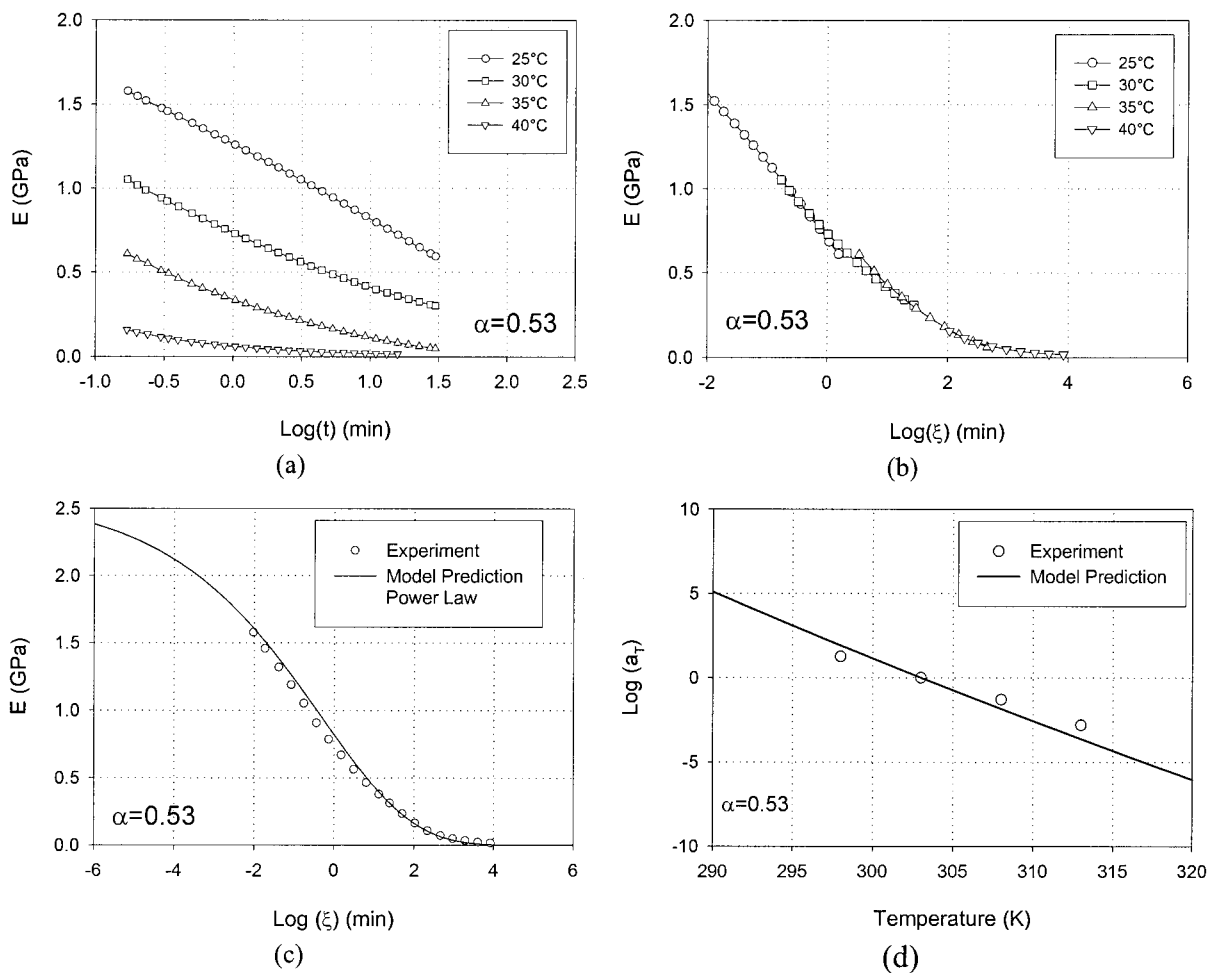


Figure 10 (a) 30-min stress relaxation profiles at different temperatures for $\alpha = 0.53$. (b) Master curve. (c) Modulus prediction compared with the experiment. (d) Shift factor prediction compared with the data.

FM73 adhesive were cured for 70 min at 80°C resulting in a final degree of cure of 0.53. Because of the low resin degree of cure, cutting specimens and placing them into the DMA apparatus had to be done especially carefully to prevent specimen damage. The measured stress relaxation modulus is shown in Figure 10(a). The time–temperature superposition was applied to obtain the master curve as shown in Figure 10(b). It should be emphasized that the curves that are related to temperatures lower than the reference temperature should be shifted to the left and those that are related to the higher temperatures should be moved to the right. As shown in Figure 10(c), very good agreement was found between model predictions and the experimental measurements for this degree of cure. Good agreement was also found between predicted and observed shift factor, as shown in Figure 10(d).

CONCLUSIONS

The development of stress relaxation behavior of FM73M adhesive during cure was presented. A num-

ber of plates were made using different cure cycles to obtain specimens with different degrees of cure. The glass-transition temperature at each degree of cure was measured using dynamic mechanical analysis (DMA) at a frequency of 1 Hz. Stress relaxation tests at different temperatures were performed using DMA in stress relaxation mode. For each degree of cure the maximum temperature was kept less than the glass-transition temperature to prevent curing during test. Time–temperature superposition was used to obtain master curves and shift functions at each degree of cure. It was observed that the adhesive stress relaxation behavior is greatly influenced by its cure state.

Different constitutive models were examined for their ability to describe adhesive relaxation modulus development during cure. A single relaxation time in a Maxwell model is typically insufficient to represent a real polymeric material. The Prony (exponential) series covers a spectrum of relaxation times but requires a substantial number of parameters to describe material behavior. A simple three-parameter model consisting of a stretched exponential with cure-dependent terms was ultimately selected. This equation was

fitted to experimental measurements using a least-squares technique and the Levenberg–Marquardt algorithm. The results indicate that among the parameters the relaxation time strongly depends on the cure state. The other model parameters could be considered to be constant, independent of adhesive degree of cure.

To establish a correlation between relaxation time and degree of cure, it was assumed that the evolutions of glass-transition temperature and stress relaxation time are influenced by the same mechanisms during cure. The empirical DiBenedetto equation was used to obtain an expression for glass-transition temperature as a function of degree of cure. Based on the DiBenedetto equation, a new expression was proposed to describe the stress relaxation time as a function of degree of cure. Time-shift functions were modeled using a simplified form of the Vogel equation with cure-dependent coefficients. Good correlation between experimental relaxation modulus measurements and model prediction was observed.

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