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Evolution of viscoelastic behavior of a curing LY5052 epoxy resin in the glassy state

Sibin Saseendran*, Maciej Wysocki and Janis Varna

Abstract The aim of this work is to develop a methodology to analyze the influence of the curing history on the viscoelastic storage modulus. Two different experimental approaches are presented exposing the material to various cure temperature and cure time sequences. The evolving viscoelastic properties are characterized using standard Dynamic Mechanical and Thermal Analysis (DMTA) equipment. Therefore, the present study is limited to infinitesimally small strains and linear viscoelasticity only. The methodology is demonstrated using the LY5052 epoxy resin system for its storage modulus $E'$ in the frequency domain. Results indicate that evolution of thermo-viscoelastic properties could be indeed assumed independent of the cure history for the investigated LY5052. We observe that the shift factor in the reduced time expression for the viscoelastic model examined in this paper is a product of two shift functions, namely the temperature and cure shift functions.

Keywords Thermosetting resin, curing, mechanical properties, thermal analysis


Introduction

Traditionally, composites have been developed using trial and error methods resulting in an expensive development process. This is in particular true for the development of manufacturing processes, where many experimental loops are necessary before an efficient manufacturing process is established. Therefore, the present trend in composites design is towards virtual methods, in particular within the aerospace and transportation industry, which pushes the boundaries of virtual computer-aided engineering (CAE) towards new modeling areas. However, to enable the aforementioned trend it is necessary to increase the understanding of the physics of phenomena. New modeling methodologies and tools are necessary to reduce developmental costs incurred by developing new components. One such area considered here is the prediction of manufacturing induced residual stresses and their evolution with time, where the definition of a simplified viscoelastic model for simulation may lead to improved results.

The development of residual stress in composites is caused by different factors. Thermally induced residual stresses in composite materials are caused by the mismatch between coefficients of thermal expansion (CTE) of the matrix and the reinforcements. The magnitude of these residual stresses depends on the difference of CTE between the matrix and the reinforcements multiplied by the temperature change $\Delta T$ and other elastic or viscoelastic factors. Because of the fact that the CTE for the polymer is higher than the CTE for the fibers, the generated thermal residual stresses are tensile in the matrix and compressive in the fibers. Another source of residual stress is the result of chemical shrinkage and reduction of free volume of the matrix during curing. This happens when the polymer molecules undergo end linking reactions at elevated temperatures during curing sometimes in the presence of hardening agents or accelerators to form long and interconnected chains in three dimensions. This pulls together the molecules inward tightly and the polymer matrix goes from a liquid into a solid. As a consequence of this process, the free volume of the matrix is reduced and this inevitably adds pressure on the fibers in the form of internal stress distributed across the entire volume of the part. While thermally and chemically induced stresses contribute to the bulk of the residual stresses in the composite, studies also indicate...
tool-part interaction, moisture absorption, and aging of the matrix as contributing factors after curing.

The fundamental challenge in the modeling of residual stresses is the lack of experimental methods to develop fundamental understanding of the physics in the manufacturing process in order to design and develop appropriate constitutive models. Presently the common material behavior used in the determination of residual stresses is the Cure Hardening Instantaneous Linear Elastic (CHILE) model. Though the model is good in the terms that it is simple to characterize and implement, it is not clear how valid this assumption of linear elastic behavior is in detail. This is of concern, especially when one considers that a majority of the composites do not behave in a linear elastic manner. There exists research where viscoelastic behavior is assumed. The question that arises is as to whether the material properties during curing are linearly or nonlinearly viscoelastic.

In order to develop materials with the correct processing behavior, it is not just sufficient to take into account the viscosity of the polymer. Elasticity and time dependence of a polymer are equally important to control the processability of a polymer. A method to look at the complete rheological response of a material quickly is the dynamic mechanical and thermal analysis (DMTA) of polymers. One such technique is to study the relaxation behavior of the polymer using a DMTA instrument to obtain relaxation data at high frequencies. This extends the range of the instrument and provides insight to the material behavior at extended time scales. Thereby DMTA measurements provide a kind of fingerprint of the material and allow calculating elasticity and the material’s time dependence at processing temperatures. This is particularly useful in the composites industry to try and understand the complex thermomechanical phenomena that occur during manufacturing of composite parts and the impact these phenomena have on the part being manufactured when subject to various constraints.

Experimental studies have been performed in order to characterize the development of viscoelastic properties during curing. Using rheometer Eom et al. characterized the viscoelasticity development during curing process for tetra glycidyl-4,4′-diaminodiphenyl methane epoxy with an anthranilic acid amide hardener using various curing temperatures. The obtained values relate to the shear storage modulus development over the curing process. In their work, Eom et al. have been able to determine that the time-temperature shift factor has a linear dependence on cure temperature. It was, however, not established whether the tested material is independent on its curing history. O’Brien et al. have performed experiments with neat epoxy resins (difunctional epoxide with a diethyltoluene diamine hardener) using a single cure temperature and have found that the degree of cure has no effect on the elastic response of the material. O’Brien et al. have only focused on one cure temperature to assess the viscoelastic response of the epoxy system which is inconclusive while determining the role of cure temperature in viscoelastic response development. O’Brien et al. also noted that the peak equilibrium relaxation modulus varies significantly between the fully cured and uncured states and hence hinting at a possible interdependence of the equilibrium modulus and degree of cure. Further, in the work by Thorpe and Poursartip, an attempt to develop a model for a carbon fiber-reinforced MTM 95-1 epoxy system was performed. Characterization was performed in the solid composite in a DMTA and the liquid neat resin in a rheometer. The findings have concluded that a thermo-rheologically simple time-temperature superposition is insufficient to characterize viscoelastic behavior. The study also concluded that the glassy state storage modulus is independent of the degree of cure, a behavior which is also confirmed by Sadeghinia et al. in the shear modulus domain, working with Novolac EPN1180 epoxy and bisphenol-A hardener. Furthermore, it is thought that using a carbon fiber-reinforced resin system as opposed to a neat resin sample may affect results regarding the storage modulus from the tests that have been performed in the solid state. To isolate the storage modulus of the resin from the storage modulus of the composite, this work has used a general rule of mixtures where the values of transverse modulus at 20GPa and fiber volume fraction at 0.589 for the composite have been assumed. Suzuki et al. reported that the form of a master curve generated through time-temperature superposition principles is dependent on the cure temperature and time and both these parameters are to be considered separately. However, in their work, Suzuki et al. have not made an attempt to study cure kinetics of the diglycidyl ether of bisphenol-A (DGEBA) and methyl anhydride hardener system and subsequent comparisons with the cure state of the resin. In the work by Simon et al., a model for the calculation of the evolution of shear storage modulus that takes inputs of cure kinetics from a conventional model has been formulated for a Hexion 8551-7 epoxy system. This model incorporates time-temperature superposition and time-cure state superposition in thermosets. The model has been only tested at a single frequency of 1 Hz in a rheometer, to which the model agreed well with experimental data and it is unclear if the same is applicable to higher or lower frequencies. An attempt to model a cure dependent evolution of the storage modulus on a tetrafunctional epoxy with an amine hardener system based on a modified form of the Kohlrausch–Williams–Watts (KWW) equations has been performed in the work by Zarrelli et al. Yeong et al. have ascertained that since most of the residual stresses develop at post-gelation it is appropriate to look for ways to model stress relaxation at such post-gelation conditions. Their effort focused primarily on the stress relaxation behavior of DGEBA samples cured with multifunctional amine hardener to a particular degree of cure using several different temperatures. The fundamental assumption in is that the relaxation modulus depends on the cure state on an a priori basis, while a real-time assessment on the cure state is necessary for viscoelastic evolution of the modulus. Adolf and Martin have done preliminary assessment of the influence of cure on viscoelastic properties by developing a time-cure superposition method. This method uses horizontal and vertical shifting of DMTA data in the time domain, to arrive at master curves. The vertical shift accounts for the change in the equilibrium relaxation modulus with
changing degree of cure which has never been accounted for in other similar works. They worked in the shear modulus domain and have not conducted an in-depth analysis of the curing behavior of the material under test. They have ascertained that viscoelastic functions at differing degrees of cure should superpose if the appropriate vertical and horizontal shifts are applied to the DMTA data.

This work is a part of a larger research project towards improved understanding and development of models for curing, residual stress and shape distortion. The present contribution is towards method development for characterization of the thermo-viscoelastic properties in the glassy state. The aim is to investigate the dependence of the viscoelastic response on curing time, curing temperature and degree of cure and thus support development of a model that includes the dependency of the relaxation modulus on all three factors. In this work, we focus specifically on the tensile storage modulus (\(E\)) using two different approaches. In the first approach, master curve for a given cure and test temperature, which are identical, is obtained by shifting the curves corresponding to different cure times. Then the master curves for different temperatures are reduced to a “super-master curve 1” for a certain reference temperature. In the second approach, first the master curve for certain degrees of cure is obtained by performing frequency scans at various temperatures and then a “super-master curve 2” is obtained for a certain reference curing time and curing temperature. Assuming that the shift factor can be expressed as a product of two shifts, both approaches should lead to the same result – coinciding “super-master” curves 1 and 2. The methodology is demonstrated and the used assumption validated using the LY5052 epoxy resin system.

Characterization methodology

Material

The resin system used for the characterization of the thermo-viscoelasticity consisted of Araldite LY5052 epoxy resin with Aradur HY5052 hardener from Huntsman. LY5052 is a low viscosity resin with a long pot life and a maximum attainable glass transition temperature of 130 °C after post-cure. According to the manufacturer, LY5052 is a blend of butanedioldiglycidyl ether and epoxy phenol novolac resin and HY5052 is a mixture of cycloaliphatic polyamine, isophorone diamine, 2,4,6-tris(dimethylaminomethyl) phenol, and salicylic acid. Prior any experimental procedure, the resin and hardener were mixed in the ratio 100:38 by weight and stirred thoroughly, taking care not to include air bubbles.

Viscoelastic characterization

The thermo-viscoelastic characterization of the resin system was performed using a TA Instruments Q800 DMA instrument with available three-point bending and single cantilever modes. Prior to the actual material characterization, both loading modes were evaluated for their characteristics. For both loading modes, the procedure consisted of a frequency scan at various temperatures to obtain a master curve using fully cured neat resin samples of LY5052/HY5052. The scan was performed at a frequency range of 200, 100, 10, 1, 0.1, and 0.01 Hz and a temperature range of 23 to 200 °C in 10 °C increments. It was observed that the three-point bending mode induces scatter in the results at higher temperatures. Therefore, all the subsequent experiments were performed using the single cantilever mode for all samples including partially cured specimens.

The experiments performed using the single cantilever mode required using samples that are not fully cured. Consequently, a method of manufacturing samples was designed such that the samples could be manufactured quickly and easily without an intermediate stage of making plates and cutting them down to size, which would be difficult considering that the samples are not fully cured. Molds were made from a silicone rubber with dimensions of the tool leading to samples of dimensions of 17.5 × 2.8 × 3 mm as specified by TA Instruments for a single cantilever mode specimen. The mold was then sandwiched between two plates of Teflon-coated steel. The assembly was then clamped securely to prevent leakage once the mixed resin was poured into the mold. The mold assembly was then preheated in a convection oven to the required temperature before the resin was poured into it. Once the resin was poured into the mold, it was left to cure for various predetermined times and temperatures to attain a certain degree of cure predicted by cure kinetics. The details of the cure characterization and the cure kinetic models used for this purpose have been explained in detail in Ref. 15. After that, the mold was removed from the oven and the samples were cooled instantly using a coolant spray (to prevent additional curing) and ‘peeled’ out from the mold. Three samples were produced at a time with identical degrees of cure with this method. Sides of the samples were then polished using a Struers Rotopol-1 polishing machine making them ready for DMA testing. The samples were assessed visually to determine if they are deformed or damaged while being mounted onto the DMTA, especially for samples that had low degrees of cure since they were most often in the transition or rubbery zones.

Samples were cured at a constant temperature, viz. 23, 40, 60, and 80 °C for certain times in order to induce a predetermined degree of cure. The curing temperatures have been chosen in such a way that they were rather in equally spaced intervals and also so that the reaction rate was slow enough to be controllable to ensure limited post curing happens during testing at elevated temperatures. Table 1 shows the curing times used for each of the four temperatures. In the DMTA, characterization of the storage modulus using single cantilever mode, a frequency scan range 200, 100, 10, 1, 0.1, and 0.05 Hz was used.

Material model describing the viscoelastic behavior of the partially cured resin has to account for the mechanical testing temperature (\(T\)), the curing temperature (\(T_c\)), and the curing time (\(t_c\)). In the simplified viscoelastic material model which we examine in this paper, we assume that only the reduced time depends on the curing parameters. The stress (\(\sigma\))–strain (\(\varepsilon\)) relationship is hence described by

\[
\sigma = G_0 \dot{\varepsilon} + \int_0^{t_c} C(\psi - \psi^0) \frac{d\varepsilon}{dt} \, dt, \tag{1}
\]

where \(G_0\) is an integrating function, \(\Delta C\) is an independent relaxation function and they do not depend on mechanical testing temperature and curing parameters. \(\psi\) is the reduced time that depends on the curing parameters and is given by

\[
\psi = \frac{t_c}{t_c^*},
\]

where \(t_c^*\) is the reference curing time.
In this paper, the two-step shifting procedure described is used to identify functions $\log a_i(T)$ and $a_i(T, t_i)$. The DMTA experiments and data reduction were split into two different approaches reflecting the two possible sequences of shifting described above.

**Approach 1**: Samples cured at a particular temperature were also tested at the same temperature, i.e. $T = T_c$. In the frequency domain, we obtain several storage modulus curves corresponding to different curing times. We shift them to obtain master curve finding shift factor which reflects the curing time effect for a given temperature. Then we change the temperature repeating all testing and data reduction. Finally, the master curves for different temperatures are shifted creating the “super-master curve” to obtain the temperature dependence of the shift factor.

**Approach 2**: curing was at 60 and 80 °C with curing times given in Table 1. The frequency scan for storage modulus was performed at 23, 40, 60 and 80 °C. The first step in data reduction is temperature shifting of data corresponding to certain cure state. Master curves for different cure states are obtained and temperature shift factors identified. Then horizontal shift to these master curves is applied to obtain the shift factor reflecting the effect of the cure state.

Regarding the factor $a_i(T, t_i)$ (see Section Results and analysis), we found that using the cure time as a parameter instead of degree of cure $\alpha$ results in simple linear shift function with coefficients dependent on cure temperature $T_c$.

Traditionally, for polymers the factor $a_i(T)$ is shown to be approximately related by the Williams–Landel–Ferry (WLF) equation, given by

$$\log a_i(T) = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}}$$


where $c_1$ and $c_2$ are temperature dependent constants and $T_{ref}$ is the reference temperature. Care was taken to ensure that the degree of cure was not changing during the experiments. This was achieved using a different sample for each temperature. Since each of the DMA tests last approximately 10 min, the difference in degrees of cure from start to finish was negligible as confirmed by the DSC characterization. The applied strain on the sample in all DMTA tests was in the order of 0.01%.

### Results and analysis

#### Approach 1
Fixing the cure and test temperature, $T = T_c$, the storage modulus vs. frequency curve was obtained for several values of the curing time. As an example DMTA curves for samples tested and cured at 40 °C at various cure states are shown in Fig. 2. These curves were then shifted horizontally to create a master curve corresponding to an arbitrary selected reference curing time as shown in Fig. 3. This procedure was repeated for all four values of $T = T_c$. The master curves thus obtained along with the values of the logarithmic shifts used to construct the master curves are shown in Figs. 4(a)–(d). The shifting procedure was performed such that the master curves are deemed continuous. As observed in Fig. 4, for each cure temperature, the shift factor is a rather linear function of the cure time.

---

**Table 1** Curing temperature and times

<table>
<thead>
<tr>
<th>Temperatures (°C)</th>
<th>Curing times (hours)</th>
<th>Total number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>14.75; 17; 18; 19;</td>
<td>6</td>
</tr>
<tr>
<td>40</td>
<td>21; 24</td>
<td>9</td>
</tr>
<tr>
<td>60</td>
<td>3.5; 4; 4.5; 5; 5.5; 6; 6.5; 7; 7.5</td>
<td>28</td>
</tr>
<tr>
<td>80</td>
<td>1.25; 1.5; 1.75; 2; 2.25; 2.5; 3; 0.5; 0.75; 1; 1.25</td>
<td>16</td>
</tr>
</tbody>
</table>
The curing time-related shift factors can be easily recalculated to the degree of cure using $T_c$ and the cure kinetics model. In this work, we have chosen to use a well-established cure kinetic model by Kamal which describes the reaction rate as an analytical function of temperature and degree of cure as detailed in Equation 5,\textsuperscript{15}

$$\frac{d\alpha}{dt}(T, \alpha) = Ae^{-\frac{B}{R}T} (\alpha^m - \alpha)^n,$$

(5)

where $\alpha$ is the degree of cure, $A$ is the pre-exponential rate constant, $T$ is the temperature in Kelvins, $B$ is the reaction energy, $R$ is the ideal gas constant, $m$ and $n$ are constants independent of cure temperature that are obtained from fitting experimental data from the DSC using standard least-squares fit. Moreover, the $\alpha$ is defined as

$$\alpha = 1 - \frac{H}{H_{\text{tot}}},$$

(6)

where $H$ is the residual heat of reaction and $H_{\text{tot}}$ is the total heat of reaction which has been determined as 482 J/g for the given resin system.\textsuperscript{15} $\alpha_{\text{max}}$ is defined as the maximum degree of cure attained at various curing temperatures. The values for $\alpha_{\text{max}}$ are obtained for each cure temperature ($T_c$) from the isothermal DSC experiments performed in\textsuperscript{15} and fitted to obtain the relationship $\alpha_{\text{max}} = 0.002T_c + 78.2$.

However, the slopes of the linear shift factor curves in Fig. 4 are slightly different; it depends on $T_c$. It was determined that the slopes of the cure shift factors do not vary with cure time for a given temperature. A second-order dependence of the slope on curing temperature was observed. Based on this, we have arrived at

Figure 2  DMTA curves for 40 °C cured samples with various cure states tested at the same temperature

Figure 3  Master curve produced by horizontally shifting data in Figure 2 using an arbitrary reference cure state

Figure 4  Master curves by shifting in the curing time for a 25 °C (referenced at 19 h or 73.71%), b 40 °C (referenced at 5 h or 80.74%), c 60 °C (referenced at 1.75 h or 87.68%) and d 80 °C (referenced at 0.75 h or 93.51%) in the frequency domain (f)

Note: The shift factors used for the superposition are also shown
here \( T_c \) is the curing temperature, \( t_c \) is the time of cure, and \( t_{cref} \) is the time of cure at which a reference cure state is attained. A reference state of 80% cure was then arbitrary selected master curves in Fig. 4 recalculated to this cure state, as shown in Fig. 5. The time of cure corresponding to \( \alpha = 80\% \) for each temperature \( T_c \) is again determined from the cure kinetics model and detailed in Table 2.

The individual master curves, each corresponding to specific test temperature are now shifted again horizontally this time to account for different test temperatures. Using 23 °C (room temperature) as a reference state, the result of shifting and the shift factors for different temperatures are shown in Fig. 6. The shift factors used for the temperature shift in Fig. 6(b) are rather linear with respect to the testing temperature. It is also observed that these temperature shift factors are nearly equivalent to the WLF values for the corresponding data as described in Equation 4. The constants \( c_1 \) and \( c_2 \) in Equation 4 for the epoxy system LY5052/HY5052 are 77.59 and 433.6 K, respectively. The constants have been determined by performing frequency scans at various temperatures on a fully cured sample and then using TTS principles to obtain a master curve.

### Approach 2

The second approach is to generate master curves and to identify shift factors for samples that have been cured to a certain degree of cure at a particular temperature and then frequency scanned at various temperatures. The cure temperatures were 60 and 80 °C. For each degree of cure (\( T_c \) and \( t_c \)) the generated storage modulus curves for different test temperatures \( T \) were shifted to construct the individual master curve. It was done for each sample cured at 60 °C or at 80 °C with a specific curing time. As an example, response curves for samples cured at 60 °C for 1.5 h are shown in Fig. 7. Horizontal shifting of the data in Fig. 7 using 23 °C as a reference generates a master curve as shown in Fig. 8. All the temperature-shifted master curves so obtained are shown in Fig. 9 for 60 and 80 °C curing temperatures. In both instances, the curve representing 23 °C testing temperature was chosen as the reference curve for the construction of the master curve. Also to be noted is that, for higher testing temperatures (at 80 °C for instance) since the testing time is less than 9 min in the DMTA, no significant post curing has occurred to the samples as a result, which has been confirmed by subsequent DSC investigations.

**Table 2** Time required to attain 80% degree of cure for each temperature based on the cure kinetic model

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time to attain 80% ( \alpha ) (in minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 °C</td>
<td>1221</td>
</tr>
<tr>
<td>40 °C</td>
<td>288</td>
</tr>
<tr>
<td>60 °C</td>
<td>68</td>
</tr>
<tr>
<td>80 °C</td>
<td>19.5</td>
</tr>
</tbody>
</table>

**Figure 5** Master curves for each cure temperature with 80% degree of cure as reference state

**Figure 6** (a) Super-master curve at test temperature 23 °C (room temperature) and (b) corresponding second shift factors and the independent WLF fit

\[
\log \alpha_c(T, t_c) = C(t_c - t_{cref}), \tag{7}
\]

where

\[
C = 0.0026T_c^2 - 0.0903T_c + 1.39, \tag{8}
\]

**Figure 7** Frequency scans on samples cured at 60 °C for 1.5 hours (\( \alpha = 85.74\% \)) using various testing temperatures
of the tested samples. Additional post curing was within only 1% and hence no correction has been applied to the curves to counteract this since the change in mechanical properties would be insignificant.

The temperature shift factors obtained constructing each master curve are shown in Fig. 10 separately for curing at 60 °C and at 80 °C along with the WLF shift factors for the corresponding temperatures. The WLF shift factors are independently determined using the constants, as described in the previous section.

It can be observed that for both cases, the temperature shift factors do not change significantly dependent on curing time and the general behavior can be identified to be linear with respect to testing temperature. Hence, irrespective of cure temperature ($T_c$), the shift factors can be assumed
behavior of the system is independent of its cure history. The fact that the test temperature-related shift factors shown in Figs. 6(b) and 10 corresponding to the two approaches are identical, supports the argument that different curing histories still result in similar viscoelastic responses in the glassy state. Further, noting the limitation of the DMTA, we see some evidence that the studied material is thermo-rheologically simple and that the shift factor in the viscoelastic reduced time expression can be written as product of two shift functions: one related to test temperature effect (the common time-temperature relationship) and one related to the cure state. The product type form of the shift function results in linear summation of two shifts when logarithmic axis with respect to time or to frequency is used. It has also been observed that the shift factors for shifting in test temperature are identical to the WLF shift factors that have been independently obtained for either approach.

It can be hence concluded, that the viscoelastic material behavior at any cure state may be obtained from the super-master curves, given that appropriate shift factors are used. In comparison, this investigation agrees with the work performed by Eom et al., where the full relationship between modulus and cure time was analyzed for a single frequency. Eom et al. has concluded that time-cure superposition can be used as a tool to estimate the viscoelastic moduli as a function of cure time and temperature. In contrast, the work presented improves upon this understanding by introducing the testing temperature as a parameter by defining the shift function as a product of the temperature and cure shift factors.

The cure-related shift factors from Approach 1 for 40 °C against degree of cure and cure time is shown in Fig. 13(a) and (b). It can be observed that using cure time instead of degree of cure results in a nearly linear shift curve with a deviation from linearity of about 1%. This justifies the use of curing time instead of the degree of cure, even though they are mutually dependant. The deviation from linearity can be explained by the fact that the master curves were generated using visual references only. This deviation can be possibly avoided if an
error analysis were to be utilized to fit the curves together rather than employing a visual approach.

Additionally, to verify the accuracy of the cure kinetic model complementary tests were performed to determine the glass transition temperature (\( T_g \)) of some of the partially cured samples for the DMTA experiments. This was performed in the DSC by scanning partially cured samples from 0 to 250 °C at 20 °C/min. This experimental \( T_g \) was compared to theoretical values obtained from the standard DiBenedetto equation to derive \( T_g \) from the degree of cure,\(^{14}\) which is computed from the cure kinetic model

\[
\frac{T_g - T_0}{T_\infty - T_0} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha}
\]  

The values for \( T_g, T_\infty, \) and \( \lambda \) for the epoxy system LYS052/HY502 have been determined by Svanberg,\(^2\) as shown in Table 3. The results from the examination are shown in Fig. 14. The values obtained for \( T_g \) from the DSC tests are in close agreement with the theoretical model, hence confirming the effectiveness of the cure kinetic model described with Equation 5.

In this work, two methodological approaches to investigate the influence of curing history on viscoelastic properties were demonstrated on an LYS052 epoxy resin system. While the first approach is easy to perform and time saving, it was not adequate to provide information on the rubbery region. A more detailed understanding of the evolution into the rubbery region is provided by the second experimental approach, though it is time-consuming.

However, it is to be stressed that the above conclusions may not be in general valid for all epoxies and there is a possible dependence of the behavior on the molecular weight of the epoxy constituents. There is some indication in the open literature that high molecular weight epoxies do not necessarily obey this linear relationship for shift factors. This argument was confirmed experimentally by Mours and Winters in.\(^{16,17}\)

Another study by Emri\(^{18}\) also agrees with the observation by Mours and Winters, arguing that high molecular weight systems tend show nonlinear dependence of the shift factors on the response time. However, an in-depth investigation is required to ascertain if this behavior of high molecular weight resins applies to the methodologies described in this work.

For this particular methodology, it could be ascertained that the resin system to a certain degree obeys linear viscoelastic behavior. It is to be stressed that in the DMTA the strain level at which the material is tested is infinitesimally small, which restrains the development of nonlinearity. In conclusion, the present results represent behavior in the glassy state only and only limited information is available in the rubbery state. Therefore, an ongoing investigation is into characterization of the rubbery state and its dependence on degree of cure.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

**References**


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Table 3 Parameters in the DiBenedetto equation described by Equation 8

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>( T_g (\alpha = 0) )</td>
<td>−41 °C</td>
</tr>
<tr>
<td>( T_g (\alpha = 1) )</td>
<td>136 °C</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Figure 14 Experimental \( T_g \) values with values predicted by the DiBenedetto model

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