

# Time-Temperature Viscoelastic Behavior of an Interlaminar-Toughened Epoxy Composite

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## SYNOPSIS

Viscoelastic deformation of an interlaminar-toughened laminated composite was investigated, and effects of the interlaminar heterogeneity were examined. Dynamic mechanical experiments were performed on the laminates and neat matrix resins of the laminated composite in the temperature range of 82–210°C to probe linear time-temperature behavior. The reason for using torsional shear deformation for probing was that it usually is more dominated by the matrix. In the relatively low-temperature regime, time-temperature superposition was applicable, and the effect of the interlaminar heterogeneity was found to be not pronounced. A methodology based on the Arrhenius activation energy approach was proposed for predictions of long-term viscoelasticity of the heterogeneous-phase composite. The effects of the interlaminar toughening phase became more significant at temperatures greater than the  $T_g$  of the toughening phase and presented some limitations for accurate predictions of time-dependent behavior. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Viscoelastic (inelastic) deformation of composites with polymeric matrices under continuous long-term loading conditions may be a concern in composite structure design since viscoelastic behavior is responsible for creep, i.e., changes of strains or compliances as a function of time. Various studies on thermoplastic polymers and some epoxy composites<sup>1-4</sup> have demonstrated that polymeric materials, in general, do exhibit viscoelastic deformation to various extents. Time-temperature superposition is usually used in dealing with viscoelastic behavior of a polymeric material. Within the linear range, viscoelastic response of a material in the time domain can be "equivalent" to the temperature domain through a connecting factor. As time progresses over long duration, a material may undergo noticeable stress relaxation or creep. Viscoelastic models state that such a decrease in stiffness (modulus) or increase in compliance of the material as a function of time could be correlated quantitatively to stiffness or compliance changes at a higher temperature, but,

conveniently, within a much shorter duration of time. Through proper time-temperature superposition, equivalency may be established and used effectively for long-term prediction. Multiphase polymers could add one more dimension of difficulty in quantitative treatments of viscoelastic deformation. A model of viscoelastic behavior of a multiphase polymer was proposed by Kaplan and Tschoegl<sup>1</sup> using a Takayanagi model. This, however, had only limited success since it would require knowledge of many variables as a function of time and temperature, which usually were not readily obtained.

Because of relatively high glass transition temperatures and a highly cross-linked network structure, most advanced high-temperature epoxy composites are expected to exhibit relatively slight creep at normal service temperatures. Nevertheless, composites with a heterogeneous matrix morphology may impose additional difficulties in quantitative analyses and predictions. Toughened epoxy composites are being increasingly used in various primary structures of aircraft or other advanced applications, and most toughened composites possess a multiphase matrix, usually with the constituents exhibiting different  $T_g$ 's. For some toughened composites, the toughening phase(s) is dispersed uniformly throughout the matrix, and the main epoxy

and the toughening phases exhibit about the same glass transition temperatures. It is documented<sup>5</sup> that, within the linear stress range, the multiphase composite matrix may be treated with applicable viscoelastic models if the  $T_g$ 's of the main epoxy and the toughening phases are the same. A material may exhibit multiphase morphologies, but behave rheologically and viscoelastically simply.

However, some toughened composites have the toughening phase(s) localized in certain areas within the cured laminates, and the main epoxy and toughening phases exhibit different glass transition temperatures. A new approach in toughening advanced composites is to have the heterogeneous phase localized at the interlaminar (interply) regions of the laminates to more effectively improve the interlaminar fracture toughness. Selective introduction of heterogeneity only in localized regions of the composite matrices would help keep to a minimum the trade-offs in mechanical performances and other properties. With such an approach, toughness in advanced composites usually can be effectively enhanced by introduction of a heterogeneous morphology to the matrix. It, however, may complicate the methodology in analyzing the viscoelastic behavior of the composite.

An interlaminar-toughened composite, Toray 3900-2/T800H (6), was chosen as the model system in this study since its interlaminar morphology is known and effects of other environmental durability factors, such as galvanic reactions, have been investigated.<sup>7</sup> Using the interlaminar-toughened composite as a model system, the objective of this study was to investigate the effect of interlaminar heterogeneity on the viscoelasticity. A practical methodology to predict long-term viscoelastic durability of heterogeneous-matrix composites was proposed.

## EXPERIMENTAL

### Materials

The toughened laminated composite used in this study was fabricated from a commercially available carbon fiber/epoxy prepreg, Toray 3900-2/T800H (Toray Ind. Ltd., Japan). Curing was done using a standard cure cycle in an autoclave, i.e., a 1–2°C/min ramp rate to 177°C for 2 h. The autoclave pressure was kept at 550–620 kPa for properly consolidating the laminates during cure. The composite specimens were machined from eight plies cured

laminated panels of four different ply stackups:  $[0]_8$ ,  $[90]_8$ ,  $[\pm 45]_{2s}$ , and  $[+45/90/-45/0]_8$ .

To better distinguish individual contributions from the main epoxy vs. toughening phase to the viscoelastic properties, experiments were also performed on the epoxy matrix with no presence of carbon fiber. Better sensitivity could be obtained if the influence of carbon fiber was excluded in the analysis of viscoelasticity. Neat resin specimens, Neat-A and Neat-B, were also prepared from the two ingredient resins: Toray 3900-2(1) and 3900-2(2), respectively. Neat-A was the base epoxy resin in the prepreg, which was primarily a high-temperature epoxy resin based on a tetraglycidyl 1,4-diaminodiphenyl methane/4,4'-diaminodiphenyl sulfone (TGDDM/DDS) system. This was the resin used for primary impregnation of the prepreg during the prepregging process. In the cured composite, Neat-A constituted the intraply matrix. Neat-B was the toughening ingredient (particles), which was applied during an after-impregnation treatment. Intended for improving interlaminar damage tolerance and toughness of the cured composite, this Neat-B stayed in the interply region after cure and formed a highly heterogeneous morphology.<sup>7</sup> Viscoelastic behavior of these two ingredient resins was characterized to provide comparative information about the viscoelastic behavior of each of the constituents of the toughened composite. The dimensions of all the laminate specimens were approximately  $5 \times 1 \times 0.15$  cm. The neat resin specimens used were of the same length and width but slightly thicker at  $5 \times 1 \times 0.25$  cm.

### Procedures

Dynamic mechanical analysis (DMA) was performed on the specimens using a Rheometric RMS-800 at a series of isothermal temperatures. The two ends of the specimen were mounted onto the sample holders by clamping, and an oscillatory torsional deformation was imposed along the longitudinal direction of the specimen at a fixed frequency or at five scanning frequencies: 0.01, 0.1, 1, 10, and 100 rad/s. The temperature was kept isothermal when the five frequencies were scanned. Subsequently, the temperature was increased stepwise from 82 to 210°C ( $T_g$  of the composite) at a 20°C interval. At each isothermal temperature, the dynamic modulus of the composite was measured at these five frequencies. After completion of frequency scanning at the first isothermal temperature, the specimen in the DMA isothermal temperature chamber was brought to the next higher isothermal temperature

while the same five frequencies were scanned again. The same procedures were repeated at all incremental isothermal temperatures until experiments at the highest temperature (210°C) were completed.

The shear deformation strains imposed by the dynamic mechanical analyzer were below 0.1–0.2%. At these relatively low strain levels, the stress–strain relationship was likely in the linear range. To check reproducibility, three experiments were performed on three separate  $[0]_8$  laminates (specimens #1–#3) under the same experimental conditions and parameters.

## BACKGROUND

In a linear range, the shift factors ( $\log a_T$ ) of time–temperature superposition generally can be described by two common viscoelastic models.<sup>8,9</sup> At temperatures near or above the glass transition ( $T_g$ ) region of a material, temperature dependence of the shift factors of a polymeric material often follows the Williams–Landel–Ferry (WLF) equation with two adjustable parameters  $C_1$  and  $C_2$ , as follows:

$$\log(a_T) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

where  $C_1$  for most polymeric materials ranges from 7 to 15, and  $C_2$ , from 50 to 80.

However, mechanisms of viscoelasticity are generally different at, above, and below the  $T_g$  of the material. Since the service temperatures of most composites are usually far below the  $T_g$ 's of the matrix epoxy of the composites, the WLF equation [eq. (1)] could not be expected to be of much use for predicting the viscoelastic behavior of the composite at the service temperatures.

Below the glass transition region, an Arrhenius-type relationship is usually found to be useful in describing temperature dependence of shift factors generated from time–temperature superposition. The Arrhenius approach is based on the molecular relaxation theory, which states that the molecules in a material system “relax” differently at different temperatures and the rate of relaxation (as characterized by the relaxation time “ $\tau$ ”) at a temperature can be described using an Arrhenius equation,<sup>8,9</sup> as follows:

$$\tau(T) = A \cdot \exp(E/RT) \quad (2)$$

where  $A$  is the Arrhenius preexponent constant;  $E$ ,

the activation energy;  $R$ , the gas constant; and  $T$ , the temperature in Kelvin.

Viscoelasticity in terms of “creep” or “stress relaxation” is believed to be associated with a molecular relaxation process. When the molecules in a material system relax faster (as characterized by a shorter relaxation time  $\tau$ ), the material would relax more readily. Conversely, when the material exhibits a long relaxation time, the material would “relax” slowly. A shift factor is defined as the ratio of the relaxation time at any given temperature  $T$  to the relaxation time at a reference temperature  $T_0$ :

$$\begin{aligned} a_T &= \frac{\tau}{\tau_0} = A \exp(E/RT) / A \exp(E/RT_0) \\ &= \exp[E/R(1/T - 1/T_0)] \end{aligned} \quad (3a)$$

As noted earlier,  $E$  is the “activation energy” for the molecular relaxation process. Also note that the relaxation time ( $\tau$ ) is related to the time ( $t$ ) it takes for the molecules to relax to a given state at temperature  $T$ , as follows:

$$a_T = \frac{\tau}{\tau_0} = \frac{t}{t_0}$$

The relationship [eq. (3a)] can also be expressed as

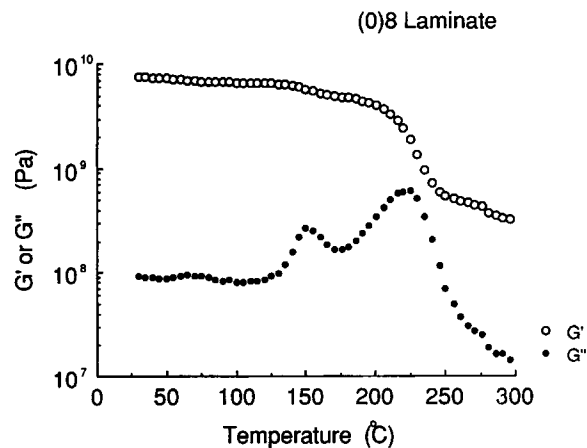
$$\ln a_T = E/R(1/T - 1/T_0) \quad (3b)$$

According to eqs. (3a) or (3b), the slope of a  $\ln(a_T)$  vs.  $1/T$  plot should yield activation energies for the shift factors. A higher activation energy  $E$  suggests that the shift factor  $a_T$  would vary to a greater extent with temperature. Thus, when compared at the same reference temperature, the material with a higher activation energy is more “viscoelastic.” Consequently, the activation energy of shift factors can be used as a quantitative measure of viscoelasticity of material systems if compared at a common reference temperature.

## RESULTS AND DISCUSSION

### Time–Temperature Behavior of Laminates

Figure 1 shows the storage and loss moduli as a function of temperature for the  $[0]_8$  laminate. Two relaxation peaks were observed in the loss modulus curve: one at 145°C and the other at 220°C. The higher one at 220°C was the  $T_g$  of the main base epoxy and is labeled as  $T_{g1}$ . The lower relaxation

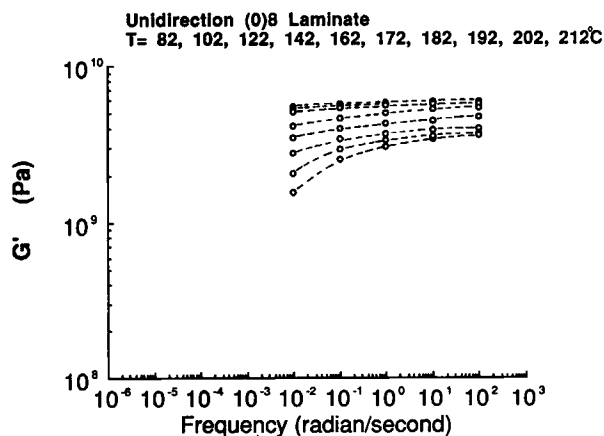


**Figure 1** Storage and loss moduli of the  $[0]_8$  laminate as a function of temperature.

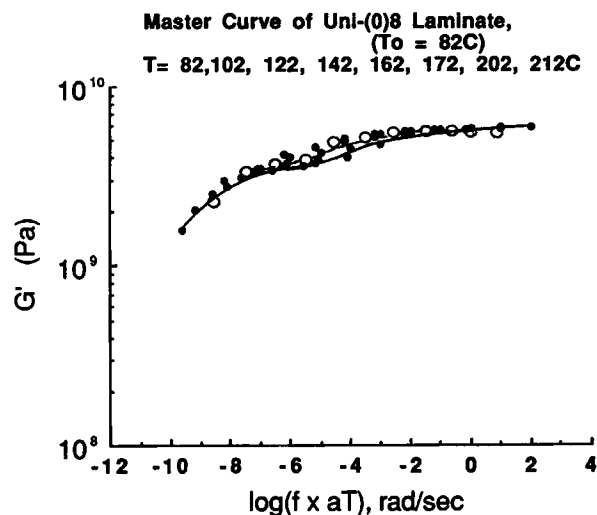
temperature at  $145^\circ\text{C}$  was contributed from the interlaminar heterogeneous phase and is labeled as  $T_{g2}$ .

Figure 2 shows the storage dynamic mechanical moduli of the  $[0]_8$  (specimen #1) laminate as a function of frequency (time) at several isothermal temperatures between  $T = 82$  and  $212^\circ\text{C}$ . Note that all the dynamic modulus data acquired at the four different isothermal temperatures were plotted in a common set of logarithmic axes of  $G'$  vs. frequency (time) in order to perform time-temperature shifting. Results from all three  $[0]_8$  laminates showed the same features and excellent agreement was observed.

A master curve was constructed by using time-temperature shifting relative to a reference temperature of  $82^\circ\text{C}$ . With the modulus curve at  $82^\circ\text{C}$  as



**Figure 2** Moduli of the  $[0]_8$  laminate as functions of frequency ( $1/\text{time}$ ) at isothermal temperatures of  $82$ – $212^\circ\text{C}$ .



**Figure 3** Master curves of  $[0]_8$  laminates: (solid circle) specimen #1; (open circle) specimen #3.

the reference, the curves at three other higher temperatures were shifted, one at one time, to the left to construct a smooth, continuous curve. After shifting, a fairly smooth “master” curve was formed. Similarly, shifting was performed on the  $[0]_8$  laminate (specimen #3). Both master curves were plotted on the same graph for direct comparison, which showed quite good reproducibility. Figure 3 shows that both “master curves” covered a total time (in unit of seconds) of approximately 10 orders of magnitude ( $10^{10}$  s) with  $82^\circ\text{C}$  as the reference temperature. In addition, both master curves exhibited a minor drop at an intermediate time, which could be attributed to the toughening phase. Note that the left-hand side of the  $\log(\text{frequency})$  axis represented low frequencies or, equivalently, long times. Also keep in mind that the master curve was based on a reference temperature of  $82^\circ\text{C}$ . If predictions of viscoelastic deformation at any other temperatures are desired, a master curve can be similarly generated with a new reference.

Figure 4 shows the shift factors of the three unidirectional  $[0]_8$  laminates (specimens #1–3) plotted as a function of  $1/T$ , in the fashion of the Arrhenius relationships [eq. (3b)]. The shift factors plotted in this figure were obtained from time-temperature superpositions on the modulus results of the three unidirectional  $[0]_8$  laminate specimens. Apparently, the results of shifting were quite reproducible. All the shift factors fell into two linear relationships with the breakpoint at approximately  $T = 140$ – $145^\circ\text{C}$ . The slope of the  $\log a_T$  vs.  $1/T$  plots yielded an activation energy  $E$  of  $33.0$  kcal/mol in the tem-

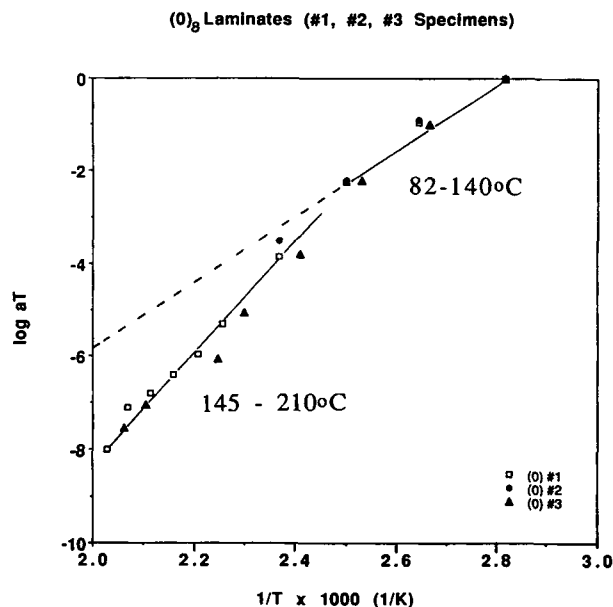


Figure 4 Shift factors plotted as a function of  $1/T$  for the  $[0]_8$  laminates (specimens #1, #2, and #3).

perature range of 82–140°C and 52.9 kcal/mol in the temperature range of 145–210°C.

Interestingly, the temperature location of the breakpoint coincided roughly with the  $T_g$  of the toughening particles (145°C). This suggested that the breakpoint at 145°C apparently was related to the toughening phase present in the interlaminar region of the laminate. Note that above  $T_g$  of the toughening phase the experimental  $\log a_T$  vs.  $1/T$  plots seemed to be slightly scattered. This deviation could be explained: The major reason was that the temperature was approaching the  $T_g$  of the primary

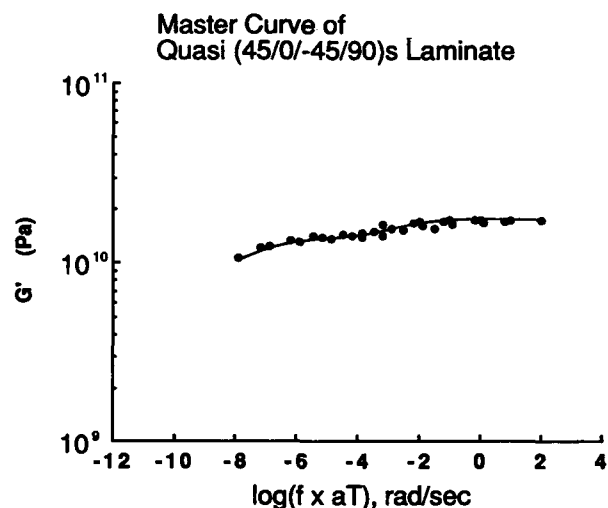


Figure 5 Master curve of the  $[-45/90/45/0]_s$  laminate.

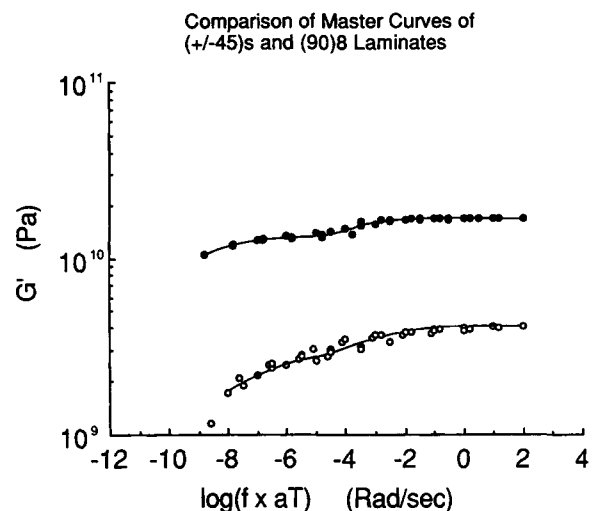


Figure 6 Comparison of master curves of the  $[\pm 45]_s$  and  $[90]_8$  laminates.

epoxy phase. Although the viscoelastic behavior primarily reflected the relaxation of the main epoxy phase, the interlaminar heterogeneity might contribute and complicate the behavior. Because of non-Arrhenius-type contributions from the toughening phase, though accounting for only a small portion of the composite matrix, the apparent activation energies exhibited some slight scattering in their values.

Modulus data of the  $[-45/90/45/0]_s$  (quasi-isotropic) laminate were also plotted as a function of frequency at several isothermal temperatures from  $T_0 = 82$  to  $T = 212^\circ\text{C}$ . Using the procedures described earlier, a master curve for the quasi-isotropic laminate was generated and is shown in Figure 5. The master curve of the quasi-isotropic laminate also exhibited a minor drop characteristic of the toughening phase at an intermediate time of  $\log(\text{frequency}) = -5$  to  $-6$  rad/s.

Similarly, the master curves of the  $[90]_8$  and  $[\pm 45]_s$  laminates were also generated by time-temperature shifting, which are both shown in Figure 6 on the common coordinate axes for direct comparison. Again, both curves exhibited a minor drop at approximately the same intermediate time ( $\log f = -5$  to  $-6$  rad/s). The intermediate drop in the modulus curves, as discussed earlier, was attributed to the toughening phase.

The shift factors for these laminates from the time-temperature shifting were obtained from  $\log aT$  vs.  $a/T$  plotting. Again, the shift factors fell into a linear relationship with two different slopes in two temperature ranges: 82–140°C and 145–210°C, with the breakpoint at approximately  $T$

**Table I** Activation Energies of Shift Factors for Various Laminates and Neat Resins

Samples	<i>E</i> (kcal/mol) at Two Temperature Ranges	
	82–140°C (Low, below $T_{g2}$ )	145–210°C (High, above $T_{g2}$ , below $T_{g1}$ )
<b>Laminates</b>		
$[0]_8 : 1^a$	33.9	51.8
$[0]_8 : 2$	32.0	53.4
$[0]_8 : 3$	33.2	53.4
Average	33.0	52.9
$[+45/90/-45/0]_8$	25.1	52.0
$[90]_8$	33.2	45.0
$[\pm 45]_{2s}$	27.4	51.8
<b>Neat resins</b>		
Neat-A	31.2	31.2
Neat-B	37.1	89.9

<sup>a</sup> Three separate experiments were performed on the  $[0]_8$  laminates to confirm reproducibility of the results of time-temperature shifting.

= 140°C. The values of the shift factors for these laminate are listed in Table I.

### Effects of Ply Orientation

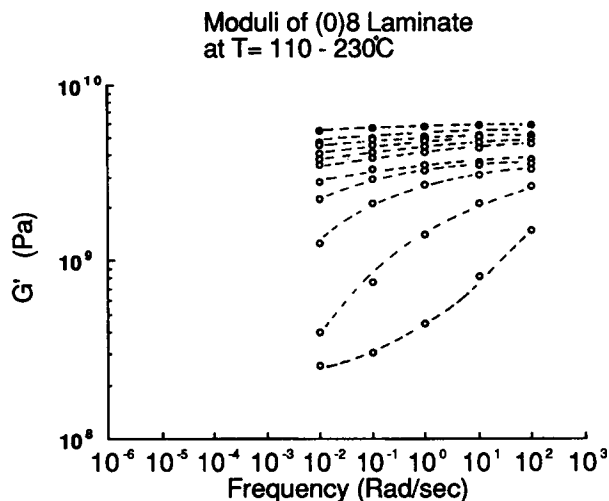
Ply stackups in the laminate specimens were chosen in this study such that the specimens would be deformed in directions where the modulus was dominated by the matrix. For dynamic deformation using the Rheometric, a torsional shear on the plane perpendicular to the length direction was dominated by the matrix for a unidirectional  $[0^\circ]_8$  or  $[90^\circ]_8$  laminate. On the other hand, the torsional shear deformation was expected to be less dominated by the matrix and more by the fiber for the  $[-45/90/45/0]_8$  and  $[\pm 45]_{2s}$  laminates, which were also investigated in this study for comparing with the unidirectional laminates.

From Table I, the activation energies for all the laminates in the temperature range of 82–140°C (below  $T_{g2}$ ) can be ranked in the following order:  $[-45/90/45/0]_8 = [\pm 45]_{2s} < [90]_8 = [0]_8$ . As discussed, the activation energy can be taken as a quantitative measure of the viscoelastic nature of a material, and this comparison illustrates the influence of ply stackups of the laminates on the viscoelastic behavior at temperatures below  $T_{g2}$ .

When subjected to a torsional shear deformation, quasi-isotropic and crossply orientations were the “least viscoelastic” and the  $[90]_8$  and  $[0]_8$  ply ori-

entations were the “most viscoelastic” of all the laminates examined. Interestingly, this trend coincides with the trend of variation of shear moduli for various laminates. The quasi-isotropic and  $[\pm 45]_{2s}$  laminates exhibited higher moduli than those of the unidirectional  $[0]_8$  or  $[90]_8$  laminates when subjected to torsional shear deformation at the same temperatures. A shear deformation normal to the length direction of a  $[90]_8$  or  $[0]_8$  laminate was dominated more by the matrix, whereas the same type of deformation to a quasi-isotropic laminate was dominated more by the carbon fiber. Since the laminate modulus reflected the relative dominance by ply orientation of the carbon fiber, the viscoelasticity as measured by the “activation energies” apparently was similarly influenced by the ply orientation.

At higher temperatures between  $T_{g2}$  and  $T_{g1}$ , however, the activation energy seems to be quite constant, which suggests that the viscoelastic deformation might be independent of ply orientation as well as the presence or absence of the carbon fiber. At these higher temperatures, the activation energies for all laminates,  $[0]_8$ ,  $[90]_8$ ,  $[\pm 45]_{2s}$ , and  $[+45/90/-45/0]_8$ , were about the same and between 52 and 53 kcal/mol. Possible explanations are offered here: As the matrix material softened at temperatures above  $T_{g2}$ , the viscoelastic behavior of the composite was increasingly dominated by the matrix resin and the toughening phase to such an



**Figure 7** Moduli as functions of frequency at isothermal temperatures 110–230°C.

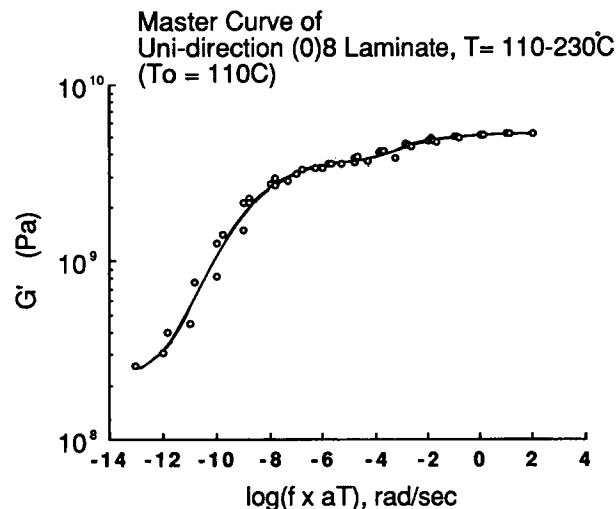
extent that the effect of carbon fiber and its orientation was masked. In their study on viscoelastic behavior of a single-phase epoxy composite, Brinson et al.<sup>3</sup> also reported that the shift factors were quite independent of ply orientations at elevated temperatures near  $T_g$ .

#### Extension of Master Curves

For predictions at longer times, master curves covering a wider time domain would be needed, which would require modulus data generated at temperatures well above the reference temperatures (82°C). To further extend the width of the time domain of interest, modulus data at temperatures at or above the epoxy glass transition temperature might be required. Figure 7 shows the moduli curves of the  $[0]_8$  laminate (specimen #4) as functions of frequency at several isothermal temperatures from 110 to 230°C. With  $T_0 = 110^\circ\text{C}$  as the reference temperature, a master curve covering an extended range of time (14 orders of magnitude in seconds) was generated as shown in Figure 8. At an intermediate time ( $\log f = -5$  rad/s), the master curve exhibited the familiar minor drop characteristic of the toughening phase. A dramatic drop in the modulus occurred at about  $\log f = -8$  rad/s, which was caused by molecular relaxation of the main epoxy phase.

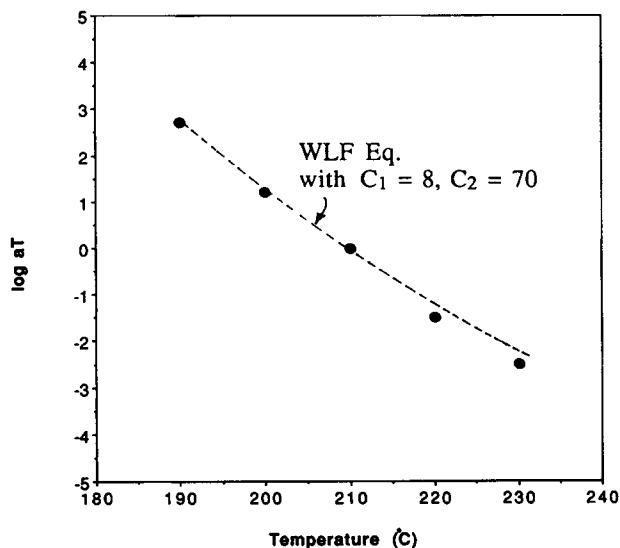
#### Viscoelastic Behavior at $T_g$

The shift factors for the  $[0]_8$  laminate (specimen #4) in the lower-temperature range (110–170°C) were found to agree well with the results in Table I



**Figure 8** Master curve of extended time for the  $[0]_8$  laminate at  $T_0 = 110^\circ\text{C}$ .

for the other  $[0]_8$  laminates (specimens #1–3). In the higher-temperatures range from 190 to 230°C, however, the Arrhenius-type relationship might not be applicable. Figure 9 shows that the experimental  $\log a_T$  data for the  $[0]_8$  laminate can be described well by the WLF [Eq. (1)] relationship. In comparing the WLF fitting with the experimental shift factors data, there appear to be some slight deviations at the high-temperature end. Experimental difficulties might have contributed to this deviation. Data acquired using the Rheometric DMA equipment were usually less reliable at temperatures

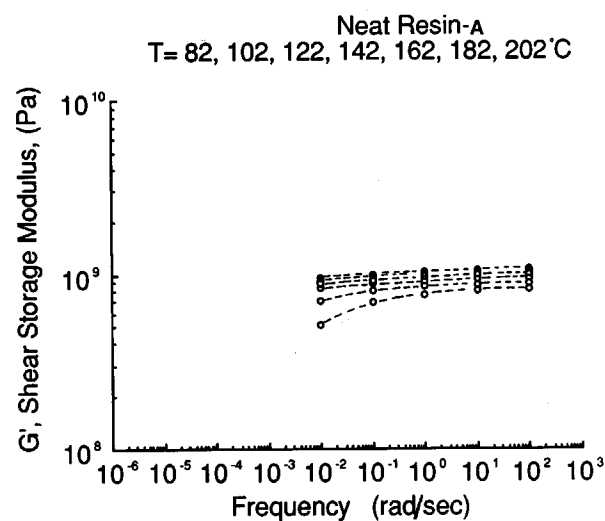


**Figure 9** Experimental shift factors data (solid circle) for the  $[0]_8$  laminate in comparison with the WLF equation (dotted curve) with  $C_1 = 8$ , and  $C_2 = 70$ .

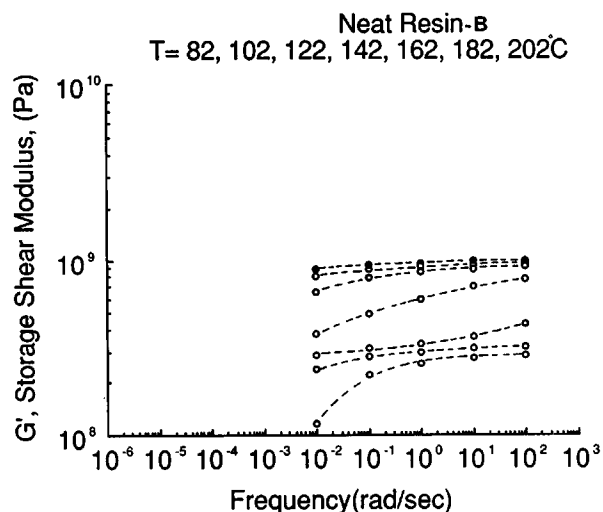
above the glass transition temperature, where the material started to soften significantly and specimen gripping by the clamps was made difficult.

When deformation is within a linear stress-strain range, most polymeric materials exhibit simple viscoelastic behavior below and at the glass transition region.<sup>3,5</sup> However, some researchers argued that under high stresses coupled with high temperatures a polymeric material may exhibit a nonlinear viscoelastic behavior. For nonlinear deformation to a unidirection composite, the Schapery theory<sup>10</sup> has been applied to describe viscoelastic behavior. Ha and Springer<sup>11</sup> also applied such an approach to model nonlinear time-temperature behavior of homogeneous-matrix composites at elevated temperatures.

Under a dynamic shear deformation, the epoxy matrix of the toughened composite was found to behave linearly in its viscoelastic deformation. This might be interesting, but predictions of the toughened epoxy composite could not be made from the experimental data generated at temperatures near the glass transition temperature of the epoxy phase ( $T_{g1}$ ). Mechanisms and activation energy for the viscoelastic behavior of the composite could differ dramatically at, below, and above the glass transition temperature. As a result, errors might arise if attempts were made to extrapolate the data generated at temperatures near  $T_{g1}$  in order to predict viscoelastic behavior of the composite at much lower temperatures. Better predictions usually should be made by extrapolating experimental data generated at temperatures below  $T_{g1}$ .



**Figure 10** Moduli of Neat-A as functions of frequency at isothermal temperatures of 82–202°C.



**Figure 11** Moduli of Neat-B as functions of frequency at isothermal temperatures of 82–202°C.

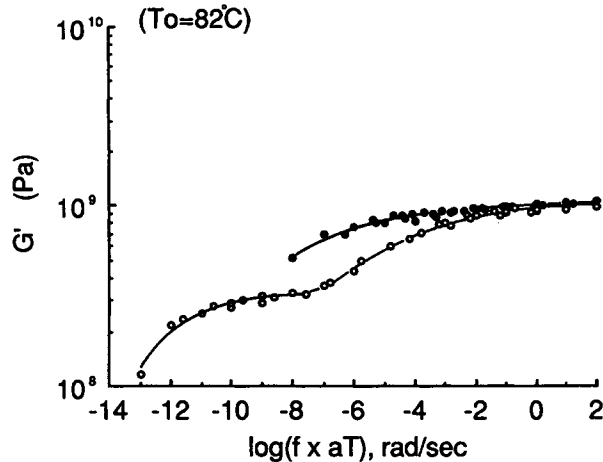
#### Matrix Resins and Effects of Toughening Phase

There were two major ingredients, the main base epoxy and the toughening particles, in the matrix of the interlaminar-toughened composite. They might contribute differently to the observed viscoelastic properties of the composite. In laminates, effects of toughening particles could possibly be masked by the reinforcing carbon fiber. By excluding the carbon fiber and evaluating the constitutive neat resin components, the viscoelastic contributions from the two individual matrix components were compared and effects of the toughening particles on the viscoelastic behavior could be observed more clearly.

Figure 10 shows the modulus data of Neat-A as functions of frequency at several isothermal temperatures. Similarly, Figure 11 shows the moduli of Neat-B at several isothermal temperatures. A comparison showed that the shear moduli of Neat-B exhibited much greater sensitivities to temperature than did Neat-A. Obviously, the presence of the toughening phase in a greater content in Neat B enhanced viscoelastic deformation.

Time-temperature shifting was performed on both sets of data. Figure 12 shows that the master curves for Neat-A and Neat-B plotted on the same graph for convenient comparison. The presence of the toughening particles was responsible for the observed difference in the moduli results between Neat-A and Neat-B. The master curve of Neat-A, which contained no toughening particles, exhibited no intermediate drop in the master modulus curve until an apparent drop starting at  $\log f = -8$  rad/





**Figure 12** Master curves of (solid circle) Neat-A and (open circle) Neat-B.

s, which was due to molecular relaxation of the main epoxy phase. On the contrary, the master curve of Neat-B exhibited a prominent drop in the modulus at an intermediate time of  $\log f = -5$  rad/s. The drop in the master curve for Neat-B resin was exactly at the same location in which a drop in the master modulus curves was observed in all the laminate specimens. This characteristic drop, as discussed earlier, was attributed to the molecular relaxation of the toughening particles phase with its  $T_g$  at  $145^\circ\text{C}$ . Note that the modulus drop at the intermediate time was more prominent in Neat-B resin than were the drops in all the laminates containing Neat-B in the interlaminar regions. This apparently was due to the much greater content of the toughening phase in Neat-B than in the heterogeneous matrix of the various laminates.

Figure 13 shows the shift factors as a function of inverse temperature ( $1/T$ ) for both Neat-A and Neat-B resins. Interestingly, the shift factors for the base epoxy Neat-A fell into a linear relationship throughout the temperature range of  $82$ – $210^\circ\text{C}$ . By contrast, the shift factors for Neat-B resin fell into two distinct linear regions, with the distinct breakpoint near  $140^\circ\text{C}$ . As discussed earlier, this feature also characterized the  $\log a_T$  vs.  $1/T$  relationships for all the laminates containing the toughening phase. The difference of the shift factors at, below, and above  $T_{g2}$  (i.e.,  $T_g$  of Neat-B) suggests that the mechanism of viscoelastic behavior of the toughened composite might be different.

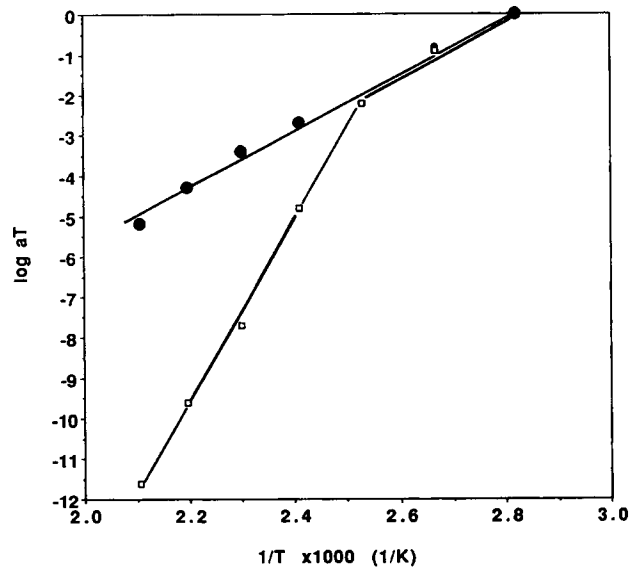
For comparison, the activation energies for Neat-A and Neat-B resins are also listed in Table I. The comparison of the results of Neat-A and Neat-B resins revealed the effect of the toughening phase

on the viscoelastic behavior. Below  $T_{g2}$  ( $145^\circ\text{C}$ ), the activation energy for the shift factors of Neat-A was  $32$  kcal/mol, which was not much different from the activation energy ( $37$  kcal/mol) for Neat-B. Above  $T_{g2}$ , however, the difference was much greater ( $31.2$  kcal/mol vs.  $89.9$  kcal/mol), indicating that above  $T_{g2}$  the toughening phase more significantly dominated the viscoelastic behavior. The toughening phase, due to its lower  $T_g$  than the main epoxy  $T_g$ , not only resulted in more viscoelastic deformation of the composite, but also made predictions more limited and probably less accurate. Limitations of predictions of long-term viscoelastic deformation originated from the fact that a longer-time prediction would require use of experimental modulus data generated at high temperatures, usually at or above the  $T_g$  of the toughening phase. This created a dilemma. The mechanisms of viscoelastic deformation could be expected to differ significantly at, above, and below the  $T_g$ . Inaccuracy in predictions might occur if above- $T_g$  data were used to predict viscoelastic behavior at temperatures below the  $T_g$ . Apparently, the greater the percentage of the toughening phase, the greater its effect would be on viscoelastic deformation.

It is proposed that the activation energy is an additive sum of the contributions from the constitutive components, as follows:

$$E = E_A\omega_A + E_B\omega_B \quad (4)$$

where  $E$ ,  $E_A$ , and  $E_B$  are the activation energies of



**Figure 13** Shift factors plotted as a function of  $1/T$  for (solid circle) Neat-A and (open square) Neat-B resins.

the heterogeneous matrix, Neat A, and Neat B, respectively, and  $\omega_A$  and  $\omega_B$  are the weight fractions of Neat A and Neat B in the heterogeneous matrix, respectively. A resin content determination of the prepreg was performed and the weight fractions,  $\omega_A$  and  $\omega_B$ , were estimated to be about 0.58 and 0.42, respectively. This equation applies when there is no influence from the carbon fiber. A comparison of the activation energies of the various laminate specimens with different ply stackups demonstrated the influence of fiber and fiber orientation on the viscoelasticity. However, a torsional shear on a  $[0]_8$  laminate is apparently dominated by the matrix. As a result, the viscoelastic deformation of the laminate and the matrix resin would be similar. The carbon fiber exercises almost no influence as far as viscoelasticity is concerned. As discussed earlier, this could also be demonstrated by the fact that the values of the torsional shear moduli of the  $[0]_8$  laminate were comparable to those of the Neat resin specimen. The estimated results of activation energy according to eq. (4) for the matrix-dominated  $[0]_8$  laminate was 33.7 and 58.5 kcal/mol for the lower-temperature range (82–140°C) and the higher-temperature range (145–210°C), respectively. The two values agreed quite well with the experimental values of 33.0 and 52.9 kcal/mol, respectively, for the  $[0]_8$  laminate.

## CONCLUSIONS

An interlaminar-toughened composite was used as a model for studies on time-temperature behavior in the linear range. Despite the multiphase morphology in the interlaminar region of the toughened composite, time-temperature superposition was found to be applicable at relatively low-temperature regimes where the composite was in the linear viscoelasticity range. The toughening constituent was introduced only in the interply regions and such interlaminar heterogeneity effectively improved delamination resistance of the laminated composite. With this type of modification, the effect on the mechanical viscoelastic behavior of the laminate was minimal, unless the temperature was higher between the  $T_g$  of the toughening phase and the  $T_g$  of the main epoxy phase. Activation energies of the shift factors were found to be useful as a quantitative measure of viscoelasticity for heterogeneous matrix composites. Effects of the interlaminar toughening

phase on the viscoelastic deformation of the toughened composite were quantified.

The methodology developed in this study could be applied for predictions of long-term changes of modulus of the composite under prolonged, say years, loading. Complications and limitations in making long-term predictions were primarily caused by the presence of the toughening particles phase that exhibited a relatively lower glass transition temperature than the primary epoxy phase. Using the procedure described in this study, the limitations were expected to cause only relatively minor errors in predictions.

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