

# Creep and Stress Relaxation Modeling of Vinyl Ester Nanocomposites Reinforced by Nanoclay and Graphite Platelets

Ahmad Almagableh, P. Raju Mantena, Ahmed Alostaz

Composite Structures and Nano-Engineering Research, University of Mississippi, University, Mississippi 38677

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**ABSTRACT:** This article discusses the viscoelastic behavior of a vinyl ester (Derakane 411-350) reinforced with 1.25 and 2.5 wt % nanoclay and exfoliated graphite nanoplatelets during short-term creep and relaxation tests with a dynamic mechanical analyzer. Linear viscoelastic models are generally composed of one or more elements such as dashpots and springs that represent the viscous and elastic properties. Stress relaxation data from the dynamic mechanical analyzer have been used to obtain the elastic parameters based on model constitutive equations. The standard linear solid model, which is a physical model, has been used for predicting the creep deformation behavior of the vinyl ester nanocomposites over a wide temperature range. Some correlations have been made with the mechanical model, such as the effect of temperature on the deformation behavior, which is well explained by the

dashpot mechanism. At lower temperatures, higher creep compliance has been observed for the vinyl ester versus the nanocomposites, whereas at temperatures near the glass-transition temperature of the vinyl ester, creep compliance in the nanocomposites is closer in magnitude to that for the vinyl ester. The creep response of the pure vinyl ester and its nanocomposites appears to be modeled reasonably well at temperatures lower than their glass-transition temperatures. A comparison of the predictions and experimental data from the creep tests has demonstrated that this model can represent the long-term deformation behavior of these nanoreinforced materials reasonably well. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1635–1641, 2010

**Key words:** creep; nanocomposites; viscoelastic properties

## INTRODUCTION

Composite materials with polymer matrices exhibit viscoelastic behavior that is directly related to the molecular structure and formulation differences. A polymer at a specific temperature and with a specific molecular weight may behave as a liquid or a solid according to the timescale at which its molecules are deformed. In crosslinked polymers, the crosslinking acts to decrease the viscous component of viscoelastic behavior because the chains are prevented from slipping past one another.

Understanding the viscoelastic properties of composite materials is essential for the design and analysis of advanced structures. To determine the creep

behavior of a given material, a constant stress is applied to a specimen maintained at a constant temperature, and the strain data are collected as a function of time. When a load is applied, instantaneous deformation occurs as a pure elastic response. This deformation is followed by rapidly decreasing deformation called primary deformation.<sup>1</sup> This is then followed by steady-state linear deformation called secondary deformation. The creep behavior of a polymer also depends heavily on the material temperature during testing, and the highest rate of deformation occurs around the glass-transition temperature ( $T_g$ ).

The creep behavior of many plastics has been fitted to an analytical relationship similar to those proposed for metals. Findley<sup>2</sup> demonstrated that the creep strain ( $\epsilon$ ) and time ( $t$ ) could be related by the following equation:

$$\epsilon(t) = \epsilon_0 + mt^n \quad (1)$$

where  $\epsilon_0$  is the instantaneous strain and  $m$  and  $n$  are material constants that depend on both the stress and temperature. The restriction of this approach is that it does not provide a physical representation for creep deformation behavior under different loading conditions.

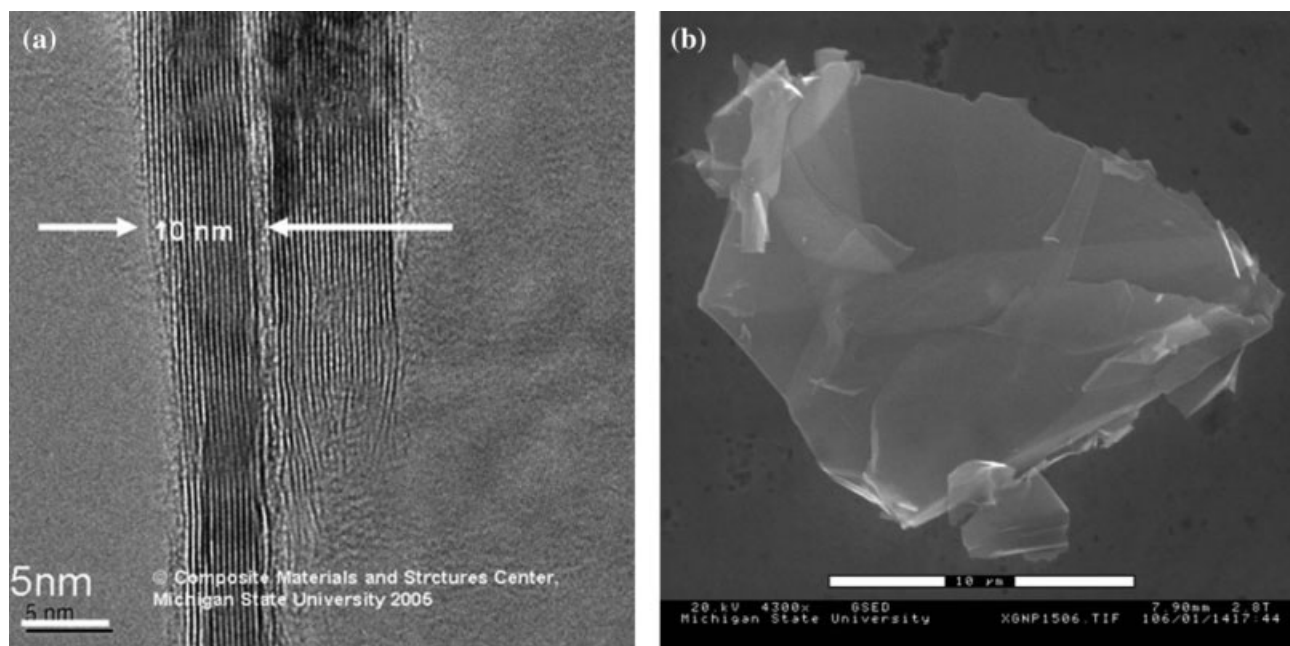
Bakis and Temple-Boyer<sup>3</sup> studied the tensile creep response of coupon-type specimens made of epoxy

Correspondence to: A. Almagableh (amalmag1@olemiss.edu).

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**Figure 1** Morphology of xGnPs: (a) edge view (transmission electron microscopy) and (b) lateral view (scanning electron microscopy).<sup>8</sup>

reinforced with single-walled carbon nanotubes (up to 3 wt %). Master creep compliance curves were constructed at a reference temperature of 40°C on the basis of the time–temperature superposition principle, and a Findley-type creep law for the creep strain was fit to the master curves according to eq. (1).

Many physical models have described the time-dependent mechanical behavior of polymers. Most of these models have been developed to characterize the strain rate dependence, creep, and stress relaxation over the viscoelastic regime.<sup>4–6</sup> Linear viscoelastic models are generally composed of one or several elements such as dashpots and springs that represent the viscous and elastic properties. The Kelvin model, which is one of the simplest models, consists of a linear spring and a dashpot in parallel, and this model can be used to represent the behavior of a solid polymer component at the beginning of loading.<sup>1</sup> At longer times, the predicted deformation approaches a fixed value, and it returns to an undeformed condition after load removal.

Thermoset vinyl ester matrices are becoming increasingly important in industrial applications because of their enhanced mechanical properties. They exhibit characteristics similar to those of epoxy resins as well as unsaturated polyester resins. Advantages include a high tensile strength and stiffness, low cost, process versatility, and good chemical resistance. The deformation behavior of a vinyl ester polymer over a wide range of strain rates (0.0001–1/s) and over a wide range of temperatures [room temperature

(RT) to 100°C] was investigated by Plaseied and Fatemi<sup>7</sup> under monotonic tensile loading and relaxation conditions. In our work, the effect of temperature on the creep deformation behavior of a vinyl ester (Derakane 411-350) and its nanocomposites with 1.25 and 2.5 wt % nanoclay and exfoliated graphite nanoplatelets (xGnPs) was investigated. The objective was to develop constitutive models to describe the viscoelastic behavior and characterize the temperature-dependent mechanical response of vinyl ester nanocomposites.

## EXPERIMENTAL

### Material preparation

Clay and graphite in conventional composites exist as layered materials, with the layers held together by van der Waals forces without any intercalation or exfoliation. Exfoliated nanocomposites, however, have exfoliated and dispersed graphite platelets with a 1-nm thickness and widths of several hundred nanometers. Figure 1(a,b) shows the morphology with transmission electron microscopy and scanning electron microscopy from both the edge and lateral views of xGnPs inside a polymer.<sup>8</sup> The distance between the layers was in the range of 10–30 Å, and the size of the layered graphite extended from several hundred nanometers to several micrometers.

Square plates of the Derakane 411-350 vinyl ester and its nanocomposites with nominal dimensions of 254 × 254 × 9.9 mm<sup>3</sup> (10" × 10" × 0.39") were

prepared at the Composite Materials and Structures Center of Michigan State University. Prismatic samples with nominal dimensions of  $35 \times 10 \times 1.6 \text{ mm}^3$  were prepared from these plates and tested with a dynamic mechanical analyzer with a single-cantilever clamp fixture.

### Experimental setup

Because a material's modulus is independent of its geometry, equations relating the sample stiffness to the modulus depend on the clamping conditions, sample shape, and deformation mode. The stiffness calculation for the single-cantilever clamp used in the TA Instruments (New Castle, DE) model Q800 dynamic mechanical analyzer along with the appropriate correction factor is described. Also included are stress and strain equations calculated from the force and deformation amplitude. The maximum level of strain occurs at the sample surface, whereas the center experiences no strain at all, provided that the stress and strain equations assume linear viscoelastic behavior. The stiffness model and maximum stress and strain level equations for a rectangular cross-section sample, analyzed on a single-cantilever clamp,<sup>9</sup> are as follows:

$$E = \frac{K_S L^3}{F_C 12I} \left[ 1 + \frac{12}{5} (1 + \nu) \left( \frac{t}{L} \right)^2 \right] \quad (2)$$

$$F_C = 0.7616 - 0.02713 \sqrt{\frac{L}{t}} + 0.1083 \ln \left( \frac{L}{t} \right) \quad (3)$$

$$\sigma_x = \frac{6PL}{wt^2} \quad (4)$$

$$\epsilon_x = \frac{3\delta t F_C}{L^2 \left[ 1 + \frac{12}{5} (1 + \nu) \left( \frac{t}{L} \right)^2 \right]} \quad (5)$$

where  $E$  is the elastic modulus,  $L$  is the clamp span length,  $w$  is sample width,  $K_S$  is the measured stiffness,  $t$  is the sample thickness,  $I$  is the sample moment of inertia,  $\nu$  is Poisson's ratio,  $F_C$  is the clamping correction factor,  $\sigma_x$  is the stress,  $\epsilon_x$  is the strain,  $P$  is the applied force, and  $\delta$  is the amplitude of deformation.

### Test description

Derakane 411-350 vinyl ester samples with 1.25 and 2.5 wt % nanoclay and xGnPs were tested in a TA Instruments model Q800 dynamic mechanical analyzer using a single-cantilever clamp with a span of 17.5 mm and a preload stress of 3 MPa. The preload

stress of 3 MPa was chosen because the linear viscoelastic theory is applicable when stresses are low. Two samples were tested from each configuration.

Short-term creep tests were carried out by the subjection of the samples to a constant load over 30 min at isothermal temperatures in the dynamic mechanical analyzer. RT fluctuated between 28 and 30°C. A temperature range of 28–100°C was chosen as this covered  $T_g$  for all the nanocomposites that were investigated. The sample was initially equilibrated at 28°C for about 4 min to ensure that the sample temperature settled down. After equilibrium, the sample was subjected to a fixed stress of 3 MPa for about 30 min. The temperature was then increased by 4°C, and the aforementioned procedure was repeated until the final temperature of 100°C.

In the stress relaxation mode, the sample was held at a constant strain, and the stress level was measured as a function of time over the same temperature range. The method segments executed during the relaxation test were the same as those used in the creep test. The sample was initially equilibrated at RT for about 4 min and then displaced 0.1 mm for 30 min. The temperature was then increased by 4°C, and the process was repeated until the final temperature of 100°C.

### MODEL FORMULATION

The Maxwell model is a basic deformation behavior model for polymers; other models such as the Kelvin model and standard linear solid (SLS) are modifications of this model designed to better describe the deformation behavior.<sup>1</sup> Figure 2 shows the SLS model consisting of a Maxwell element (a linear spring and a dashpot in series) and a linear spring in parallel. This model has been chosen because it can describe stress relaxation and creep behavior and also can explain the two main deformations of plastics,<sup>10</sup> the spring represents deformations due to bending and stretching of intermolecular bonds, whereas the dashpot represents deformation due to a viscous effect. Some correlations have been made with the mechanical model, such as the effect of temperature on the mechanical behavior, which is well explained by the dashpot mechanism. For instance, at high temperatures, the viscosity in the dashpot decreases, and this results in greater extensions, whereas at lower temperatures, the dashpot becomes more viscous, and less deformation takes place; this is similar to the creep response observed at RT.

In the SLS model, the total stress ( $\sigma_{\text{tot}}$ ) is decomposed into the rate-dependent stress component in the spring ( $E_2$ ) and dashpot ( $\eta$ ) and the rate-independent equilibrium stress ( $\sigma_1$ ) in the spring ( $E_1$ ). The strain in the Maxwell element ( $E_2, \eta$ ) is the same

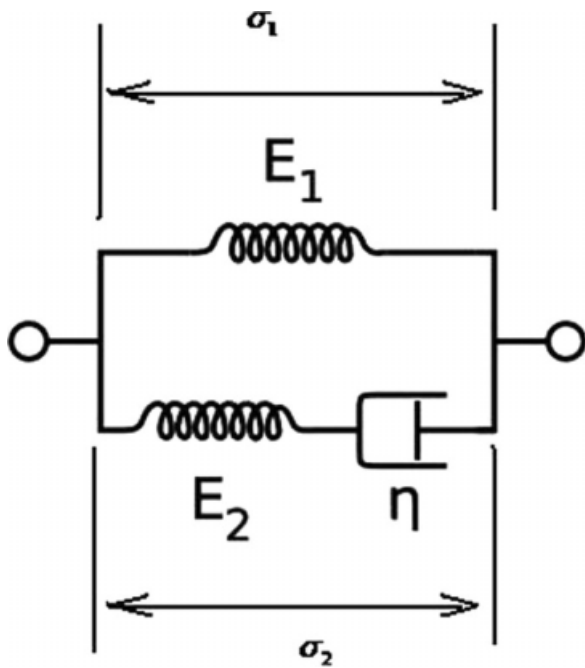


Figure 2 Schematic of the SLS model.

as that in the elastic spring parallel to it and can be substituted by the total strain ( $\epsilon$ ).<sup>7</sup>

The elastic constitutive equation in the spring follows Hooke's law:

$$\sigma_1 = E_1 \epsilon \tag{6}$$

$$\sigma_{tot} = \sigma_1 + \sigma_2 \tag{7}$$

The governing equation for the Maxwell element is

$$\frac{\sigma_2}{\eta} + \frac{1}{E_2} \sigma_2' = \epsilon' \tag{8}$$

where  $\epsilon'$  and  $\sigma_2'$  are time derivatives of the total strain and the stress component in the Maxwell element, respectively. With eqs. (6)–(8), the governing equation for the total stress in the SLS model can be obtained as follows:

$$\frac{d\epsilon}{dt} = \frac{(d\sigma_{tot}/dt) + \frac{E_2}{\eta} (\sigma_{tot} - E_1 \epsilon)}{E_1 + E_2} \tag{9}$$

The solution of eq. (9) defines the stress–strain relationship at a constant strain rate for the proposed model, whereas the creep behavior can also be modeled with eq. (9), with  $d\sigma_{tot}/dt = 0$  and  $\sigma_{tot} = \sigma_0$ . Then, the governing equations for this model under creep and stress relaxation are reduced to the forms given in eqs. (10) and (11), respectively:

$$\sigma_0 = E_1 \epsilon + \frac{\eta}{E_2} (E_1 + E_2) \epsilon' \tag{10}$$

$$0 = \frac{d\sigma}{dt} + \frac{E_2}{\eta} (\sigma - E_1 \epsilon) \tag{11}$$

RESULTS AND DISCUSSION

The initial portion of a typical stress–strain curve for plastics loaded in tension under a constant strain rate is linear and follows Hooke's law.<sup>3</sup> As expected, the shape of the creep and relaxation curves for these vinyl ester nanocomposites is strongly dependent on the temperature. As an illustration, the effect of temperature on the creep and relaxation behavior of the pure vinyl ester and the 2.5 wt % nanoclay reinforced samples over 30 min is shown in Figures 3(a,b) and 4(a,b), respectively. The creep deformations in the initial (pure elastic) portion are relatively

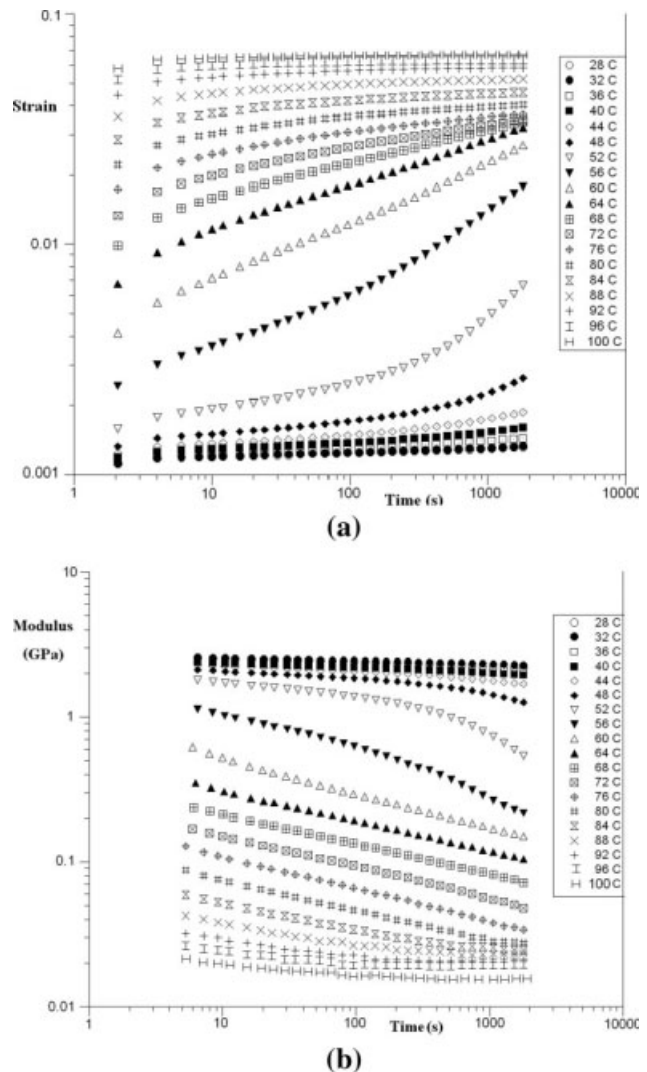
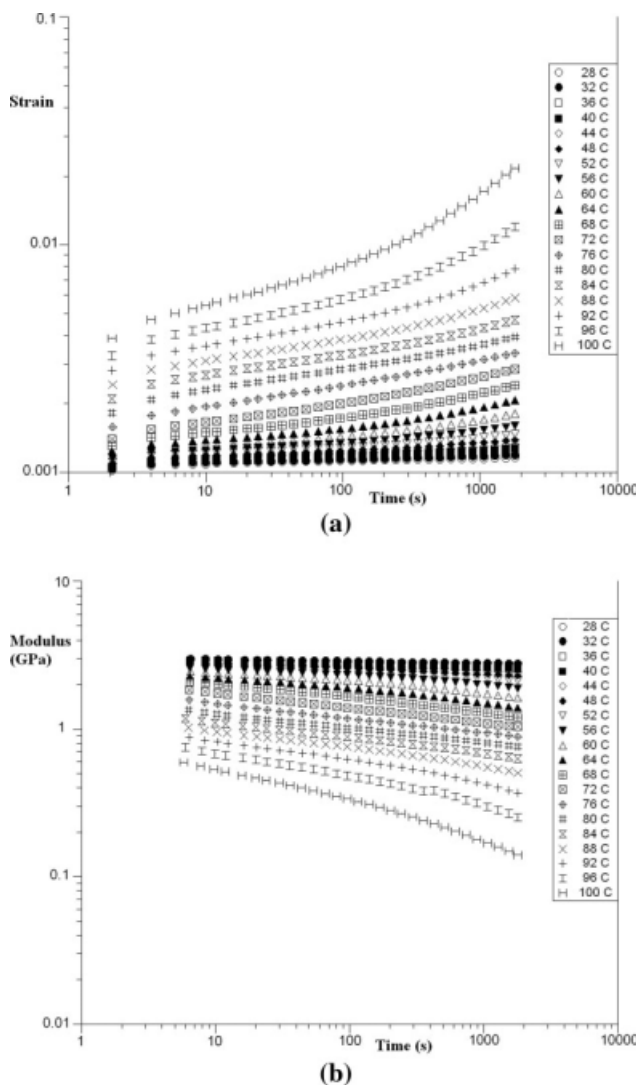


Figure 3 (a) Creep strain and (b) relaxation modulus for the pure vinyl ester.



**Figure 4** (a) Creep strain and (b) relaxation modulus for 2.5 wt % nanoclay vinyl ester.

small and are associated with bending and stretching of intermolecular bonds. However, the deformation that occurs beyond the proportional limit is similar to a straightening of the folded molecular chains, which is recoverable but not instantaneously. Thus, the mechanical response appears to exist in the viscoelastic linear region, in which no permanent deformation due to intermolecular slippage occurs.

At a lower temperature, much higher creep compliance was observed for the vinyl ester in comparison with the nanocomposites. At temperatures beyond  $T_g$  of the pure vinyl ester, creep compliance in the nanocomposites became closer in magnitude to that for the vinyl ester. Also, the rubbery region was more prominent for the pure vinyl ester, as indicated by the dramatic drop in the modulus at temperatures greater than its  $T_g$  (66°C). The 2.5 wt %

nanoclay vinyl ester, however, still behaved as a solid with a modulus around 0.3 GPa beyond its glass transition.

**Development of the modified SLS model**

Data from the relaxation experiments at a given temperature were used to calculate  $E_1$  in the SLS model, which was associated with the rate-independent equilibrium stress or was approximately the same as the stress–strain curve without any viscosity effect. The initial modulus of the given model ( $E$ ) is the sum of the moduli of the two linear springs, that is,  $E_1 + E_2$ , which is also obtained from relaxation data at a time equal to zero. The relationship between  $E_1 + E_2$  and  $E$  as a function of temperature was determined for the pure vinyl ester by the curve fitting of the relaxation data:

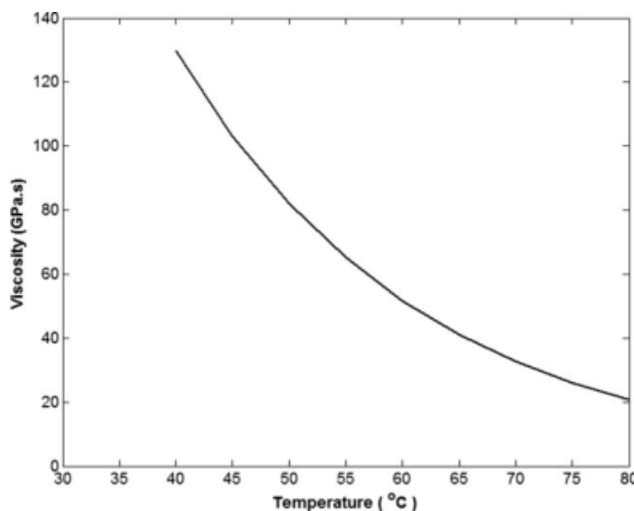
$$E = -10^{-6}T^4 + 0.0004T^3 - 0.034T^2 + 1.27T - 13.5 \tag{12}$$

$$E_1 = 29.86 \exp(-0.082T) \tag{13}$$

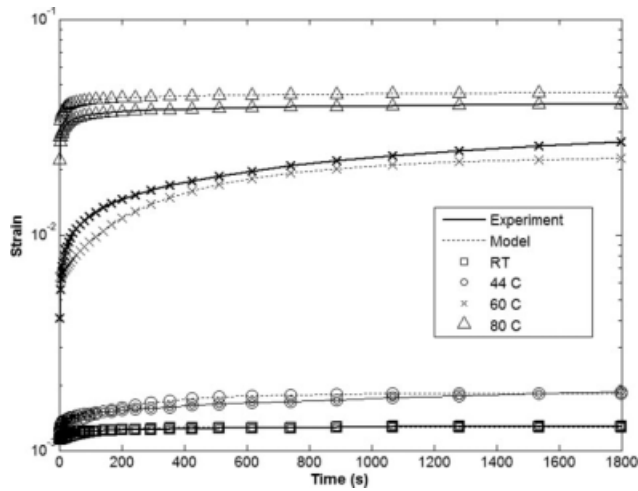
$E_2$  was subsequently derived by the subtraction of  $E_1$  in eq. (13) from  $E$  in eq. (12) at different temperatures. The variation of  $E_2$  with temperature is thus given by

$$E_2 = -10^{-6}T^4 + 0.0004T^3 - 0.034T^2 + 1.27T - 13.5 - 29.86 \exp(-0.082T) \tag{14}$$

On the basis of this analysis, the solution of eq. (10) defines the creep strain response as per the SLS model:



**Figure 5** Relationship between  $\eta$  and the test temperature (°C) in the SLS model for the pure vinyl ester.



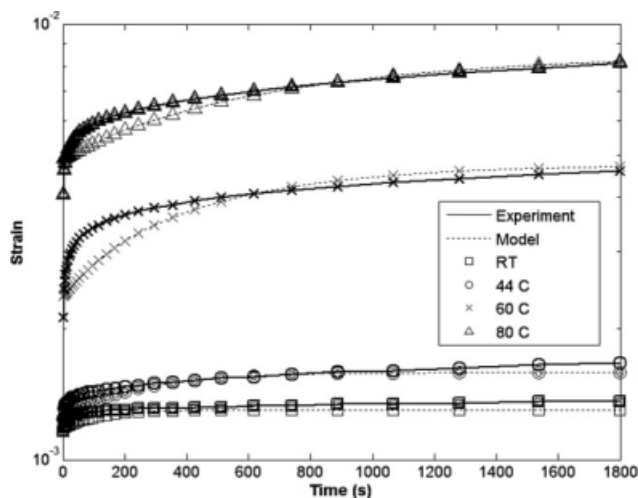
**Figure 6** Predicted and experimental results of the creep strain versus time for the pure vinyl ester at selected temperatures on the basis of the viscoelastic model.

$$\varepsilon(t) = \frac{\sigma_0}{E_1} \left[ 1 - \frac{E_2}{E_1 + E_2} \exp(-t/\rho) \right] \quad (15)$$

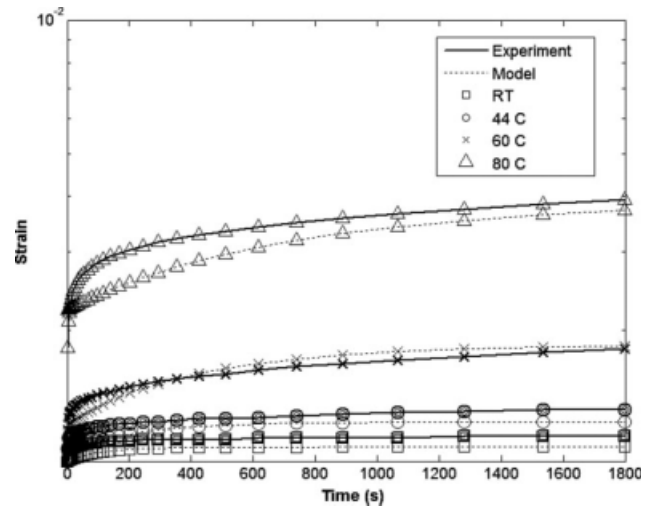
where

$$\rho = (\eta/E_1 E_2)(E_1 + E_2) \quad (16)$$

The parameter  $\rho$  is a constant proportional to the viscous effect in the model as expressed in eq. (16). To find an optimized value for  $\rho$ , a least-squares curve-fitting program in Microsoft Excel was applied to fit eq. (15) for all vinyl ester nanocomposites to the creep strain data curves obtained from creep experiments at room temperature ( $T_r$ ). The viscosity



**Figure 7** Predicted and experimental results of the creep strain versus time for the 1.25 wt % nanoclay vinyl ester at selected temperatures on the basis of the viscoelastic model.

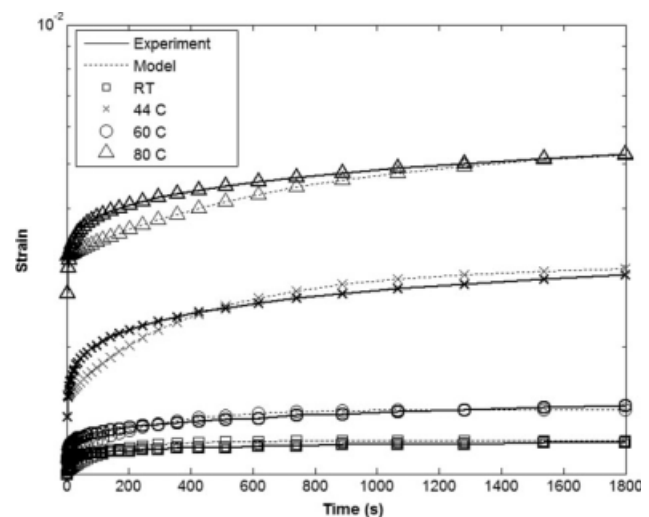


**Figure 8** Predicted and experimental results of the creep strain versus time for the 2.5 wt % nanoclay vinyl ester at selected temperatures on the basis of the viscoelastic model.

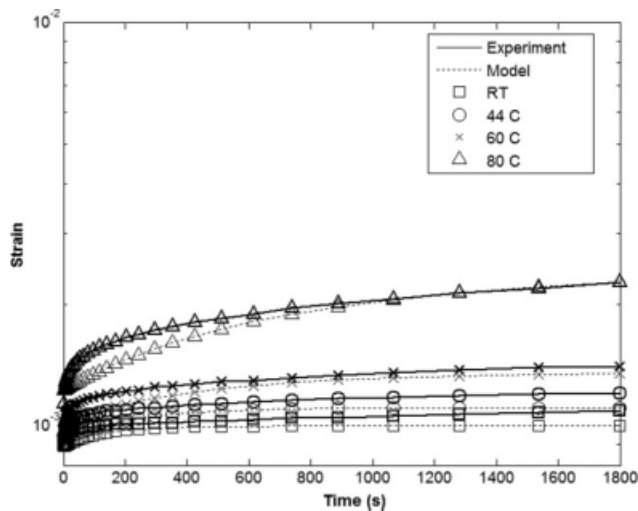
parameter ( $\rho$ ) was then modified in a way similar to that suggested by Khan et al.<sup>11</sup> to predict the actual creep behavior of all the nanocomposites at a specific operating temperature ( $T$ ):

$$\rho = \text{Constant} \left( \frac{T_r}{T} \right)^m \quad (17)$$

The value of  $m$  was calculated to be 0.44 from the least-squares curve fitting. Figure 5 shows  $\eta$  as a function of temperature for the pure vinyl ester, and as expected,  $\eta$  decreased when the temperature increased and vice versa, reflecting the physical behavior of the dashpot mechanism.



**Figure 9** Predicted and experimental results of the creep strain versus time for the 1.25 wt % graphite platelet vinyl ester at selected temperatures on the basis of the viscoelastic model.



**Figure 10** Predicted and experimental results of the creep strain versus time for the 2.5 wt % graphite platelet vinyl ester at selected temperatures on the basis of the viscoelastic model.

**Comparison of the model predictions with the dynamic mechanical analysis test results**

Creep strain data at representative temperatures obtained from the creep tests are plotted in Figure 6 along with the strain predicted from eq. (15), including the modified effect of viscosity in eq. (17). As can be seen from this figure, the model can predict the strain–time behavior of the pure vinyl ester reasonably well except at high temperatures (>66°C), at which the onset of the rubbery region started earlier with complete motion of molecular segments occurring for the pure vinyl ester polymer in comparison with the nanocomposites. Again, the elastic constants ( $E_1$  and  $E_2$ ) for 1.25 and 2.5 wt % nanoclay and graphite platelet reinforced vinyl ester materials were obtained from their respective relaxation data; the viscosity constant ( $\rho$ ) developed in eq. (17), however, varied with the temperature. Agreement between the model predictions and creep data for the nanocomposites was better than that for the pure vinyl ester, as shown in Figures 7–10.

**CONCLUSIONS**

The viscoelastic behavior of vinyl ester nanocomposites was characterized with creep and relaxation tests using a DMA Q800 at various isothermal tem-

peratures. The SLS model was used in this study to model the creep behavior of the vinyl ester nanocomposites. This physical model is a modification of the Kelvin and Maxwell model, consisting of a Maxwell model with a linear spring and a dashpot in series together and then both in parallel with a linear spring. After the elastic constants for this model were obtained from relaxation test data at various isothermal temperatures, predictions of creep strain behavior were performed and shown to be in reasonable agreement with the experimental data for the vinyl ester nanocomposites. The dashpot parameter of the SLS model was then modified to reflect the variation of the deformation behavior with the temperature. The predicted creep behavior based on the modified constants showed good correlations with the experimental results, especially at temperatures lower than the sample’s  $T_g$ . In summary, the modified SLS model provides a good representation of the constitutive behavior of vinyl ester nanoclay and graphite platelet nanocomposites in viscoelastic deformation regimes as a function of temperature.

The nanoclay and graphite platelet/vinyl ester composite plates were manufactured by Larry Drzal’s group at Michigan State University Composite Materials and Structures Center.

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