

Creep and Stress Relaxation Modeling of Nanoclay and Graphite Platelet Reinforced Vinyl ester Nanocomposites

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ABSTRACT

This paper discusses the viscoelastic behavior of 1.25 and 2.5 wt. % nanoclay and graphite platelet reinforced vinyl ester under short term creep and relaxation tests using a Dynamic Mechanical Analyzer (DMA). 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 DMA was used to obtain the elastic parameters based on model constitutive equations. The Standard Linear Solid (SLS) model, which is a physical model, was used for predicting the creep deformation behavior of the vinyl ester nanocomposites over a wide temperature range. This model was chosen because it can describe the stress relaxation and creep behavior of polymers and can also explain the two main deformations of plastics [1]; with the spring representing deformations due to bending and stretching of intermolecular bonds and dashpot represents deformation due to the viscous effect. Some correlations have been made with the mechanical model, such as the effect of temperature on the deformation behavior which is well explained in the dashpot mechanism. At lower temperatures, higher creep compliance was observed for vinyl ester as compared to nanocomposites, while at temperatures near the T_g of vinyl ester, creep compliance in nanocomposites becomes closer in magnitude to that for vinyl ester. Creep response of pure vinyl ester appears to be modeled reasonably well at temperatures lower than its T_g (66 C). Comparison between the predictions and experimental data from creep tests demonstrate that this model can represent the long term deformation behavior of these nano reinforced materials reasonably well.

INTRODUCTION

Composite materials with polymer matrices exhibit viscoelastic behavior which is directly related to molecular structure and formulation differences. A polymer at specific temperature and molecular weight may behave as liquid or a solid depending on the time scale at which its molecules are deformed.

In cross-linked polymers, the cross-linking acts to decrease the viscous component of viscoelastic behavior, as the chains are prevented from slipping past one another. Understanding 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 the specimen maintained at constant temperature and the strain data is collected as a function of time. When a load is

applied, an instantaneous deformation occurs as a pure elastic response. This deformation is followed by a rapidly decreasing deformation called primary deformation [1]. Then, it is followed by steady state linear deformation called secondary deformation. Creep behavior of a polymer also depends heavily on the material temperature during testing and has the highest rate of deformation around the glass transition temperature. Creep behavior of many plastics was fitted into analytical relationship similar to those proposed for metals. Findley [2] demonstrated that creep-strain and time could be related by the following equation:

$$\varepsilon(t) = \varepsilon_0 + m t^n \quad (1)$$

where ε_0 is instantaneous strain and, m , and, n , are the material constants which depend on both stress and temperature. The restriction of this empirical approach is that it does not provide a physical representation for creep deformation, recovery, and behavior under different loading conditions.

Bakis and Temple-Boyer [3] studied the tensile creep response of coupon-type specimens made of epoxy reinforced with up to 3 wt % single-walled carbon nanotubes. Master creep compliance curves were constructed at 40 C reference temperature based on the time-temperature superposition principle, and Findley-type creep law for the creep-strain was fit to the master curves according to Equation (1).

Many physical models have described the time dependent mechanical behavior of polymers. Most of these models are developed to characterize the strain rate dependence, creep and stress relaxation over the viscoelastic regime [4, 5]. Linear viscoelastic models are generally composed of one or several elements such as dashpots and springs that represent the viscous and elastic properties. 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 [1]. 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 due to their enhanced mechanical properties. They exhibit characteristics similar to epoxy resins, as well as unsaturated polyester resins. Advantages include high tensile strength and stiffness, low cost, process versatility and good chemical resistance. The deformation behavior of vinyl ester polymer at a wide range of strain rate (0.0001-1/s) and temperatures (room temperature, RT to 100C) was investigated by Plaseied and Fatemi [6] under monotonic tensile loading and relaxation conditions. In our work, the effect of temperature on creep deformation behavior of vinyl ester and its nanocomposites with 1.25 and 2.5 wt.% nanoclay and graphite platelets was investigated.

The objective is to develop constitutive models to describe the viscoelastic behavior and characterize the temperature dependent mechanical response of vinyl ester nanocomposites.

MODEL FORMULATION

The Maxwell model is a basic deformation behavior model for polymers; other models such as Kelvin model and Standard Linear Solid (SLS) are modifications of this model to better describe the deformation behavior [1]. Figure 1 shows the Standard Linear Solid model consisting of a Maxwell element (linear spring and 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 [7]; the spring represents deformations due to bending and stretching of intermolecular bonds, where as the dashpot represents deformation due to 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 in the dashpot mechanism [1]. For instance, at high temperatures, the viscosity in the dashpot decreases resulting in greater extensions, while at lower temperatures the dashpot becomes more viscous and lesser deformation takes place similar to the creep response observed at RT.

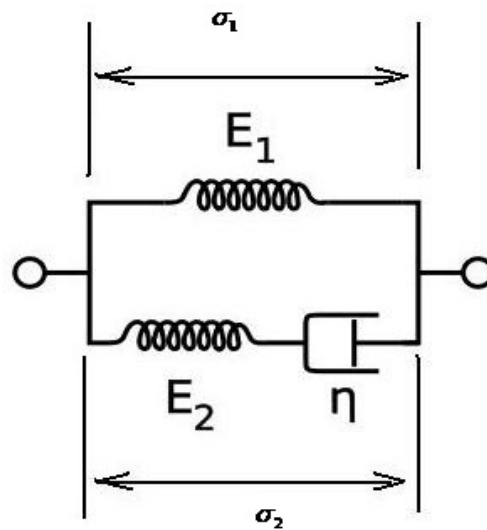


Figure 1. Schematic of the Standard Linear Solid (SLS) model.

In the SLS model, the total stress is decomposed into rate dependent stress component in the spring E_2 and dashpot η and rate independent equilibrium stress (σ_1) in the spring E_1 . The strain in the Maxwell element (E_2, η) is the same as the one in the elastic spring parallel to it, and can be substituted by total strain ϵ [6]. The elastic constitutive equation in the spring follows Hook's law:

$$\sigma_1 = E_1 \varepsilon \quad (2)$$

$$\sigma_{tot} = \sigma_1 + \sigma_2 \quad (3)$$

The governing equation for Maxwell element is:

$$\frac{\sigma_2}{\eta} + \frac{1}{E_2} \sigma_2' = \varepsilon' \quad (4)$$

Using Equations (2), (3) and (4), the governing equation for the total stress in Standard Linear Solid model can be obtained as

$$\frac{d\varepsilon}{dt} = \frac{(d\sigma_{tot}/dt) + \frac{E_2}{\eta}(\sigma_{tot} - E_1\varepsilon)}{E_1 + E_2} \quad (5)$$

The solution of Equation (5) defines the stress-strain relationship at a constant strain rate for the proposed model, while the creep behavior can also be modeled using the same Equation with $\frac{d\sigma}{dt} = 0$, $\sigma_{tot} = \sigma_o$. Then the governing equations for this model under creep and stress relaxation are reduced to the forms given in Equations (6) and (7), respectively.

$$\sigma_o = E_1\varepsilon + \frac{\eta}{E_2}(E_1 + E_2) \varepsilon' \quad (6)$$

$$0 = \frac{d\sigma}{dt} + \frac{E_2}{\eta}(\sigma - E_1\varepsilon) \quad (7)$$

EXPERIMENTAL SETUP

Since a material's modulus is independent of its geometry, equations relating the sample stiffness to the modulus depend on clamping conditions, sample shape and deformation mode. The stiffness calculation for the single cantilever clamp type along with the appropriate correction factor is described. Also, included are stress and strain equations calculated from force and deformation amplitude. The maximum level of strain occurs at the sample surface, while the centre experiences no strain at all, providing stress and strain equations assume linear viscoelastic behavior. The stiffness model, maximum stress and strain level equations for a rectangular cross section sample, analyzed on the single cantilever clamp [8] are given as:

$$E = \frac{K_s}{F_c} \frac{L^3}{12 I} \left[1 + \frac{12}{5} (1 + \nu) \left(\frac{t}{l} \right)^2 \right] \quad (8)$$

$$F_c = 0.7616 - 0.02713 \sqrt{\frac{L}{t}} + 0.1083 \ln\left(\frac{L}{t}\right) \quad (9)$$

$$\sigma_x = \frac{6 P L}{w t^2} \quad (10)$$

$$\varepsilon_x = \frac{3 \delta t F_c}{L^2 \left[1 + \frac{12}{5} (1 + \nu) \left(\frac{t}{l} \right)^2 \right]} \quad (11)$$

where:

E = elastic modulus

L = clamp span length

K_s = measured stiffness

t = sample thickness

I = sample moment of inertia

ν = Poisson's ratio

F_c = clamping correction factor

σ_x = stress

ε_x = strain

P = applied force

δ = amplitude of deformation

TESTS DESCRIPTION

Vinyl ester samples with 1.25 and 2.5wt. % of nanoclay and graphite platelets were tested in a TA Instrument Model Q800 DMA using single-cantilever clamp with a span of 17.5 mm and a pre-load stress of 3 MPa. The preload stress of 3 MPa is

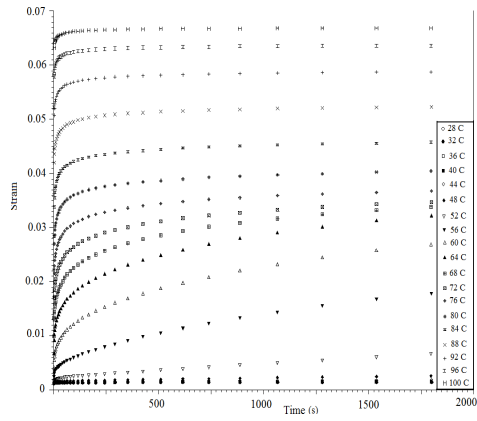
chosen based on the fact that Linear viscoelastic theory can be applicable when stresses are low. Specimen dimensions were $35 \times 10 \times 1.6$ mm and two samples were tested from each configuration.

Short-term creep tests were carried out by subjecting the samples to a constant load over 30 minutes duration at isothermal temperatures in the DMA. The room temperature (RT) fluctuated between 28-30°C. A temperature range of 28°C through 100°C was chosen, as this covered the glass transition temperature for all the nanocomposites that were investigated. The sample was initially equilibrated at 28°C for about 4 minutes to make sure that the sample temperature settles down. After equilibrium, the sample was subjected to a fixed stress of 3 MPa for about 30 minutes. The temperature was then incremented by 4°C and the above procedure repeated till the final temperature of 100°C.

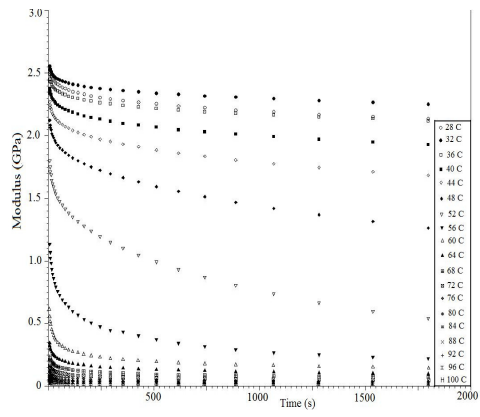
In the stress relaxation mode, the sample was held at a constant strain and the stress level measured as a function of time over the same temperature range. The method segments executed during the relaxation test was the same as that used in creep. The sample is initially equilibrated at RT for about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

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 it follows Hooke's law [3]. As expected, shape of the creep and relaxation curves for vinyl ester nanocomposites is strongly dependent on temperature. As an illustration, the effect of temperature on creep and relaxation behavior of pure vinyl ester and the 2.5 wt.% nanoclay reinforced samples over 30 minutes duration is shown in Figures 2(a,b) and 3(a,b) respectively. The creep deformations in the initial (pure elastic) portion are relatively small and associated with bending and stretching of intermolecular bonds. However, the deformation that occurs beyond the proportional limit is similar to a straightening out of the folded molecular chains which is recoverable but not instantaneously. Thus, the mechanical response appears to exist in the viscoelastic linear region, where no permanent deformation due to intermolecular slippage occurs. At lower temperature, much higher creep compliance was observed for vinyl ester as compared to nanocomposites. At temperatures beyond T_g of pure vinyl ester, creep compliance in nanocomposites becomes closer in magnitude to that for vinyl ester. Also, the rubbery region is more prominent for pure vinyl ester, as indicated by the dramatic drop in modulus at temperatures greater than its glass transition temperature (66 C). The 2.5 wt.% nanoclay vinyl ester, however, is still behaving as a solid with a modulus of 0.25 GPa beyond its glass transition.

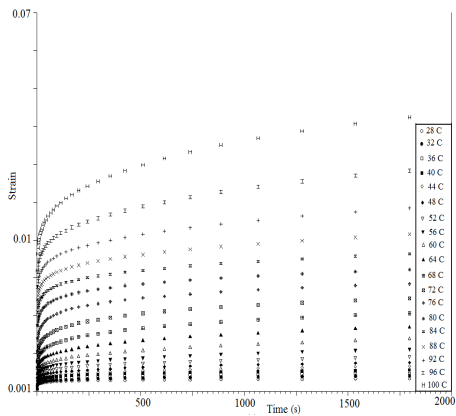


(a)

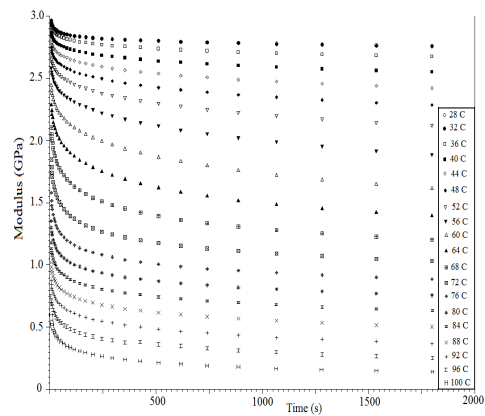


(b)

Figure 2. (a) creep-strain, and (b) relaxation modulus for pure vinyl ester.



(a)



(b)

Figure 3. (a) creep-strain, and (b) relaxation modulus for 2.5wt. % nanoclay vinyl ester.

DEVELOPMENT OF THE MODIFIED STANDARD LINEAR SOLID MODEL

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

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

$$E_1 = 29.86 \text{ Exp}(-0.082 T) \quad (13)$$

E_2 was subsequently derived by subtracting, E_1 , in Equation (13) from, E , in Equation (12) at different temperatures. Variation of, E_2 , with temperature is given by:

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

Based on the above analysis, the solution of equation 6 defines the creep-strain response as per the SLS model:

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

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

To find an optimized value for the dashpot viscosity, η , a least-squares curve fitting program in Microsoft Excel was applied to fit Equation (15) for all vinyl ester nanocomposites to the creep-strain data curves obtained from creep experiments at room temperatures. The viscosity parameter, η , was then modified, similar to that suggested by Khan et al. [9], to predict the actual creep behavior of all nanocomposites at a specific operating temperature. Therefore, η , in equation (15) is modified as:

$$\eta = \text{constant} \cdot \left(\frac{T_r}{T} \right)^m \quad (17)$$

where T_r (K), T (K) and, m , are the room temperature, operating temperature and material parameter, respectively. The value of, m , was calculated to be 2.27 from

the least-square curve fitting for all nanocomposites. Figure 4 shows the dashpot or fluid viscosity (η) as function of temperature for pure vinyl ester; and as expected, η , decreases when temperature increases and vice versa, in order to reflect the physical behavior of dashpot mechanism.

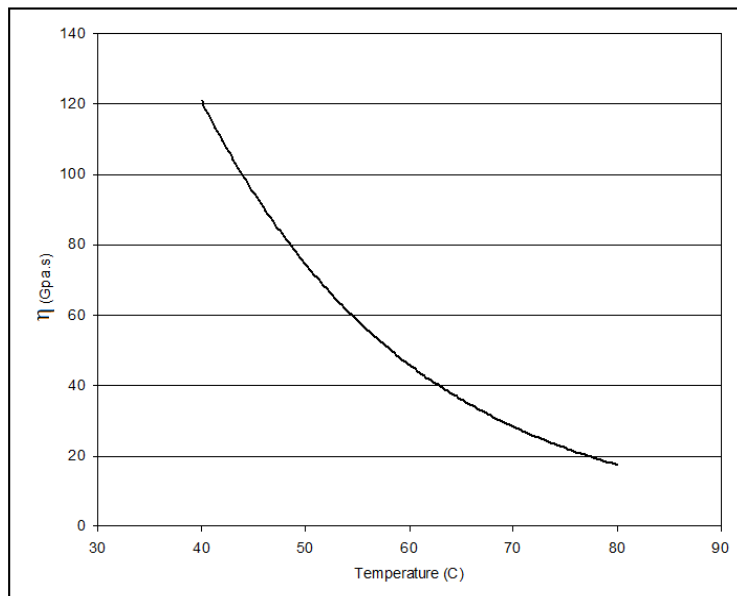


Figure 4. Relationship between viscosity (η) and test temperature (C) in Standard Linear Solid (SLS) model for pure vinyl ester.

COMPARISON OF THE MODEL PREDICTIONS WITH DMA RESULTS

Creep-strain data at representative temperatures obtained from creep tests were plotted (Figure 5) along with the strain predicted from Equation 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 pure vinyl ester reasonably well except at high temperatures (beyond 66° C) where the onset of rubbery region started earlier with complete motion of molecular segments occurred for pure vinyl ester polymer compared to other nanocomposites. Again, the elastic constants (E_1 and E_2) for 1.25 and 2.5 wt. % nanoclay and graphite platelets reinforced vinyl ester materials were obtained from their respective relaxation data; Agreement between model predictions and creep data for vinyl ester nanocomposites was better than that for pure vinyl ester as shown in Figures 6-9.

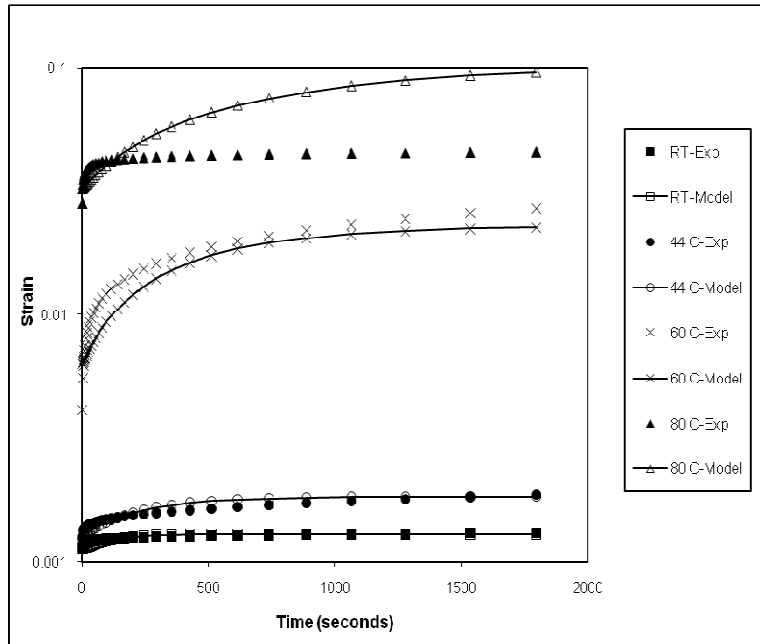


Figure 5. Predicted and experimental results of creep-strain versus time for pure vinyl ester at selected temperatures based on the viscoelastic model.

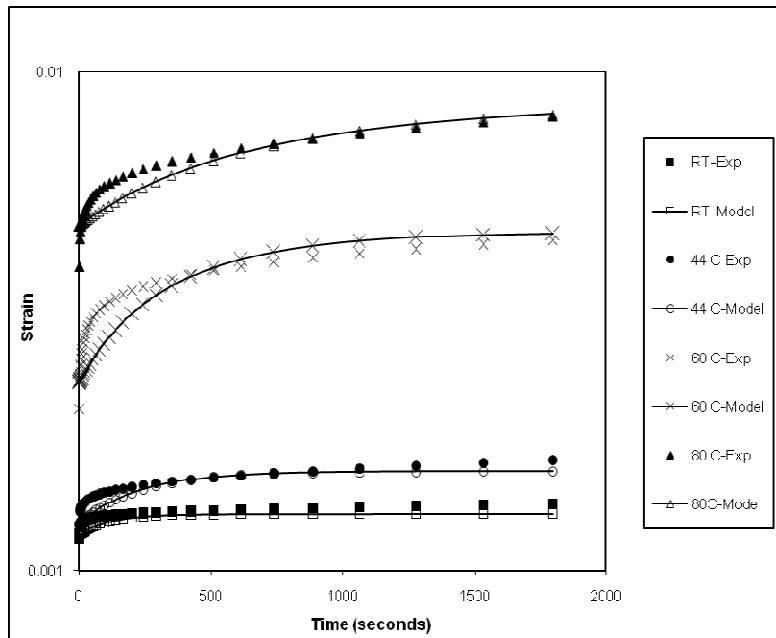


Figure 6: Predicted and experimental results of creep-strain versus time for 1.25 wt.percent nanoclay at selected temperatures based on the viscoelastic model.

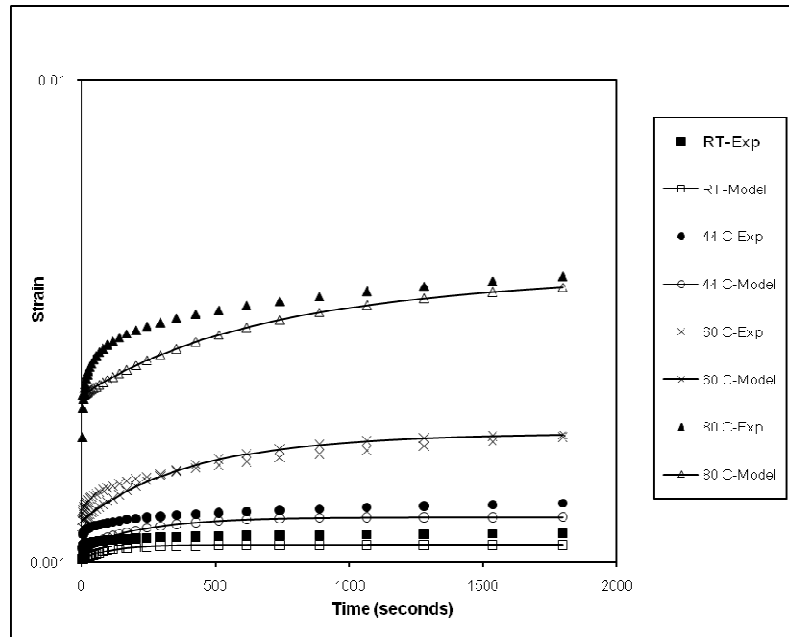


Figure 7. Predicted and experimental results of creep-strain versus time for 2.5 wt. percent nanoclay at selected temperatures based on the viscoelastic model.

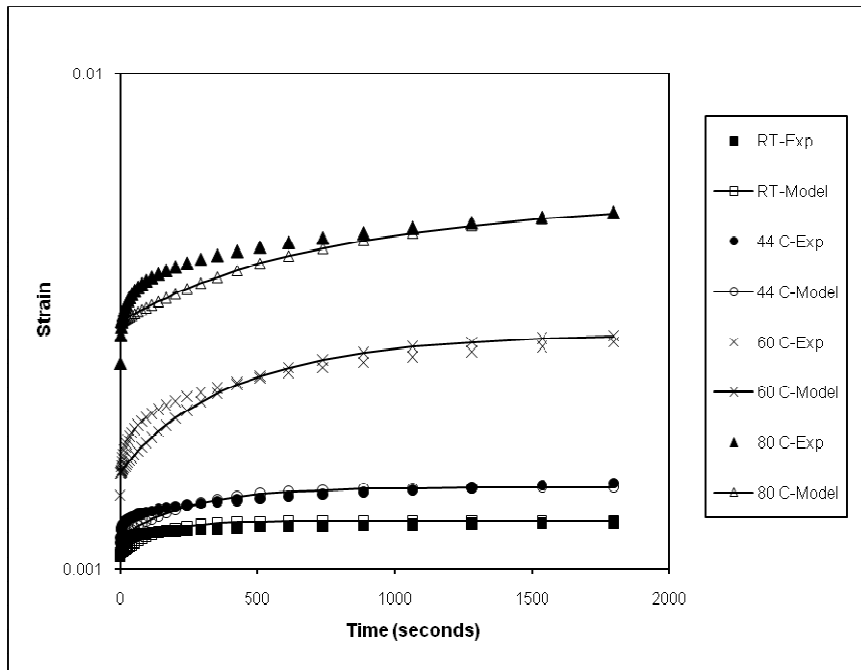


Figure 8. Predicted and experimental results of creep-strain versus time for 1.25 wt. percent graphite platelets at selected temperatures based on the viscoelastic model.

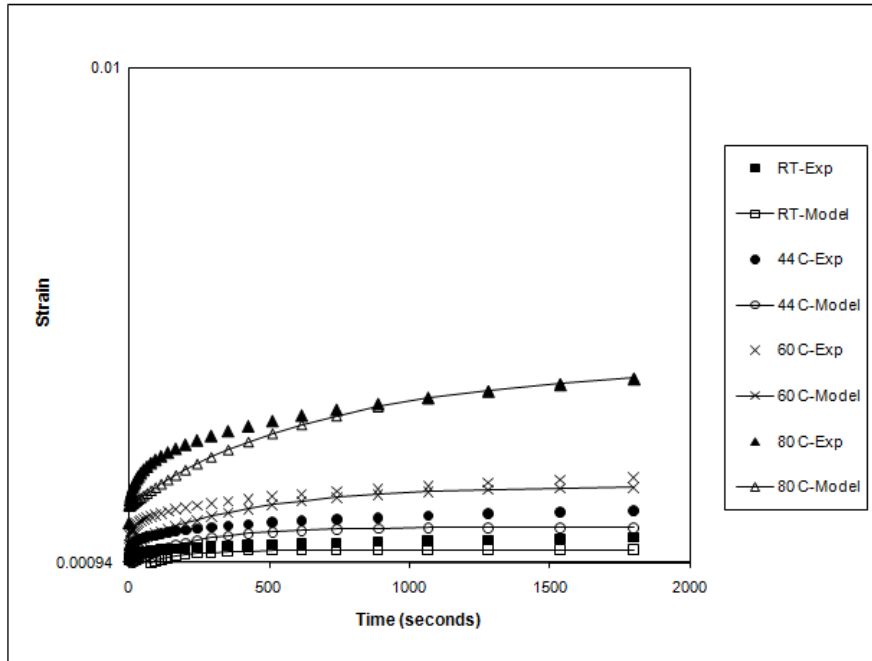


Figure 9. Predicted and experimental results of creep-strain versus time for 1.25 wt. percent graphite platelets at selected temperatures based on the viscoelastic model.

CONCLUSIONS

The viscoelastic behavior of vinyl ester nanocomposites has been characterized by creep and relaxation tests using DMA Q800 over various isothermal temperatures. The Standard Linear Solid (SLS) model was used in this study to model the creep behavior of vinyl ester nanocomposites. This physical model is a modification of 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 obtaining the elastic constants for this model 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 vinyl ester nanocomposites. The dashpot parameter of the Standard Linear Solid model was then modified to reflect the variation of deformation behavior with temperature. The predicted creep behavior based on the modified constants showed good correlations with experimental results, especially at temperatures lower than the samples T_g 's. In summary, the modified Standard Linear Solid model provides a good representation of the constitutive behavior of vinyl ester nanoclay and graphite platelet nanocomposites in the viscoelastic deformation regimes, as a function of temperature.

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