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

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Introduction

- Thermoset vinyl ester matrices are becoming increasingly important because of: high tensile strength and stiffness, low cost, process versatility and good chemical resistance
- 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
- 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.
- Linear viscoelastic models are generally composed of elements such as dashpots and springs that represent the viscous and elastic properties



Objective & Scope

- Findley demonstrated that creep-strain and time behavior for many plastics could be related by the following equation:

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

- Where ε_o is the instantaneous strain, m, and n, are material constants.
- 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 modeled by Plaseied and Fatemi 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 using a Dynamic Mechanical Analyzer (DMA).
- The objective is to develop constitutive model to describe the viscoelastic behavior and characterize the temperature dependent mechanical response of vinyl ester nanocomposites



Model formulation (Standard Linear Solid)

➤ Figure 1 shows the Standard Linear Solid model (SLS) 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 explain the two main deformations of plastics; the spring represents deformations due to bending and stretching of intermolecular bonds, where as the dashpot represents deformation due to viscous effect.

➤ Some modifications have been made to the dashpot element (η), to reflect the effect of temperature on the deformation behavior.

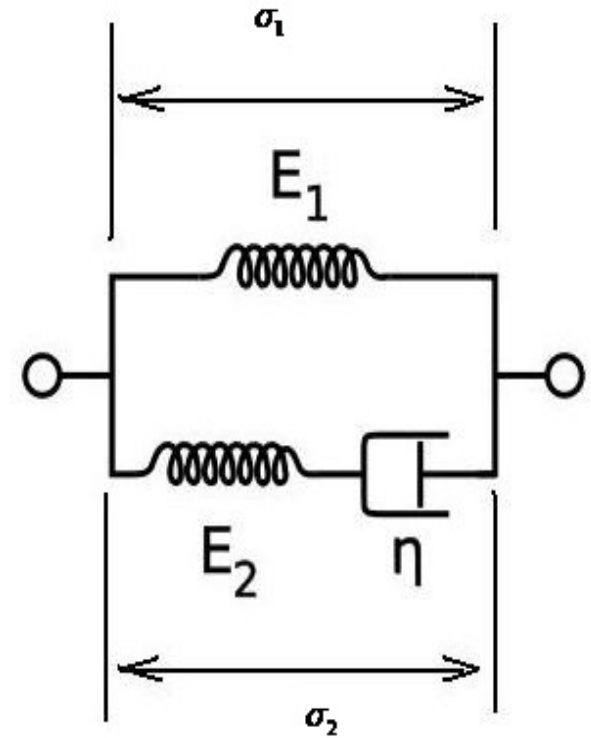


Figure 1: Standard Linear Solid model



➤ 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.

➤ In the SLS model, the total stress is decomposed into rate dependent stress component in the spring E_2 and dashpot and rate independent equilibrium stress in the spring E_1

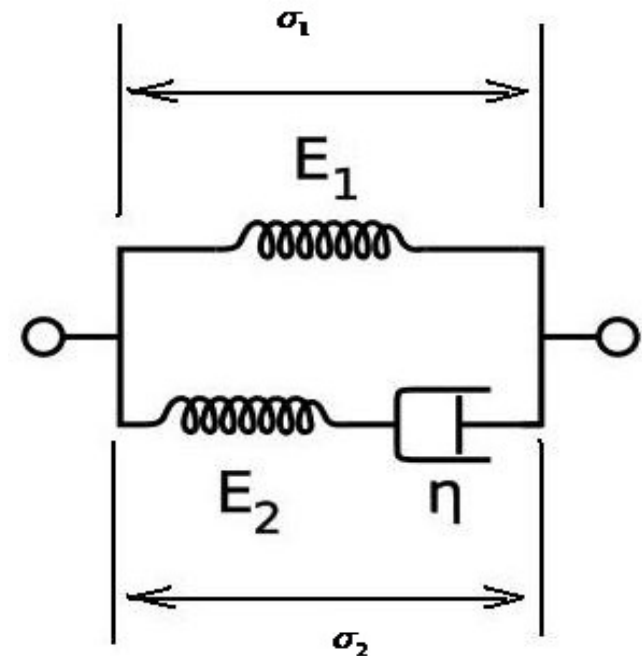
➤ The strain in the Maxwell element is the same as the one in the elastic spring parallel to it:

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

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

Equation for Maxwell element :

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



➤ Combining equations 2, 3 and 4, the governing equation for the total stress in Standard Linear Solid model can be obtained as:

$$\sigma_{tot} + \frac{\eta}{E_2} \sigma'_{tot} = E_1 \varepsilon + \frac{\eta}{E_2} (E_1 + E_2) \varepsilon' \quad (5)$$

➤ The solution of Eq. 5 defines the stress-strain relation at a constant strain rate for the proposed model, while the creep behavior can also be modeled using Eq.5 with:

$$\frac{d\sigma}{dt} = 0, \quad \sigma_{tot} = \sigma_o$$

➤ The governing equations for this model under creep and stress relaxation are described in (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

- Stress and strain are calculated from force and deformation amplitude which is measured using optical encoders in the DMA.
- The stiffness calculation for the single cantilever clamp type along with the appropriate correction factor is described as:

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

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

E = elastic modulus

F_c = clamping correction factor

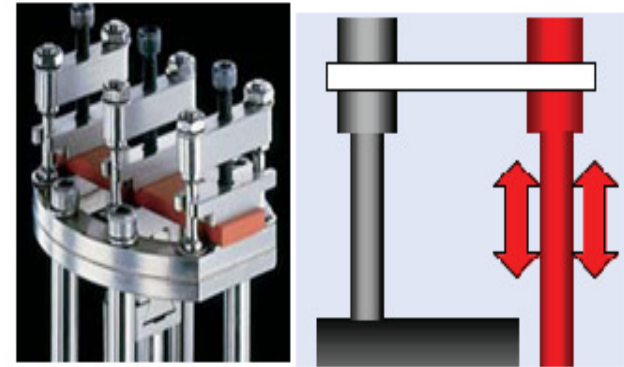
K_s = measured stiffness

L = sample length

ν = Poisson's ratio

t = sample thickness

I = sample moment of inertia



Dual / Single Cantilever



DMA test description

- Vinyl ester samples with 1.25 and 2.5wt. % of nanoclay and graphite platelets were tested in a TA Instruments, model Q800 DMA using single-cantilever clamp with a span of 17.5 mm and a pre-load stress of 3 Mpa.
- **Creep**, the sample was initially equilibrated at 30 C (RT) for about 4 minutes. 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.
- **Stress relaxation**, 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 4C and the process repeated until the final temperature of 100 C.



Experimental Results

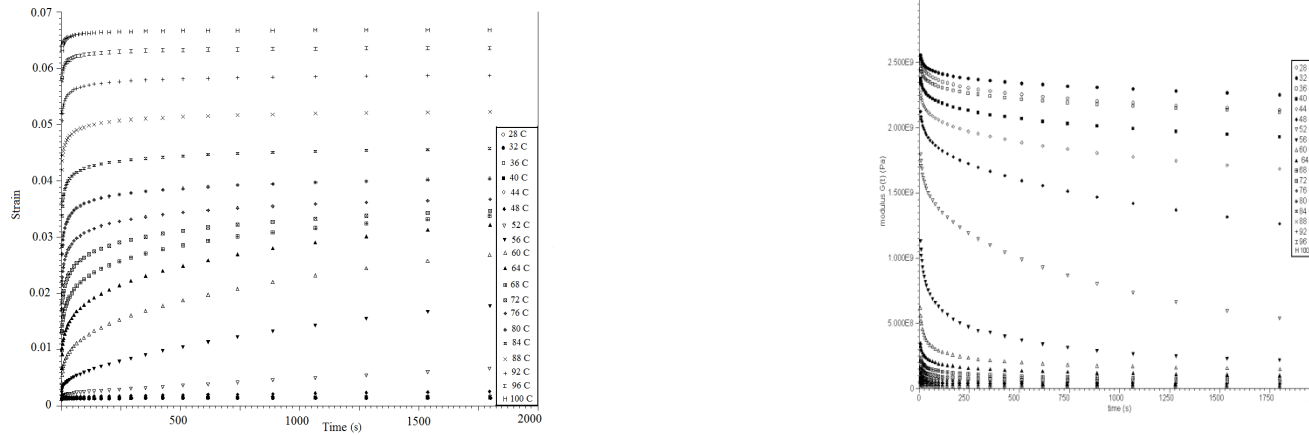


Figure 2: (a) Creep-strain, and (b) relaxation modulus for pure vinyl ester

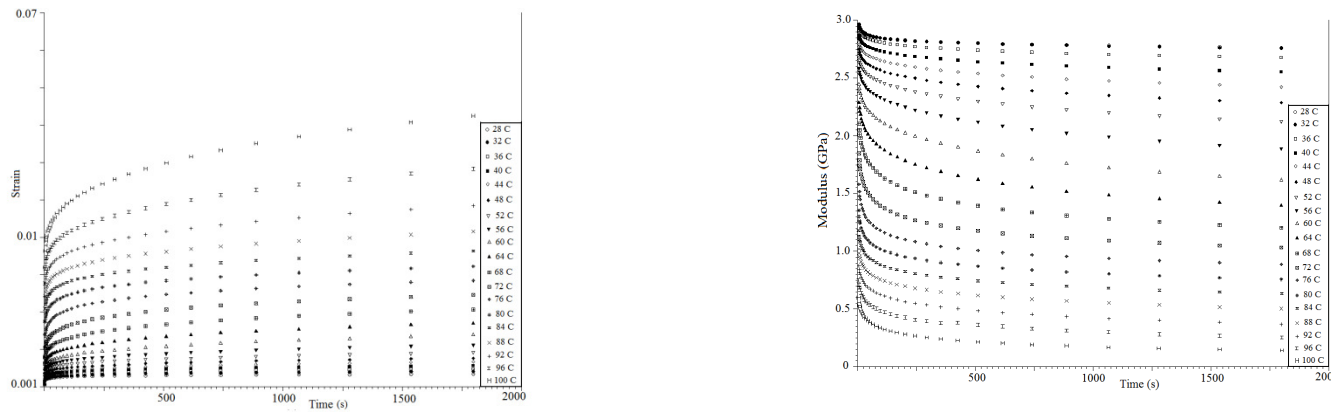


Figure 3: (a) Creep-strain, and (b) relaxation modulus for 2.5wt. % nanoclay vinyl ester.



Experimental Results

- At temperatures beyond T_g of pure vinyl ester, creep compliance in nanocomposites becomes closer in magnitude to that for vinyl ester.
- 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 (65 C).
- The 2.5 wt. percent nanoclay reinforced vinyl ester, however, is still behaving as a solid with a modulus of 0.25 GPa beyond its glass transition.



Development of the SLS 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
- The initial modulus of the relaxation curve, E , is the sum of the modulus of the two linear springs, i.e. $E_1 + E_2$
- The model governing equation for creep is:

$$\varepsilon(t) = \frac{\sigma_o}{E_1} \left[1 - \frac{E_2}{E_1 + E_2} \text{Exp}(-t / \rho) \right] \quad (10)$$

$$\text{where } \rho = (\eta / E_1 E_2) (E_1 + E_2) \quad (11)$$

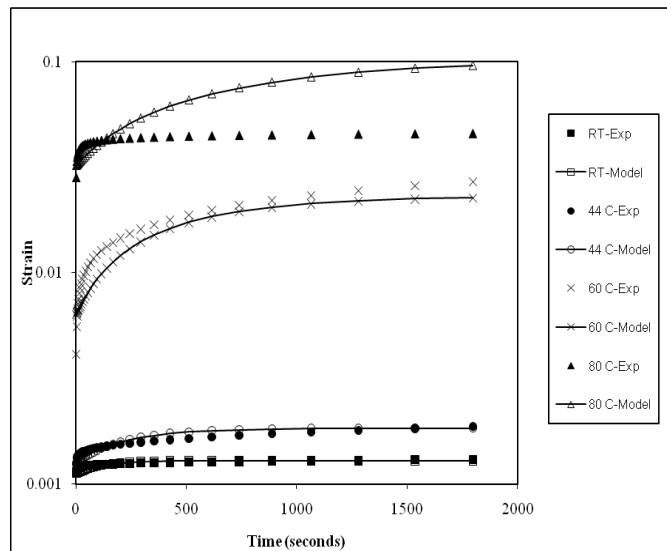
- Viscosity effect in the dashpot is modified to reflect the deformation behavior at elevated temperatures:

$$\eta = \text{constant} \left(\frac{T_r}{T} \right)^m \quad (12)$$

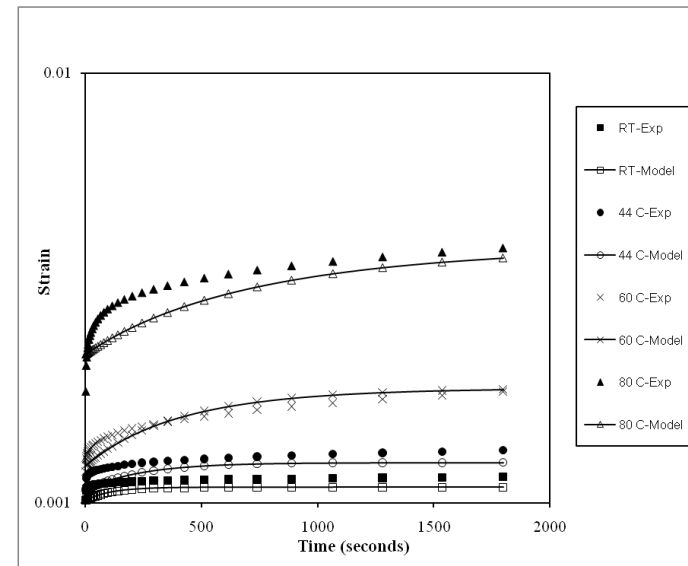


DMA results and model predictions

- The model can predict the strain-time behavior of pure vinyl ester reasonably well, except at higher temperatures beyond 65 C (T_g).
- Agreement between model predictions and creep data for vinyl ester nanocomposites was better than that for pure vinyl ester as shown (Figure 4-b).



(a)



(b)

Figure 4: Predicted and experimental results of creep-strain versus time for (a) pure vinyl ester and (b) 2.5 wt.% nanoclay.



DMA results and model predictions

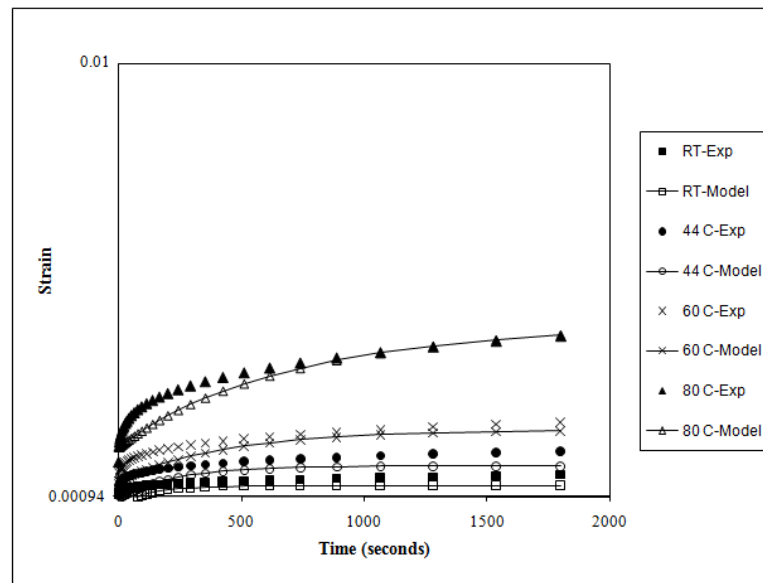


Figure 4: Predicted and experimental results of creep-strain versus time for 2.5 wt.% graphite platelet based on the viscoelastic model



Conclusion

- 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 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 .
- The predicted creep behavior based on the modified model showed good correlations with experimental results, especially at temperatures lower than the samples T_g s.



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Thank You

Questions ?



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