Modeling of Creep Behavior for Graphene Filled Vinyl Ester Nano-Composites

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Abstract

The creep resistance of thermoset vinyl ester-based nanocomposites is studied by adding different weight percents of exfoliated graphite filler, characterized at different temperatures under constant loading. The creep response of these nanocomposites was analyzed using the TA Instruments Model Q800- DMA. Results showed that the nano-filler at some temperatures may hinder slippage and reorientation of polymer chain that, in turn, shows higher creep resistance for nanocomposites than the neat matrix. At a lower temperature, poor creep resistance was observed for neat matrix as compared to nano materials tested; however, at elevated temperatures (beyond the glass transition temperature), creep resistance in nanocomposites becomes close to that of neat vinyl ester.

To fully understand the complex creep deformation of polymeric based nanocomposites, a physical modeling is conducted to study the structure-property relationship as a function of filler content. Parametric studies for the suggested model, along with variations in the simulated model parameters, illustrate various deformation mechanisms. The predicted results from the models quite well agree with the obtained experimental results.

1. Introduction

Nanoparticles that may be dispersed on nanoscale would outcome in extremely great interaction between these particles and the matrix resin. For example, an interphase of 1 nm wide corresponds to about 30% of the total volume in case of nano-structure as compared to 0.3% of the total volume of polymer in case of micro filler composites [1].

Applications of polymeric-based nanocomposites involve marine composite structures: particularly lightweight glass/carbon polymeric based composites. Sandwich composites with balsa and foam cores are presently being featured in number of navy applications such as in surface ship deck structures, radar mast and boat hulls. Several new and emerging cores have been explored in sandwich construction to provide enhanced mechanical properties.

Many studies on creep performance of various materials were carried out and showed improvements in creep performance associated with filling nanoparticles into various polymer. Creep recovery is particularly noteworthy in engineering applications. Therefore, understanding the creep mechanism of polymer-based nanocomposites requires combined experimental characterization and efficient modeling that help in establishing failure design criteria.

The effect of the clay type, clay content and temperature on creep behavior of polycaprolactone/clay nanocomposites (prepared by melt intercalation) was modeled [2]. The Kelvin-Voight models (4 parameters) along with the power-law were used to establish a correlation between the creep behavior and the nanocomposite morphology. Both, the experimental curves and the models, demonstrated that the incorporation of the clay produces a significant improvement on the creep resistance with respect to the neat matrix.

Several studies have reported both positive and negative influences of fillers on the creep resistance of polymers. For example, improvements in creep performance for multiwall carbon nanotubes/epoxy

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nanocomposite was not as high as anticipated through the use of mixture rule, indicated insufficient dispersion. However, variations in stiffness and creep strain-rate sensitivity obtained using nanoindentation showed quantifiable differences between the MWCNTs nanocomposite and epoxy specimens [3]. On the other hand, a significant improvement in tensile properties of polypropylene composites has been reported in terms of stiffening, strengthening and toughening with a low filled content of about 0.5% [4].

Based on above, modeling and simulating work, becomes a key issue in the future design of nano-based composites for engineering applications. An attempt based on the parameter analysis of the Burgers model had been accomplished [5] to explain the relationship between nano-structure and role of nano-particle toward creep performance of the bulk matrix. Results showed that the nanoparticles at some temperatures may hinder slippage and reorientation of polymer chain.

In the present study, the processed brominated 510A-40 vinyl ester is proposed to be used in the composite sheets of sandwich structures with fire-resistant foam layered in between to decrease flammability combined with enhanced flexural rigidity [6].

A previous investigation on this class of vinyl ester resin systems [7] discussed the effects of nano-filler addition to this resin against dynamic-loading applications. In this article, an attempt is made to model creep performance and the structural long-term durability from molecular structure prospective and establish future design criteria for these nanocomposites.

2. Experimental

2.1. Materials and Creep Measurements

Nanocomposites were prepared by dissolving around 3 kg of vinyl ester resin with various concentrations of graphite platelets in a one gallon container for 4 hours. The above resin-solution was blended for two minutes using FlackTek speed mixer running at 3000 rpm speed. The well-mixed vinyl ester resin solution with graphite nano platelets was discharged into a 0.33 m x 0.33 m x 0.01m mold, let to rest for 30 minutes at ambient temperature, and then was post cured at 80°C for 3 hours.

Creep tests were conducted in flexural mode under different temperatures using the TA Instruments Model Q800 [8]/ dynamic mechanical analysis (DMA). The specimens for the creep and stress relaxation tests were 35 x 10 x 1.6 mm size. The creep-strain was measured as a function of the time. Prior to the creep tests, the stress level was derived from the proportional limit in stress-strain diagrams of the tensile tests and was fixed at 3 MPa. Low applied load ensures the creep measurements remained in linear viscoelastic deformation regime.

The testing temperature was in the range of 30–150°C, incremented in 5°C steps, and the isothermal tests were run on each specimen over 30 minutes duration in the DMA. The sample was initially settled at room temperature (30°C) for about 4 minutes.

2.2. Stress-Relaxation Measurements of Nanocomposites

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, were 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 as in creep test and the process repeated until the final temperature of 150°C.

3. Theory

DMA tests were performed in accordance with ASTM D4065-01: "Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report Procedures" [9]. TA Instruments Mode Q800 DMA is a controlled stress with a Combined Motor and Transducer (CMT) machine in which the motor applies a force and displacement sensors measure strain. Force and amplitude are the raw signals recorded by the machine. The stiffness calculation for single-cantilever clamp type used in the TA Instruments Model Q800 DMA along with the appropriate correction factor is described below. The maximum level of strain occurs at the sample surface, while the centre experiences no strain at all, providing stress and strain are within the linear viscoelastic region.

4. Results and Discussion

4.1. Dynamic Properties

DMA spectra in the form of creep-strain as a function of temperature are plotted and demonstrated in Figures 1-3 for all nano-specimens, respectively. Creep deformation in the initial (pure elastic) segment is observed to be relatively small, associated with twisting and stretching of intermolecular bonds [10]. In the results shown, there was no evidence of creep rupture, which would require a longer time/temperature and maybe a larger load. As expected, these materials are viscoelastic in character, and, therefore, the shape of creep and relaxation curves is totally dependent on temperature. Creep strain increased with temperature, and, at the same time, similar behavior was exhibited by the nanocomposites. It is worth mentioning here that with the temperature rise from 100°C to 125°C the creep strain increases by 300% approximately at t = 1800 s for pure polymer (Figure not shown). Thus, the value of the creep-strain in response toward the temperature change is very sensitive. Moreover, results shown in Figure 3 can also indicate that creep strains of nanocomposites were lower than that of the neat matrix at all test temperatures and this implies that the creep behavior is improved by the addition of nanotubes. For example, the strain values at 82°C were reduced by 17%, and 23% compared to brominated vinyl ester when the contents of xGnP were 1.25 wt.%, and 2.5 wt.%, respectively. In addition, it is also observed that the creep strain rate decreased with the incorporation of xGnP.
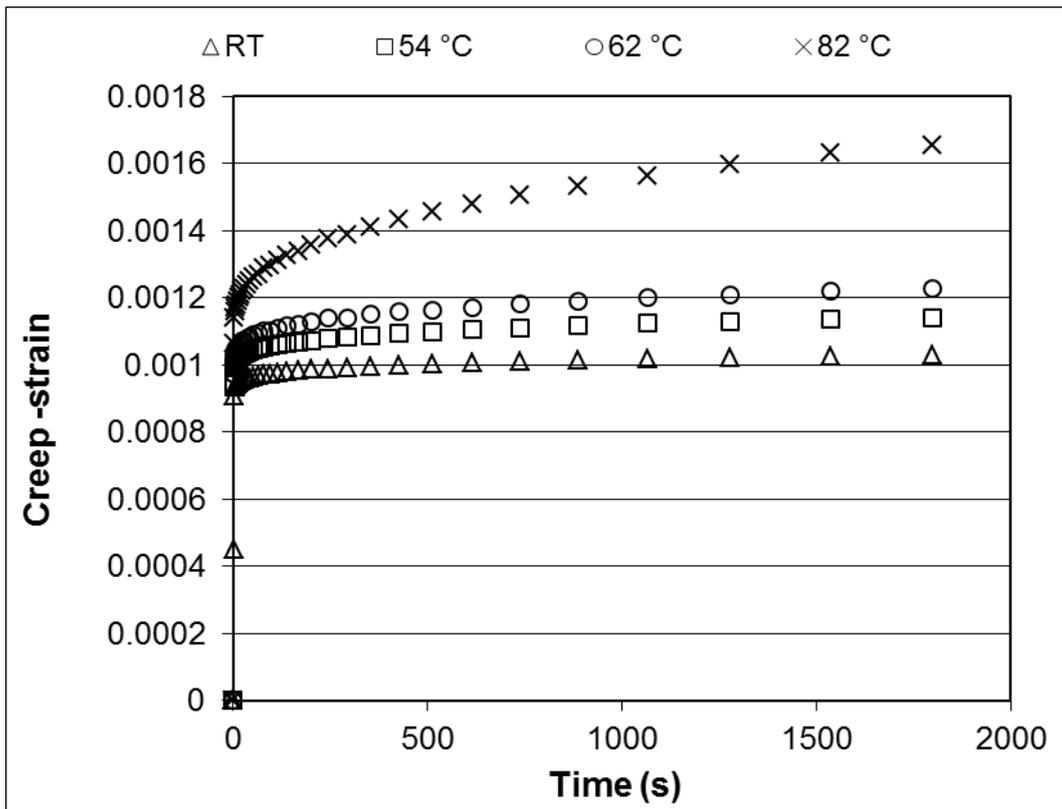
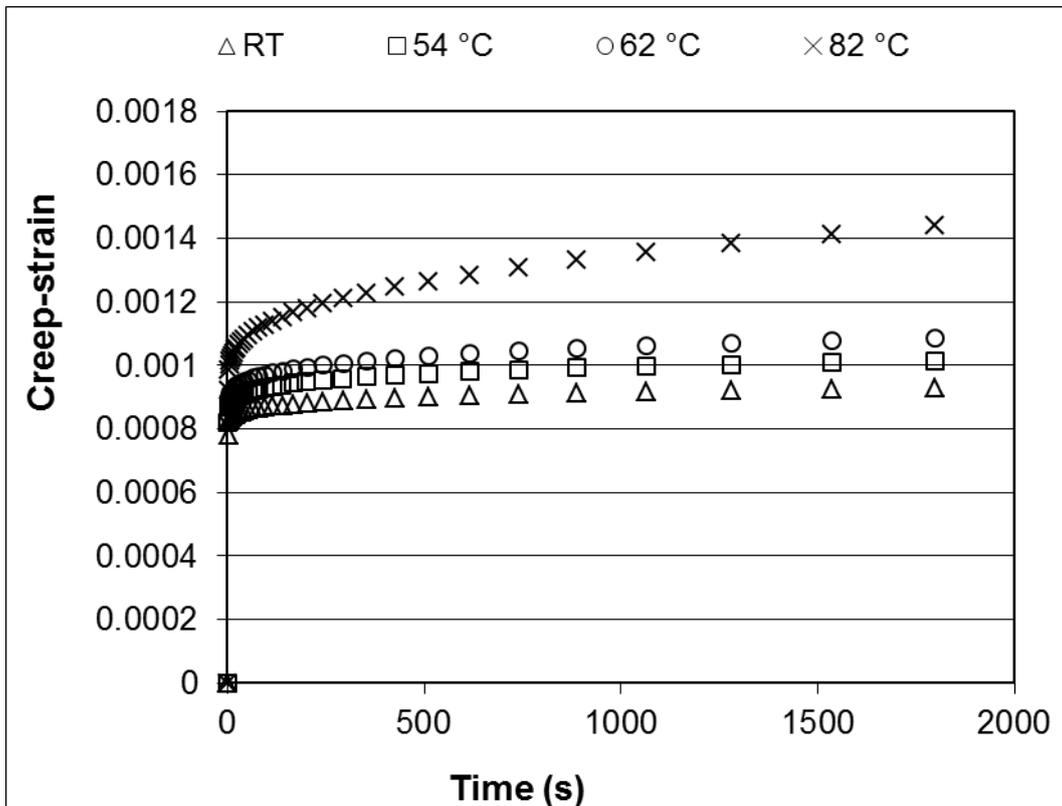**Figure 1.** Creep-strain versus time for brominated vinyl ester.

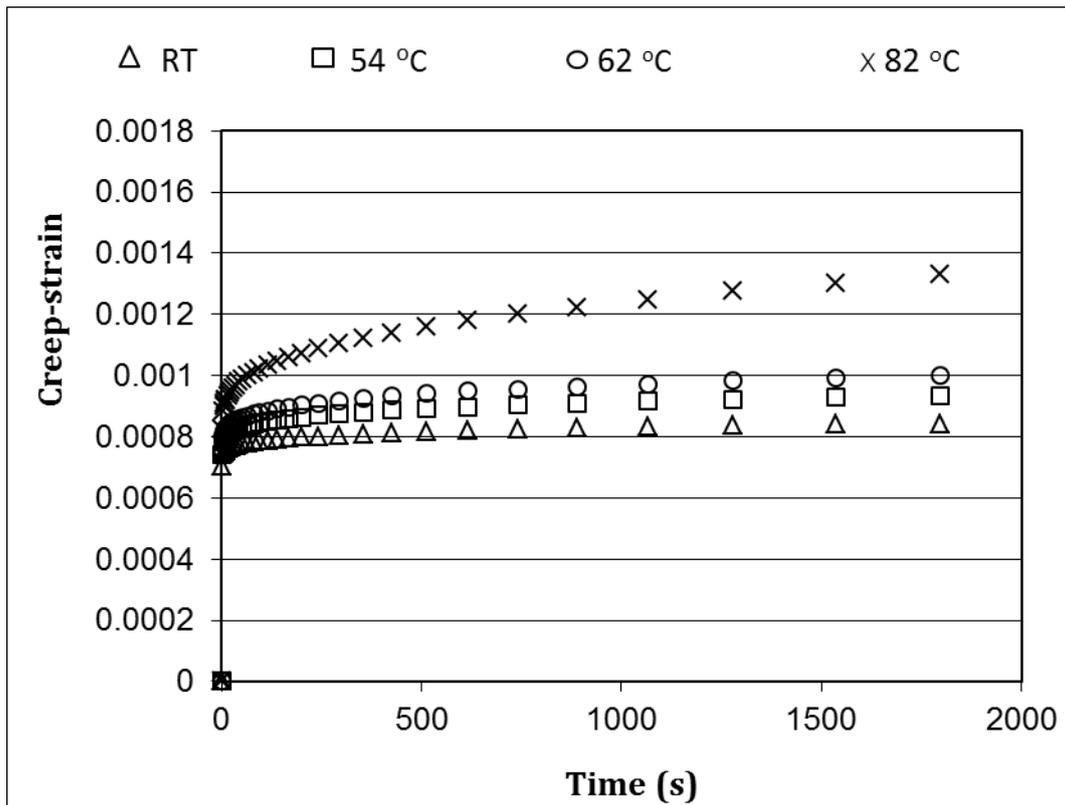**Figure 2.** Creep-strain versus time for 1.25 wt% graphite platelet vinyl ester

Figure 3. Creep-strain versus time for 2.5 wt%. graphite platelet vinyl ester.

4.2. Physical Model Formulation

Figure 4 shows the Standard Linear Solid Model that consists of a Maxwell element (linear spring and dashpot in series) and a linear spring in parallel. This model has been selected because it can explain two main deformations of plastics [8]; the spring represents deformations due to twisting and extension of intermolecular bonds, where as the dashpot refers to viscous deformation.
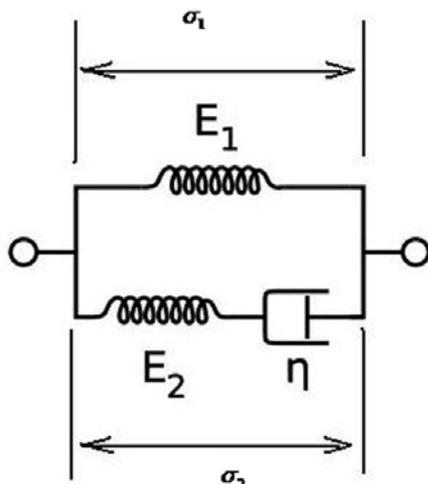

Figure 4. Schematic of the Standard Linear Solid model.

In the proposed viscoelastic model, the total stress at time t can be analyzed into time-rate dependent stress component in the spring E_2 and dashpot η (Maxwell element), and constant stress part (σ_1) in the spring element E_1 .

Thus, the total stress as per the Standard Linear Solid model is given as:

$$\sigma_o = E_1\varepsilon + \frac{\eta}{E_2}(E_1 + E_2)\ \varepsilon' \tag{1}$$

Based on the above suggested model, the creep-strain response is:

$$\varepsilon(t) = \frac{\sigma_o}{E_1}\left[1 - \frac{E_2}{E_1 + E_2}\ Exp(-t\ E_1E_2/\eta\ (E_1 + E_2))\right] \tag{2}$$

Where ε and σ_o are creep-strain and the applied stress in the creep experiment, respectively.

To simulate the model elastic parameters, data from the stress-relaxation experiments at a given temperature were accompanied. The relaxation modulus, according to the model, obtained from stress-relaxation data at quite large time, is basically representing E_1. E_1 alternatively can describe the elastic deformation in the crystalline structure, associated with no amorphous deformation or viscosity effect. In general, a polymer with large value of stiffness, E_1, may indicate highly crystalline structure. Accordingly, the neat resin exhibits higher values of E_1 with addition of nano-filler under all temperatures.

The total modulus (E_1+E_2), provided in the constitutive model, determines the immediate elastic creep strain (at time equal zero), which could be instantaneously recovered on the removal of creep load. In general, the composites showed greater values of (E_1+E_2) with the addition of filler compared to neat matrix at all temperatures. Among the nanocomposites, 2.25 wt. % appears to be the one with peak total elasticity, second is 1.25 wt.%, and finally is the neat matrix which depicted

that the addition of nanoparticles was helpful in reinforcing the elasticity of the crystalline polymer as shown in Table 1. Moreover, it is worth mentioning that the change in variation of (E_1+E_2) value from one level of nano-filler loading to another illustrated the diverse reinforcing role of nanoparticle. For example, the total modulus increased by 3% in response to addition of 1.25 wt.% xGnP to the resin network, and this figure was magnified to become 22 % when the level of nano-filler was upgraded from 1.25 to 2.25 wt.%.

On the other hand, the elasticity dictated from total stiffness (E_1+E_2) of each specimen showed a decreasing affinity with temperature; it was easy to recognize that the substance materials became softer at higher temperatures and the stiffness was therefore reduced with diminished instantaneous modulus. For example, close to the glass transition temperature, the chain-segments of polymer began to travel and thus the elastic stiffness of substance material was decreased as compared to the one measured at room temperature.

ross linking density in general restricts the chain-movement from complete segmental motion at high temperatures where deformation is mainly viscous, it is typically given as the mean molecular weight between cross-links, is an important feature governing the mechanical properties of vinyl ester resin. Moreover, cross-linking can be altered by controlling the molecular weight of vinyl ester oligomers, and concentration of nano-filler in the matrix as well.

Cross linking density can be quantitatively evaluated as per Equation (3) which implies that cross-linking density, V, is dependent on Plateau or relaxation modulus in rubbery region, $G0^n$, temperature T, and the universal gas constant R.

$$V = G_o^n / RT \qquad (3)$$

On comparing the modulus in the rubbery regions for vinyl ester with 2.5 wt.% and neat matrix as shown in Figure 5 (a, b), no major variation in plateau modulus was observed as opposed to the addition of nano-fillers. The influence of nano-filler addition in cross linking mechanism as per the above equation is not encouraging. As a result, the mechanism of hindering intermolecular slippage appears to be poor within rubbery region, and, therefore, the creep resistance in nanocomposites at elevated temperatures remains unaffected with regard to neat vinyl ester.

E_2 was subsequently developed in the model by subtracting E_1 from (E_1+E_2), at a specific temperature. The time-dependent E_2 might be associated with the stiffness and viscous deformation due to intermolecular slippage, damage from crystallized polymer or straightening out of the folded amorphous chains which is recoverable but not instantaneously. The retardant spring

modulus E_2 and the dashpot viscosity η of each material showed conflicting dependency on temperature, E_2 increases with increasing temperature. The viscosity element η was much more dependent on temperature rather than concentration of nano-filler, unlike E_1 and E_2. Among the tested specimens, the viscosity η, showed comparatively slight changes between the neat matrix and the nano-specimens at specific temperature, which accounts that the dashpot viscosity was not much altered by the addition of nano-particles. Rather, viscous deformation as per the model (Maxwell unit) is mainly governed by temperature effect, and the relationship can be correlated as follow:

$$\eta = \text{constant} \ (T/T_r)^m \qquad (4)$$

Where T_r is the reference temperature which is considered here as room temperature, m is a constant.

Table 1: The simulated parameters of the standard linear solid model

Material	Temp (^{o}C)	E_1 (MPa)	E_1+E_2 (MPa)	E_2 (MPa)	η (MPa.h)
Pure *VE*	30	2929	3160	231	7.6
	42	2750	3038	288	18.7
	62	2347	2801	454	65.2
	82	1683	2510	827	171.4
VE+1.25 wt.%	30	3002	3250	248	7.6
	42	3067	3405	338	18.7
	62	2627	3157	530	65.2
	82	1951	2858	907	171.4
VE+2.5 wt.%	30	3576	3971	395	7.6
	42	3404	3852	448	18.7
	62	2937	3596	659	65.2
	82	2175	3272	1098	171.4

Creep-strain data, at representative temperatures obtained from the creep tests, are plotted in Figure 6 through 8 along with the strain predicted including the modified effect of viscosity in Equation 4. As can be seen from these Figures, the model can predict the strain-time behavior of pure vinyl ester reasonably well except at high temperature (beyond 80°C) where the onset of rubbery region started with complete motion of molecular segments occurred for pure vinyl ester and its nanocomposites at temperature around 110°C. Agreement between model predictions and creep data for all nanocomposites is quite well.
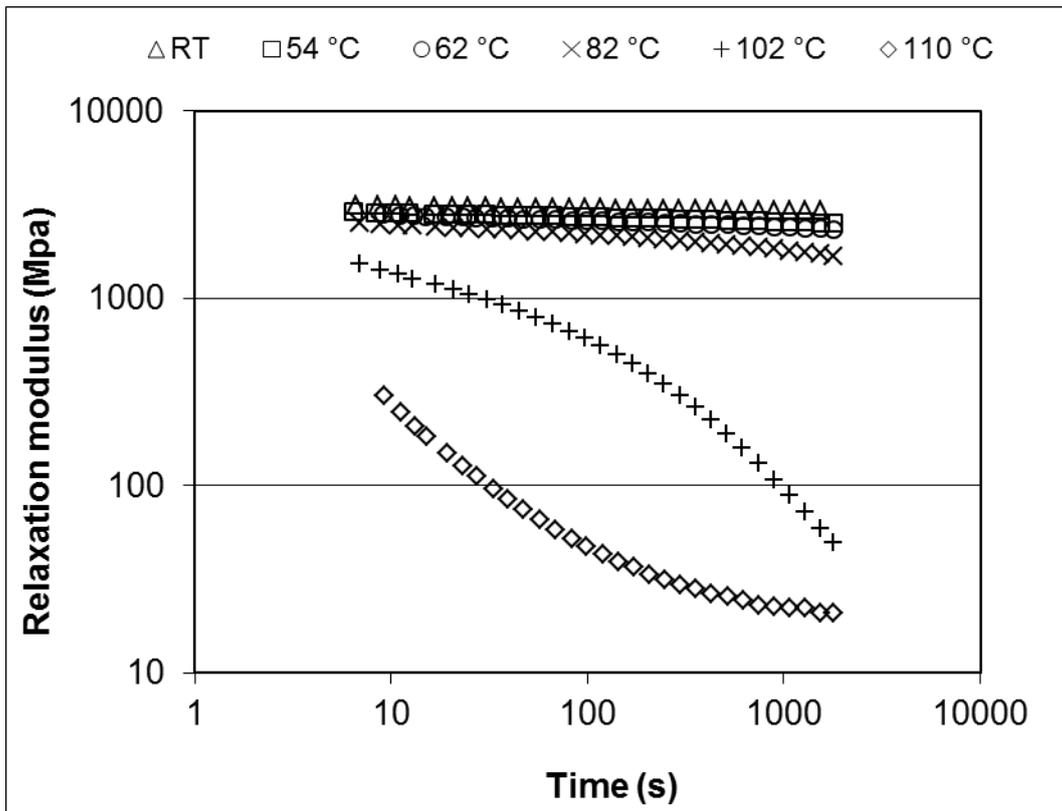
(a)   Brominated vinyl ester and
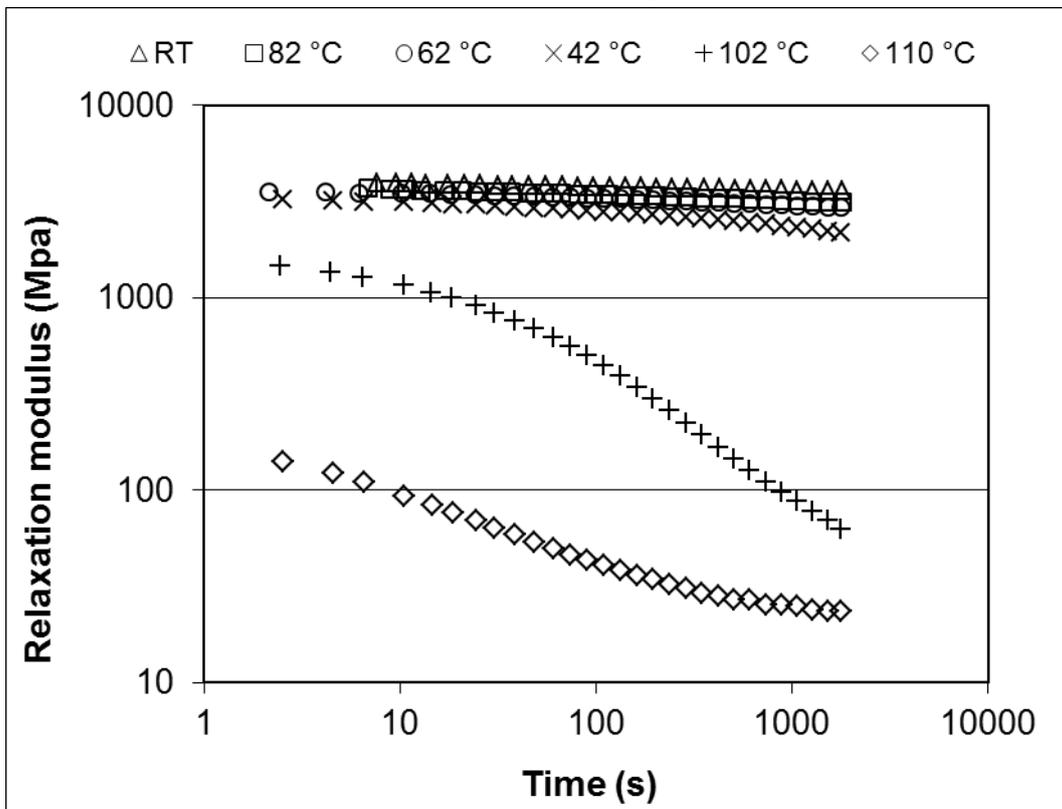
(b) Brominated vinyl ester with 2.5 wt.% graphite.
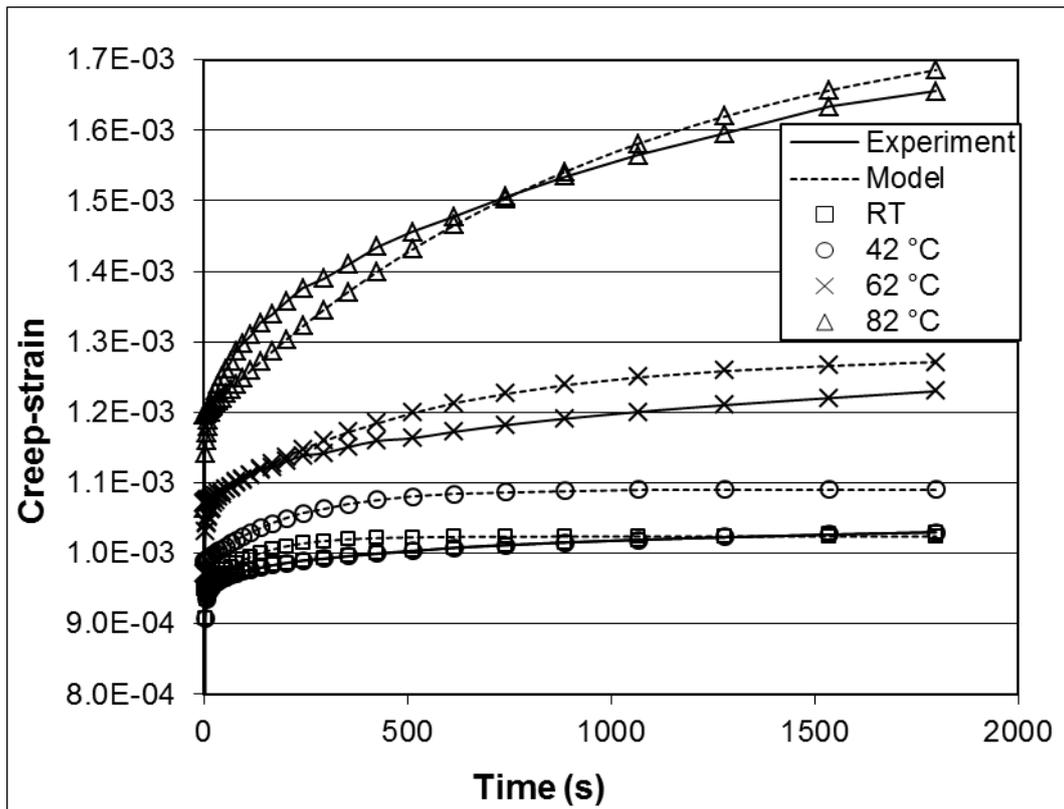
Figure 5. Relaxation modulus versus temperature.

Figure 6. Predicted and experimental results of creep-strain versus time for brominated vinyl ester at selected temperatures based on the viscoelastic model.
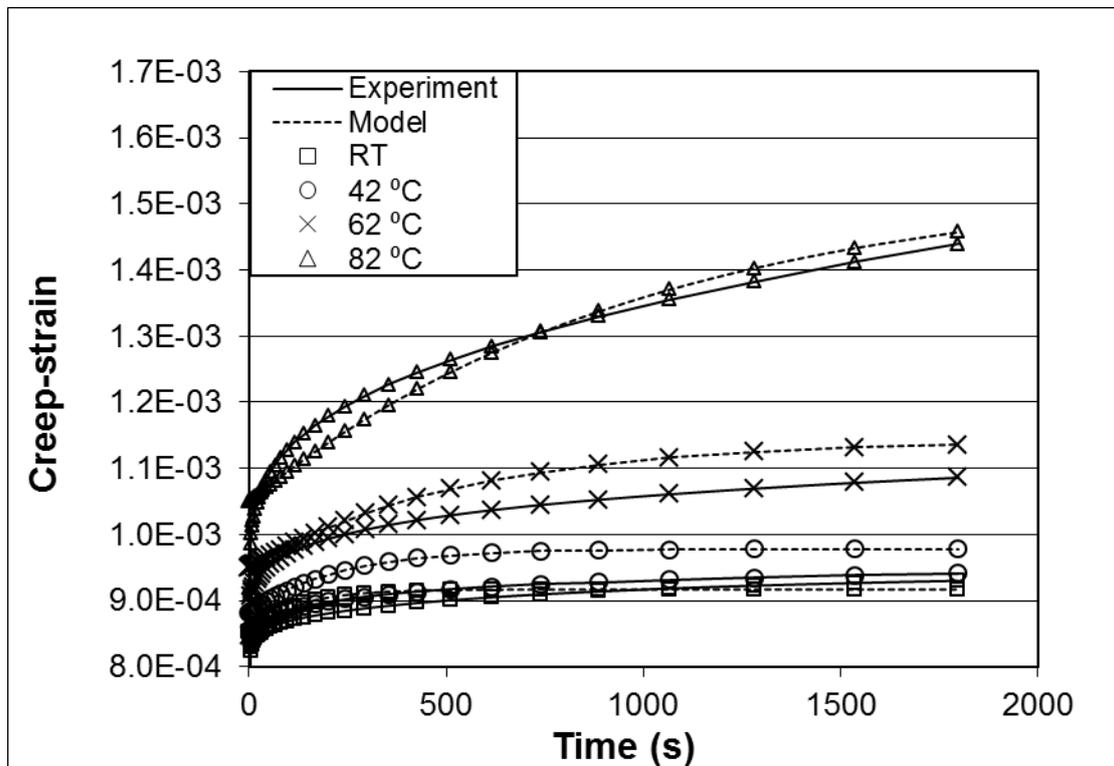

Figure 7. Predicted and experimental results of creep-strain versus time for 1.25 wt%. graphite platelet vinyl ester at selected temperatures based on the viscoelastic model.

Figure 8. Predicted and experimental results of creep-strain versus time for 2.5 wt%. graphite platelet vinyl ester at selected temperatures based on the viscoelastic model.
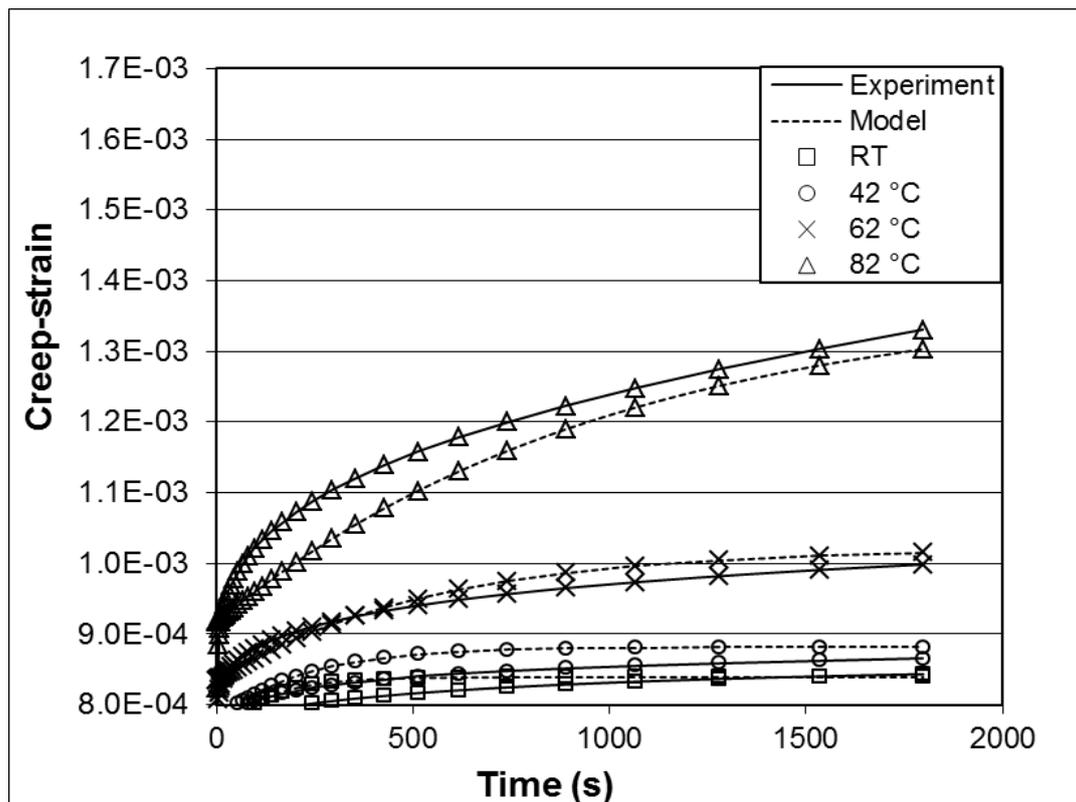
5. Conclusions

The creep behavior of brominated vinyl ester and its nanocomposites were characterized in creep and relaxation tests using DMA Q800 over various isothermal temperatures. The standard linear solid model was established and developed to understand the relationship of nano-filler/structure property for these nano-materials. The variation in the simulated parameters in the proposed model describes the mechanism of nano-filler toward creep deformation in different regimes. The key findings of the present study are listed below:

- Poor creep resistance was observed for vinyl ester as compared to nanocomposite at low temperatures, while at elevated temperatures, creep resistance in nano-specimens was close in magnitude to that of pure polymer.
- The elastic modulus for the crystalline structure, simulated as (E_1+E_2) in the model, was observed to increase with nano-filler addition under all temperatures.
- The role of nano-particles toward cross-linking and hindering molecular slippage was found to be insensitive to filler addition at temperatures greater than glass transition temperatures.
- The viscous deformation was totally governed by the predicted model elements: E_2 and η, and was strongly dependent on temperature rather than on concentration of nano-filler.
- Analysis of microstructures for different types of nanocomposites and their impact on microscopic creep property can be suggested as a future work.

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