

Long-Term Creep Behavior of Flax/Vinyl Ester Composites Using Time-Temperature Superposition Principle

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ABSTRACT: Natural fibers have great potential to be used as reinforcement in composite materials. Cellulose, being a critical constituent of natural fibers, provides unquestionable advantages over synthetically produced fibers. Increasing demand for use of bio-based composites in different engineering and structural applications requires proper test methods and models for predicting their long-term behavior. In the present work, the time-temperature superposition principle was successfully applied to characterize creep behavior of flax/vinyl ester composites. The creep compliance vs time curves were determined and shifted along the logarithmic time axis to generate a master compliance curve. The time-temperature superposition provided an accelerated method for evaluation of mechanical properties of bio-based composites, and the results suggest that the time-temperature superposition is a useful tool for accelerated testing of long-term behavior of bio-based composites.

KEYWORDS: Creep, flax, time-temperature superposition, vinyl ester, viscoelastic

1 INTRODUCTION

In recent years, due to the advantages of their lower density and higher toughness, comparable strength and stiffness, lower cost, and their being less abrasive to equipment and tooling, natural fibers have been replacing mineral or synthetic fibers like glass or carbon fibers as reinforcement in polymer composites [1–5]. Moreover, the processing, use and removal of parts made out of traditional composites with glass, carbon or aramid fibers as reinforcement have introduced some environmental concerns. Most importantly, the removal and recycling of such components at the end of the designed lifetime is extremely challenging [6,7]. Therefore, the development and use of biodegradable and renewable fibers such as flax in bio-based composites is attractive for potentially reducing and/or eliminating these mentioned environmental concerns.

As a result of the viscoelastic nature of both the matrix [8] and the fiber [9], bio-based composites exhibit mechanical properties which are time-dependent. In recent years there have been numerous studies on the viscoelastic behavior of bio-based composites [10–14]. Although the life cycle of bio-based composites needs to be adapted to meet specific applications [15], expectations for flax fiber reinforced

composites in most engineering applications is a minimum of 10 years guaranteed service life. Therefore, one important aspect of engineering design development for these materials is long-term creep behavior predictions [16]. There are two common superposition principles that are widely used to predict and model viscoelastic behavior of polymeric materials. The first one is time-temperature superposition developed by Williams, Landel and Ferry (WLF) [17,18], and the other is the Boltzmann superposition principle [18–20]. The time-temperature superposition (TTS) principle can be applied to generate a master curve to describe long-term time-dependent deformation based on short-term creep tests at different temperatures. Use of multi-frequency or accelerated temperature measurements is an accepted way to accelerate the time-dependent creep response of bio-based composites. As mentioned, the use of bio-based reinforcement as well as the use of thermoset resins are increasing [21,22]. There have been studies of long-term behavior and application of time-temperature superposition method to long continuous natural fibers/thermoplastic composites [23,24] and wood/thermoset composites [25,26]. However, to the authors' best knowledge there have not been any studies on applications of mentioned superposition and methods to flax fiber reinforced thermoset composites. A thorough understanding of creep behavior and applications of existing models to bio-based fibers/thermoset resin composites is valuable for the further development of

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their applications in more engineering and structural applications. In this study, the time-temperature superposition principle is utilized to generate a creep compliance master curve for flax/vinyl ester composites.

2 THEORY

2.1 Flexural Creep

Creep is a measure of the stability of a material and is of great importance for applications where a material needs to sustain load for a long period of time [27,28]. Three-point bend testing is one of the methods used to measure creep. Direct measurements of time dependence of strain can be expressed in the form of creep compliance. Creep compliance $J(t)$ (1/MPa) in flexure is defined as the time-dependent strain per unit stress and is calculated with the following equation [29]:

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = \frac{4bd^3D(t)}{Pl^3} \quad (1)$$

where $D(t)$ is the instantaneous deformation (mm), P is the applied load (N), b is the width of the specimen (mm), d is the depth of the specimen (mm), and l is the support span (mm). Each material exhibits a unique creep compliance, therefore creep compliance is a material property [30]. In three-point bending, by choosing appropriate support span, it is assumed that the entire deformation is due to flexural stress and the deformation due to shear is negligible [27].

2.2 Boltzmann Superposition Principle

The Boltzmann superposition principle indicates that the effect of mechanical history can linearly be added to determine the total strain response of a single load. The main assumptions for this principle are that (i) the strain of the material depends on the complete loading history of the material, (ii) each loading event should be considered independent, and (iii) the total strain is the addition of strains after each independent event. This principle is expressed with different equations [31, 32]. John Ferry [18] used the following equation to find the total strain $\gamma(t)$ after a sequence of finite stress changes σ_i each at any given time u_i :

$$\gamma(t) = \sum_{u_i=-\infty}^{u_i=t} \sigma_i J(t - u_i) \quad (2)$$

where J is the creep compliance. When performing creep tests at different temperatures, each temperature step can be considered as a loading event. Therefore,

strains from creep measurements at different temperatures can linearly be added together to calculate the total strain [33].

2.3 Williams-Landel-Ferry Equation

The basis for time-temperature superposition is the Doolittle equation which relates viscosity of a material, η , to the free volume fraction, f , and has the following form [34,35]:

$$\eta = A \exp\left(\frac{B}{f}\right) \quad (3)$$

In this equation A and B are material constants. It is widely assumed that free volume fraction is only dependent on temperature change and effect of moisture is neglected and [34,36,37]:

$$f - f_0 = \alpha_T(T - T_0) \quad (4)$$

where α_T is the coefficient of thermal expansion of the material, and f_0 is the free volume fraction at temperature T_0 . The Doolittle equation expresses that the mechanical behavior of a viscoelastic material at different time scales is equivalent to changing their temperatures [37], therefore the temperature shift factor is defined as $a_T = \eta/\eta_0$, where η_0 is the material viscosity at T_0 . By taking the logarithm of the sides of this equation and substituting Equation 4 and Equation 3 into the resulting equation, the WLF equation is established as follows [17, 18]:

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (5)$$

where C_1 and C_2 are empirical constants which depend on material type and reference temperature, T_0 .

2.4 Arrhenius Equation

Arrhenius relation or rate-process theory, discusses the relation between rate of reaction and temperature. In the case of creep, Arrhenius equation defines the shift factor as ratio of strain rate at a reference temperature to strain rate at an elevated temperature and has the following form [38]:

$$\ln\left(\frac{\dot{\varepsilon}_r}{\dot{\varepsilon}}\right) = \ln(a_T) = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_r}\right) \quad (6)$$

where $\dot{\varepsilon}_r$ and $\dot{\varepsilon}$ are strain rate at the reference temperature T_r (K) and arbitrary temperature T (K) at which horizontal shift factor a_T is desired, respectively. In

this equation, E is the activation energy (kJ/mol) and R is the universal gas constant (J/mol.K).

Arrhenius equation assumes that creep mechanisms remain unchanged at elevated temperature T , in other words, for Equation 6 to be valid, material phase transition should be avoided and during the creep process, glass transition temperature, T_g , should not be traversed [33,39].

2.5 Time-Temperature Superposition (TTS)

Williams *et al.* [17] and Ferry [18] developed the time-temperature superposition (TTS) technique initially for amorphous materials above T_g . They mentioned that Equations 5 and 6 are valid in the range T_g+100° , and below T_g the $\log(a_T)$ increases less rapidly with decreasing temperature [17]. In the literature, TTS has been applied to predict and model long-term behavior of materials below T_g [23,40], in the range including T_g [41,42] and above T_g [43,44]. TTS is valid when temperature dependence of shift factors a_T is in forms such as WLF Equation 5 or Arrhenius Equation 6, and a_T has the same value for all viscoelastic functions. Landel and Nielsen in [27] and Tajvidi *et al.* in [45] mentioned that TTS could be applied to semicrystalline and crystalline polymers, but vertical shift factors are also needed to generate a smooth master curve. The vertical shift factors are the result of change in the structure, degree of crystallinity, and molecular level of the material. Therefore, for TTS of thermoset resins to hold, one should make sure that the resin is fully cured and that no residual curing or crosslinking of the resin occurs in the test temperature range. The creep test temperature range should be picked in the range lower than degradation of the material being tested [39,45,46]. In addition, TTS can be applicable to semicrystalline and crystalline materials if the creep test is conducted under low strain to maintain the material response in the linear viscoelastic range [45,47].

2.6 Generating Master Creep Compliance Curves

Creep compliance curves measured at different temperatures can be shifted horizontally in reference to a specific temperature to generate a master compliance curve. A master compliance curve provides information for the long-term behavior of a material at a reference temperature.

2.7 Findley Power Law Equation

According to William Findley [30], the time-dependent creep compliance of a material can be represented by a power function as:

$$J(t) = A t^n \quad (7)$$

where A is the time-dependent coefficient, t is the time and n is stress-independent coefficient. The entire creep compliance curve of a material can be expressed as:

$$J = J_0 + J(t) = J_0 + A t^n \quad (8)$$

where J_0 is the time-independent or elastic creep compliance. Equation 8 is referred to as the Findley power law equation [30].

3 EXPERIMENTAL PROCEDURE

3.1 Materials and Sample Preparation

The fiber used in this study was a linen flax, farmed and harvested by the University of Saskatchewan, Saskatoon, SK, Canada. Shive (i.e., woody core of the flax stalk) was removed by passing the fiber through a pilot line eight times at Biolin Research Inc., Saskatoon, SK, Canada. The resin used was a vinyl ester (VE) system Hydropol R037-YDF-40 with 30% styrene content generously provided by AOC Resins Co. located in Collierville, Tennessee. The hardener was a 2-butanone peroxide (Luperox DDM-9) solution, which was obtained from Sigma-Aldrich Co., St. Louis, Missouri. The mixing ratio of VE to hardener was 100 to 1 weight parts. To process the composite panels, 50±4 g of fiber roving was processed with a manual drum carder model DC-P05-B/A from Strauch Fiber Equipment Co. located in New Castle, Virginia. Composite panels were manufactured using a hand-layup compression molding process. As mentioned, for each panel, 50±4 g of fiber was placed on the mold and 250 g of resin was poured onto the fiber until the fiber was soaked with resin. A nonporous PTFE sheet was placed on top of the fiber and a caul plate with dimensions of 200 mm by 150 mm was placed on top of the fiber. The entire layup was sealed under a layer of vacuum bagging plastic and five metric tons of force was applied using a shop press. The applied force resulted in 1.6 MPa pressure over the layup. Resin soaked fibers were in the mold under this pressure for 24 hours at room temperature and then post cured at 80°C for 12 hours. In addition, to keep the moisture content of composite samples at a minimum level, all

test specimens used in this study were placed in the oven at 80°C for 24 hours prior to testing.

3.2 Mechanical Testing

Static three-point bend tests at room temperature as well as creep tests at different temperatures were carried out on flax/vinyl ester composite samples. Three-point bending tests were performed on five samples using an Instron 5567 load frame in accordance with ASTM D790 [48] to measure the flexural strength. The average flexural strength of the flax/vinyl ester composite was found to be 153±29 MPa.

To measure creep in elastomeric materials, simple equipment can be used to carry out the measurements. For rigid composite materials, in order to precisely record small deformations, a more advanced machine is required. In this study, a Dynamic Mechanical Analyzer DMA Q800 by TA Instruments, New Castle, Delaware, was used in flexural bending mode with constant stress of 14 MPa to perform isothermal creep tests. Each specimen was subjected to creep for 10 min and recovery for 10 min at each temperature step. Starting test temperature was 30°C and ending temperature was 110°C with temperature steps of 10°C. The same equipment was used in dual cantilever mode at 1 Hz scanning frequency with the temperature ramp of 3 °C/min to measure the T_g of cured vinyl ester as well as the flax/vinyl ester composite. The T_g of cured resin and composite sample was the peak of $\tan \delta$ curve obtained from the results of the DMA test.

In order to measure the degradation temperature of flax fiber as well as flax/VE composite, thermogravimetric analysis (TGA) was conducted using a TA Instruments TGA Q500 with inert atmosphere.

Specimens were heated from room temperature to 450°C with temperature ramp of 10 °C/min.

Differential scanning calorimetry (DSC) was conducted on composite samples to evaluate degree of cure of vinyl ester resin and make sure that no residual crosslinking is present in the material. DSC Q1000 by TA Instruments was used to run the analysis. Approximately 20 mg samples of material were sealed in aluminum hermetic pans and specimens were analyzed under dry nitrogen purge. Specimens were heated with the rate of 5 °C/min from 25°C to 200°C, and cooled down with the same rate to 25°C.

4 RESULTS AND DISCUSSION

Figure 1 shows $\tan \delta$ curves of cured VE resin and flax/VE composite. The peak position of $\tan \delta$ curves were used to determine T_g . The T_g of VE was determined to be 127.83°C and the T_g of flax/VE to be 126.85°C. Huo *et al.* [49] reported T_g of the same VE resin (Hydropel R037-YDF-40 with 30% styrene content from AOC resins) to be 128°C and Herzog *et al.* measured the T_g of vinyl ester resin to be 132.8°C [50].

Figure 2 shows the typical thermal behavior of flax fiber/VE composite as temperature is increased. The thermogravimetric curve in its original and differentiated state (DTG) is presented. The peaks of DTG curve are marked at 298.87°C, 368.37°C and 415.96°C and correspond to the maximum changes in the slope of TGA curve. Up to 298.87°C, which was the onset of the major weight loss, the degradation in weight was 7.2%. The significance of TGA analysis for this study was to make sure that the material under the creep test was not degrading in the temperature range the creep tests were conducted. In the range between 30–110°C that creep tests were carried out, there was a

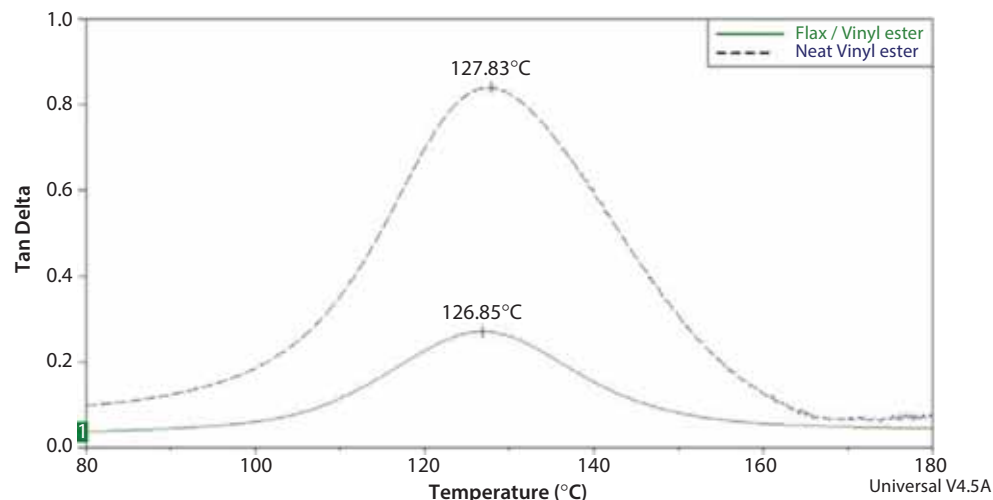


Figure 1 DMA plots of flax/VE and neat vinyl ester resin.

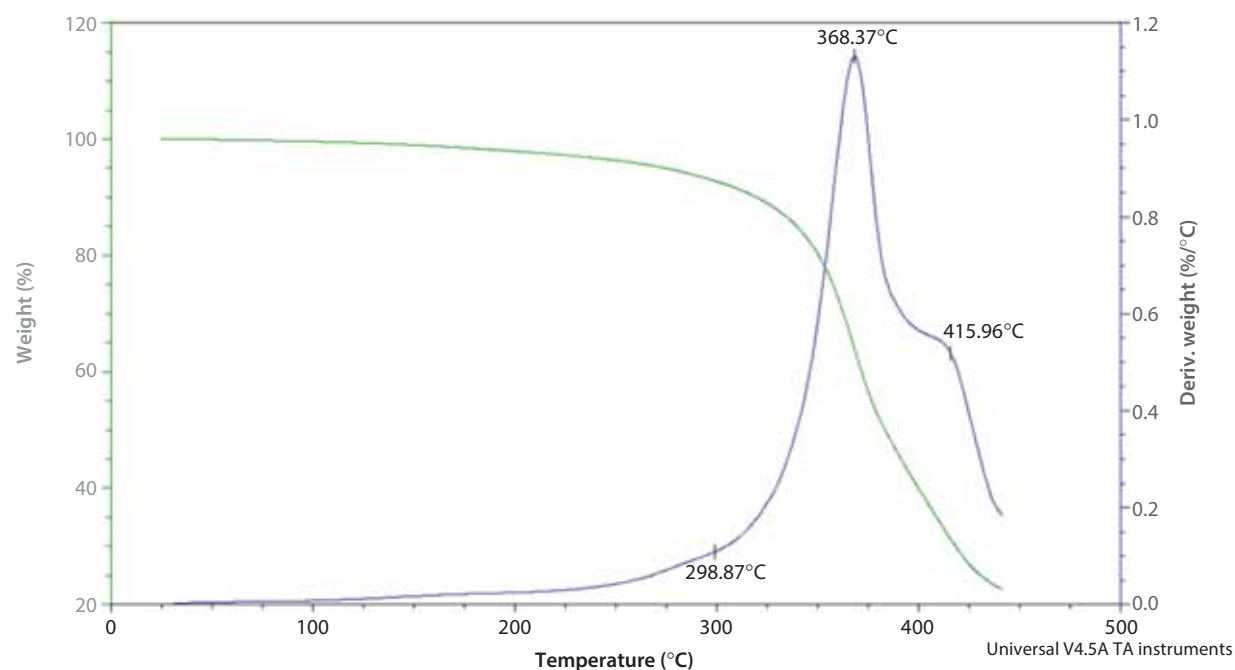


Figure 2 Thermogravimetric curve in its original and differentiated state for flax/VE composite.

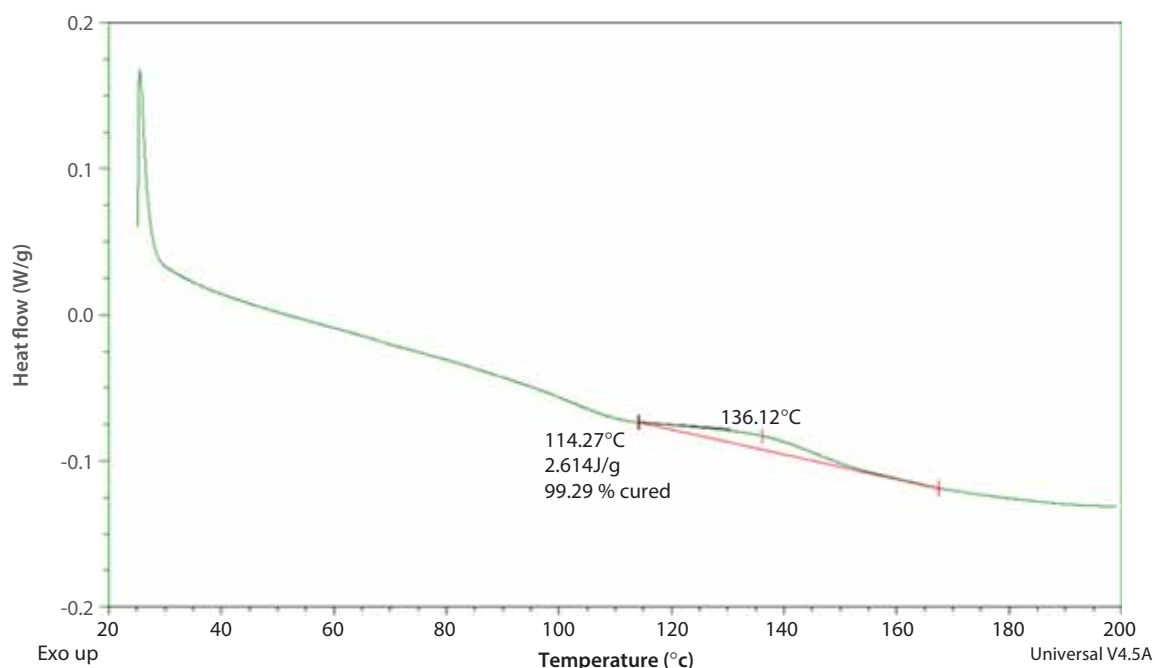


Figure 3 DSC trace for heating of flax/VE with 5 °C/min from 25°C to 200°C.

minimal 0.49% decrease in weight of specimen, indicating no degradation.

In order to make sure there was no crosslinking or curing occurring at the temperature range that creep tests were performed a DSC test was run. A typical result of the DSC analysis is presented in Figure 3. With a DSC scan, the assumption is that degree of

cure of resin is proportional to the measured heat flow [51]. Therefore, the degree of cure of resin can be calculated from the following equation:

$$\text{Degree of cure} = \frac{\Delta H_{\text{reaction}} - \Delta H_{\text{res}}}{\Delta H_{\text{reaction}}} \quad (9)$$

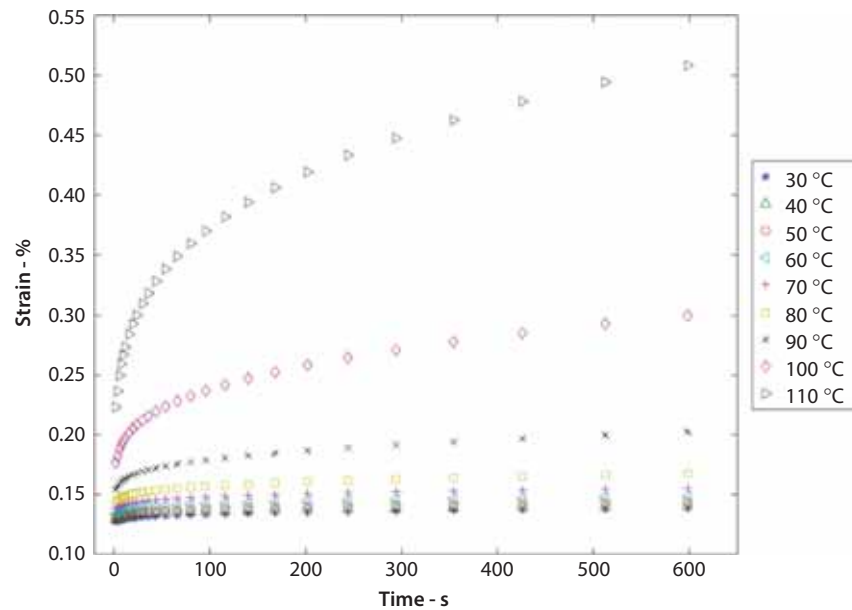


Figure 4 Creep strains vs time at different temperatures for flax/VE composite.

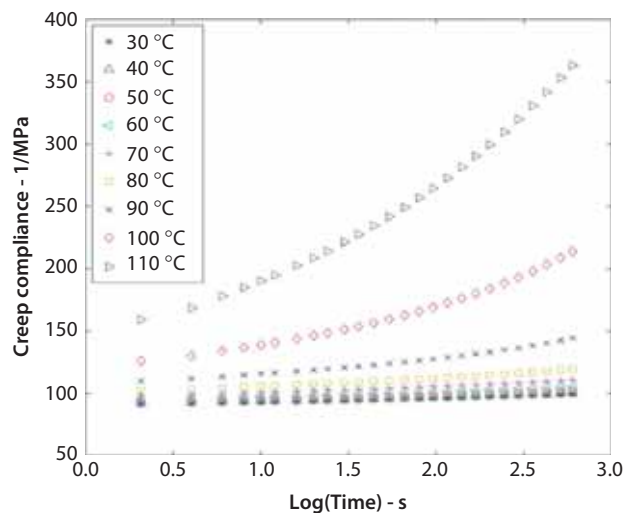


Figure 5 Creep compliance curve at different temperatures for flax/VE composite.

where $\Delta H_{\text{reaction}}$ is the total heat of reaction and ΔH_{res} is the residual heat after curing. In Figure 3, there was some residual curing approximately around 136°C and the degree of cure that was calculated automatically by the Universal Analysis software from TA Instruments was found to be 99.29%. Based on the results from DSC and TGA, it was concluded that the material does not undergo any degradation or cross-linking at the temperature range selected for the creep tests, i.e., 30–110°C.

Creep behavior of flax/vinyl ester composite at different temperatures is shown in Figure 4. With constant stress, increasing temperature accelerates the rate

that the samples are strained. The strain curves for 30°C and 40°C were very similar and nearly coincided with each other. It was from 40°C and above that the difference between creep behaviors at different temperatures could be distinguished from each other. The creep compliance curves are shown in Figure 5. As mentioned previously, creep compliance $J(t)$ is defined as the ratio of time-dependent strain to the applied constant stress.

As expected, by increasing temperature, the creep compliance also increases in a nonlinear fashion. When a polymer is under constant load, molecular rearrangements occur to minimize the localized stress. Based on the time-temperature superposition principle, higher temperatures correspond to lower frequencies, therefore at higher temperatures, material creeps faster. This is consistent with the findings of creep behavior of natural fiber reinforced composites, as seen in other studies [23,42,43].

As mentioned before, creep compliance curves at different temperatures can be shifted horizontally in reference to a selected curve to build a creep compliance master curve. By observing creep compliance and creep strain plots, the 30°C curve was selected as the reference compliance curve and all other curves were shifted to the right on the time axis to build the master curve for this composite. A MATLAB code was used to calculate shift factors in order to minimize the difference between the shifted curve and the reference compliance curve and minimize the sum of squared errors. The result of the shifted curves is shown in Figure 6. For some materials, especially if the TTS is performed below T_g , a vertical shift factor is also needed

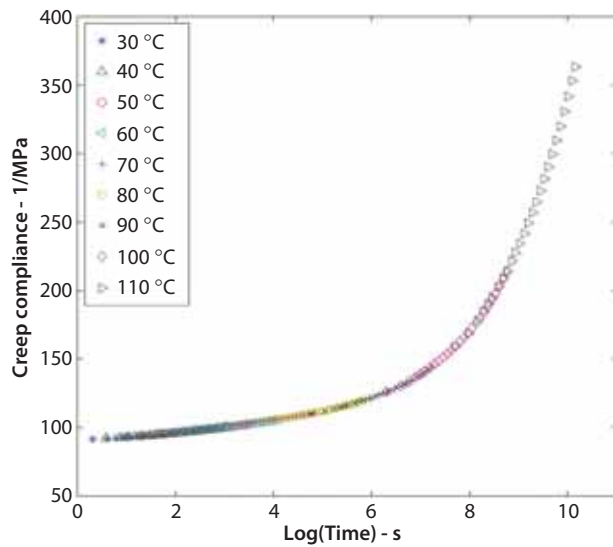


Figure 6 The master curve for creep compliance at 30°C for flax/VE composite.

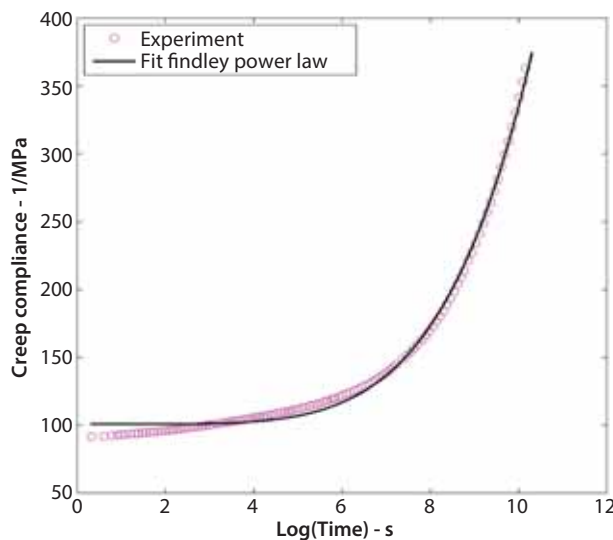


Figure 7 The master curve for creep compliance at 30°C for flax/VE composite and Findely power law fit.

in order to achieve a smooth master curve. Vertical shift factors will compensate the effect of material hygrological and thermal expansion effects [39]. In this study, a smooth master curve was achieved only with horizontal shift factors. This can be attributed to the fact that specimens were conditioned for 10 minutes at each temperature step before they were loaded for creep measurements [39].

For the compliance master curve in Figure 6, the Findley power law Equation 8 was adapted. Calculated coefficients and the resulting equation is as follows:

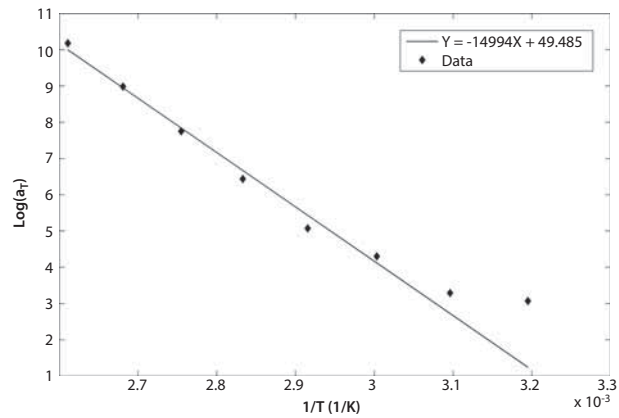


Figure 8 Arrhenius plots of horizontal shift factors.

$$J = 100.8 + 0.00135 \times t^{5.24} \quad (10)$$

The fitted curve versus experimental data is shown in Figure 7. The R-square value for the presented curve is 0.996. Despite the slight deviation from experimental data in the early stages of creep, the simulated curve agrees with the experimental results over time. Thus, there is a good agreement between the Findley power law and the experimental results.

$\text{Log}(a_T)$ is plotted vs $1/T$ (K) in Figure 8. Using least squares method, a straight line was fitted through the data points with the slope of -14994. This indicates that shift factors are governed by Arrhenius relation. With the slope of the line calculated from Figure 8, activation energy of the material was calculated from Equation 6 and was found to be 124.66 kJ/mol. In order to confirm this value, activation energy of flax/VE was also calculated using the results of TGA analysis.

4.1 Calculation of Activation Energy for Flax/VE Composite

In 1963, Horowitz and Metzger [52] proposed a method of calculating activation energy from thermogravimetric curves. They mentioned that the activation energy can be calculated from the following equation [52]:

$$\ln\left(\ln\left(\frac{W_0 - W_f}{W - W_f}\right)\right) = \frac{E(T_s - T)}{RT_s^2} \quad (11)$$

where W_0 is the weight at the beginning of the range, W_f is the weight at the end of the range, W is the weight at absolute temperature T , and T_s is the reference temperature in such a way that at T_s , $\frac{W_0 - W_f}{W_0} = 1/e^1$. Figure 9 shows plot of $\ln\left(\ln\left(\frac{W_0 - W_f}{W - W_f}\right)\right)$ vs $(T_s - T)$. For the TGA curve shown in Figure 2, T_s was found to be

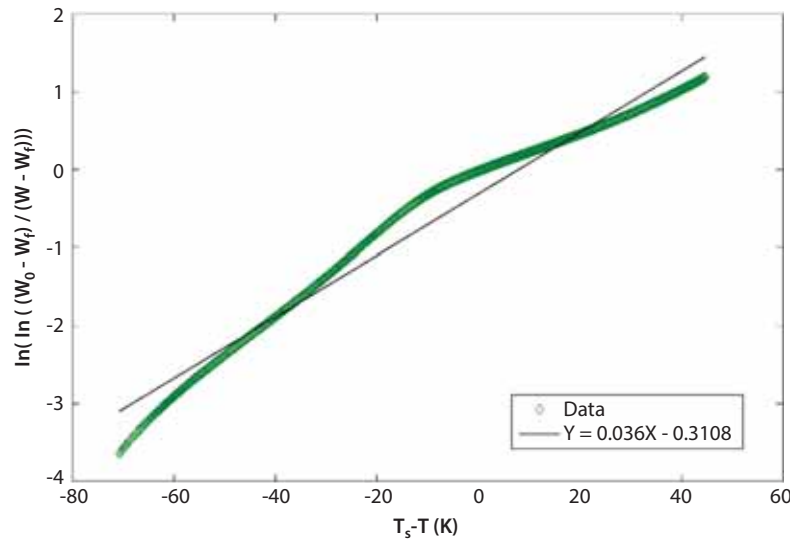


Figure 9 Calculation of activation energy for flax/VE composite.

385°C. A straight line was fitted through data points using the method of least squares. The slope of the straight line was found to be 0.036. Therefore, activation energy based on Equation 11 was 129.587 kJ/mol. Velde and Kiekens [53] used the same method and they measured activation energy of six different types of flax fiber in the air and in the nitrogen. Their average value of activation energy for flax fibers in nitrogen was 135.33 kJ/mol.

5 CONCLUSION

Creep tests with constant stress were carried out at different temperature intervals on flax/vinyl ester composite. A creep compliance master curve was generated by shifting creep compliance data along time scale in reference to the curve at 30°C. The horizontal shift factors were found to be governed by Arrhenius equation. The coefficients in Findley power law were computed and a strong agreement with 99.6% confidence level between experimental and simulated results was observed. Therefore, the resulting master curve and power law equation provides an accelerated creep characterization up to 10^{10} seconds for this composite. As a result, to predict creep behavior of a flax fiber/vinyl ester composite material in 20 years at 30°C, one can run creep tests at 100°C for 10 minutes and achieve fair accuracy.

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