Time–Temperature Superposition Principle Applied to a Kenaf-Fiber/High-Density Polyethylene Composite

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ABSTRACT: The time–temperature superposition principle was applied to the viscoelastic properties of a kenaf-fiber/high-density polyethylene (HDPE) composite, and its validity was tested. With a composite of 50% kenaf fibers, 48% HDPE, and 2% compatibilizer, frequency scans from a dynamic mechanical analyzer were performed in the range of 0.1–10 Hz at five different temperatures. Twelve-minute creep tests were also performed at the same temperatures. Creep data were modeled with a simple two-parameter power-law model. Frequency isotherms were shifted horizontally and vertically along the frequency axis, and master curves were constructed. The resulting master curves were compared with an extrapolated creep model and a 24-h creep test. The results indicated that the composite material was thermorheologically complex, and a single horizontal shift was not adequate to predict the long-term performance of the material. This information will be useful for the eventual development of an engineering methodology for creep necessary for the design of structural building products from these composites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1995–2004, 2005

Key words: composites; fibers; polyethylene (PE); viscoelastic properties

INTRODUCTION

The use of natural fibers as reinforcers and fillers in the manufacture of natural-fiber/thermoplastic composites has become more commonplace in recent years. Natural fibers have many advantageous attributes, such as low density, high specific strength and modulus, relative nonabrasiveness, ease of fiber surface modification, and wide availability. Natural fibers are also much cheaper than synthetic fibers and could replace synthetics in many applications for which cost savings outweigh high composite performance requirements.[1] The main disadvantages of natural fibers in composites are lower allowable processing temperatures, incompatibility between hydrophilic natural fibers and hydrophobic polymers, and potential moisture absorption of the fibers (and, in turn, the manufactured composite).

A challenge in using natural-fiber/thermoplastic composites is that both phases (polymer matrix and natural fiber) exhibit time-dependent properties. The long-term creep performance of these composites is of particular importance as they find increased use in structural building products. One of the greatest constraints in studying creep behavior is the relatively long time required to complete the tests. Therefore, methods that are able to predict the long-term performance of a material from short-term data have gained considerable attention. Observation suggests that the effects of time and temperature are equivalent.[2] Mechanical behaviors observed after a short time resemble those observed at cooler temperatures; those observed after a long time resemble those observed at warmer temperatures. From these observations, numerous investigators have tried to develop equations of time and temperature. The objective of this study was to evaluate the applicability of the time–temperature superposition (TTS) principle to the prediction of the creep behavior of a kenaf-fiber/high-density polyethylene (HDPE) composite.

TTS, one of the most useful extrapolation techniques with a wide range of applications, has been applied to virtually every mechanical property and every kind of plastic.[2] Many believe (e.g., ref. 3) that this superposition manifests itself from molecular behavior and, therefore, formulate equations based on the activation energy (E), such as this Arrhenius equation:

$$\ln a_T = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1}$$

where a_T is the horizontal (or time) shift factor, R is the universal gas constant, T_0 is the reference temperature (K), and T is the temperature at which a_T is desired.[2]

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Another commonly used empirical equation for TTS is the Williams–Landel–Ferry (WLF) equation, which relates a shift in temperature with a shift in time. This shifting equation is very useful if information is available for only one temperature and information must be computed for other temperatures. Conversely, if information is available at different temperatures, then more precise extrapolations and interpolations can be obtained if we direct high-temperature data to longer times to correspond to lower temperature data. The WLF equation has the following form:

$$\log a_T = \frac{17.4(T - T_g)}{51.6 + T - T_g} \qquad (2)$$

where T_g is the glass-transition temperature (K) and T is the temperature at which the test is performed (K).

Ward[4] and Van Gurp and Palmen[5] commented that TTS holds when (1) the exact matching of shapes of adjacent (time- or frequency-dependent) curves is obtained, (2) a_T has the same value for all viscoelastic functions, and (3) the temperature dependence of a_T has a reasonable form such as the Arrhenius and WLF equations [eqs. (1) and (2), respectively].

Although the TTS technique was originally developed for amorphous polymers, Nielsen and Landel[6] suggested that it could be applied to semicrystalline polymers as well, as long as a vertical shift factor, which is strongly dependent on temperature, is also employed.

The aforementioned horizontal shift factors will generally not correspond to a WLF shift factor. At least part of the vertical shift factor results from changes in the modulus of elasticity resulting from the change in the degree of crystallinity with temperature. Aging and heat treatments may also affect shift factors. For these reasons, Nielsen and Landel[6] concluded that vertical shift factors are largely empirical, with very little theoretical validity.

Ward[4] commented that TTS could not be applicable to crystalline materials because of their complex thermal behavior. However, Faucher[7] argued that the principle could be applicable to crystalline polymers if they are tested in the region in which their structure is maintained and under sufficiently low strain. The shift factors conform to an Arrhenius equation [eq. (1)].

In their work on the frequency and temperature dependence of the dynamic mechanical properties of HDPE, Nakayasu et al.[8] concluded that a simple horizontal shift along the frequency axis is not adequate to correctly superimpose dynamic loss compliance data at different temperatures. A plot of log a_T against the reciprocal of the absolute temperature gave a straight line, indicating an Arrhenius relationship. On the other hand, Mark and Findley[9] reported a successful nonlinear creep master curve obtained by only

horizontal shifting for low-density polyethylene. Again, a nearly linear relationship between the shift factors and temperature was reported, and this indicated an Arrhenius relationship.

In their study on the creep behavior of ultrahigh-molecular-weight polyethylene systems, Deng et al.[10] applied TTS to the creep data. They found that the temperature dependence of the shift factors could be described by the Arrhenius equation.

Dutta and Edward[11] also explained that isotactic polypropylene does not conform to the WLF equation. They commented that this behavior is not unexpected because polypropylene is a semicrystalline polymer and its free volume can be thought to be quantized. Therefore, it is expected to follow an Arrhenius equation for the major transitions.

Aryama et al.[12] performed tensile stress relaxation tests on polypropylene and then used TTS to shift the data. They concluded that an Arrhenius equation was sufficiently capable of explaining the temperature dependence of the shift factors.

Although many authors have indicated the possibility of shifting the viscoelastic parameters of polymers with only a single horizontal shifting, Harper and Weitsman[13] argued that the viscoelastic properties of thermorheologically complex materials could be well defined with both horizontal and vertical shift factors. Miller[14] suggested that changes in the internal structure of a material during testing require adjustments along both the vertical and horizontal axes.

Nitta and Susuki[15] superimposed the dynamic modulus/frequency curves of HDPE with both horizontal and vertical shifts. The resultant master curve was used to predict the relaxation modulus curve. However, they did not explain whether the shift factors conformed to WLF or Arrhenius equations.

Djoković et al.[16] reported that the introduction of a two-process model for stress relaxation in the standard time–temperature procedure made possible a distinct study of the viscoelastic properties of the crystal and amorphous fraction of polyethylene and polypropylene. By considering the E values and the molecular origin of the mechanical α and β relaxations in polyethylene and polypropylene, they concluded that amorphous materials are thermorheologically simple, whereas crystalline materials are complex.

One of the very few studies on the application of TTS to wood-fiber/plastic composites is that of Pooler[17] on a composite of HDPE and wood flour. Pooler concluded that this material was thermorheologically simple, so only a horizontal shifting was adequate to correctly superimpose the creep data. Dynamic mechanical analysis (DMA) tests were used to determine shift factors. However, shift factors were determined with only the storage modulus curves, and other viscoelastic parameters were ignored.

The objective of this study was to evaluate the applicability of TTS to the prediction of the creep behavior of a kenaf-fiber/HDPE composite. Three stages were planned toward this overall objective:

- Evaluating the use of horizontal and vertical shifting and two-dimensional minimization methods to obtain master curves covering a higher range of frequencies than that evaluated empirically.
- Comparing TTS master curves with actual creep test data.
- Extrapolating short-term creep data with a power-law function, predicting longer term creep data, and validating by comparison with actual long-term test data.

EXPERIMENTAL

Materials

HDPE (HiD 9035, Chevron, The Woodlands, TX), with a melt-flow index of 40 g/10 min (190°C, 2.16 kg) and a density of 0.952 g/cm^3, was used in this study as the polymer matrix. Kenaf fibers were supplied by Kengro Corp. (Charleston, MS). They contained approximately 97% bast fiber. Maleated polyethylene (MAPE) was a Fusabond C modified polyethylene (MB-100D) and was supplied by DuPont Industrial Corp (Wilmington, DE).

Compounding

The composite material used in this study consisted of 48 wt % HDPE, 50 wt % kenaf fibers, and 2 wt % MAPE compatibilizer. The ingredients were compounded in the fiber–plastic processing equipment of Teel Global Resources, Inc. (Baraboo, WI). The compounded materials were reduced in size with a pilot-scale grinder to produce granules for injection molding. The average fiber length and diameter after grinding were not determined; however, the average fiber length in the produced composite specimen was visually measured to be 1.168 mm, with a standard deviation of 0.42 mm.

Specimen preparation

The granules were injection-molded with a 33-ton Cincinnati Milacron 32-mm reciprocating-screw injection molder (Cincinnati, OH) with a length/diameter ratio of 20:1. Before the injection, all materials were dried for at least 4 h at 105°C.

Specimens for DMA and creep testing were cut from ASTM impact specimens with a woodworking table saw. They were further machined to a nominal thickness of 2 mm with a Bridgeport knee-type verti-

cal milling machine (Shelton, CT). The final specimen dimensions were 52 mm × 8 mm × 2 mm.

Frequency sweeps

Frequency sweeps were performed with a Rheometric Scientific DMTA V analyzer (Piscataway, NJ). Frequency tests were performed in a frequency range of 0.1–10 Hz, and five measurements were made in each decade. The strain amplitude was 0.1%. The measurements were carried out on a logarithmic basis and were repeated at 23, 33, 43, 53, and 63°C. A dual-cantilever fixture was used. The storage modulus, loss modulus, and tan δ values were collected during the runs and were plotted versus the frequency.

Creep tests

Short-term creep tests were performed with a DMA analyzer. The specimen dimensions and characteristics were identical to those of the described frequency sweep specimens. Creep tests were also performed at 23, 33, 43, 53, and 63°C for a total duration of 12 min. The stress level was 2 MPa. Creep tests were also performed on a dual-cantilever fixture. Each specimen was inserted into the chamber, and an 8-min soak time was applied to ensure that the specimen reached equilibrium. Then stress was applied and held constant for 12 min. During the test, strain data were collected, and they were plotted versus time. This procedure was followed for all temperatures studied in this research.

Creep modeling and TTS

According to Betten,[18] "the primary or transient creep is characterized by a monotonic decrease in the rate of creep and the creep strain can be described by the simple formula"

$$\varepsilon_c = a\sigma^n t^b \tag{3}$$

where a, n, and b depend on the temperature. ε is the creep strain and σ is the stress. Equation (3) was applied to the experimental creep data at room temperature. The RSI Orchestrator software supplied with the DMA analyzer (Piscataway, NJ) was used to perform TTS.

RESULTS AND DISCUSSION

A typical frequency sweep of the composite, as obtained from the DMA analyzer, is shown in Figure 1. The RSI Orchestrator software supplied with the DMA analyzer is capable of performing the TTS procedure for frequency scans. This is done with either a horizontal shifting procedure or a two-dimensional minimization method. In the first method, storage modu-
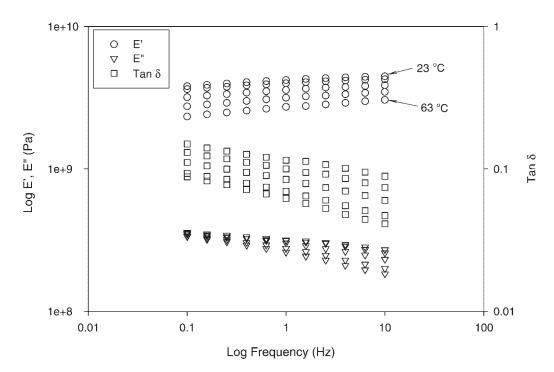
Figure 1 Frequency sweep of a kenaf-fiber/HDPE composite at different temperatures (E' = storage modulus, E'' = loss modulus).

lus curves obtained at different temperatures are horizontally moved until they superpose. The results of such shifting are presented in Figure 2.

Although a smooth curve is obtained for the storage modulus, the loss modulus and tan δ curves do not superpose satisfactorily. This means that it is not possible to use the same horizontal shift factors for all three viscoelastic parameters. This is a violation of the assumptions of TTS, in which the same shift factors are assumed to apply for all viscoelastic properties.[4,5]

Figure 2 Master curves generated by the horizontal shifting of the frequency sweep curves (E' = storage modulus, E'' = loss modulus).
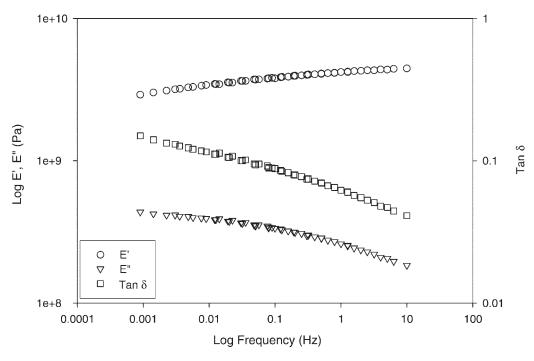
Figure 3 Master curves generated by the horizontal and vertical shifting of the frequency sweep curves (E' = storage modulus, E'' = loss modulus).

The temperature dependence of the horizontal shift factors conforms to an Arrhenius equation (r^2 (coefficient of determination) = 0.9895), and the associated E value has been determined to be 206.57 kJ/mol with the storage modulus data.

Figure 3 shows the master curves generated with the two-dimensional minimization method. Here all three sets of curves are simultaneously moved horizontally and vertically until they superpose. All three curves are very well superposed, and smooth curves have resulted. The same horizontal and vertical shift factors are used for all three viscoelastic parameters, and this conforms to TTS. However, a comparison of Figures 2 and 3 reveals that in the latter, a smaller range of frequencies is covered by the master curve. This confirms that the composite studied here is thermorheologically complex and that a vertical shift is necessary to achieve a reasonable master curve.[13] Nitta and Susuki[15] superimposed the dynamic modulus/frequency curves of HDPE with both horizontal and vertical shifts. The resultant master curve was then used to predict the relaxation modulus curve. The temperature dependence of the shift factor was also tested and found to conform to an Arrhenius equation (r^2 = 0.9904), and E was determined to be 101.01 kJ/mol.

A horizontal shifting method has been used to superpose creep data at different temperatures (Fig. 4). The same procedure has been extensively used by many authors who disregard the applicability of the shift factor to other viscoelastic properties.[8–11,19,20] The

master curve generated in this way is presented in Figure 5. The resulting very smooth curve suggests that this could be used to predict creep strain at longer times.

To determine whether the shift factors determined in frequency-scan TTS can be used for creep curves, we have applied them to creep curves (Fig. 4) obtained at different temperatures. Figure 6 shows the creep master curve generated by the application of the horizontal shift factors determined in Figure 2 to creep strain curves. The superposition is not very satisfactory, and this indicates that the use of only horizontal shifting is not adequate.

Figure 7 shows the creep master curve generated by the application of frequency horizontal and vertical shift factors to creep data. A somewhat better superposition has been obtained, and this indicates that the two-dimensional superposition method is preferable. However, as described previously, a smaller range of time is covered when the creep curves are shifted two-dimensionally.

To examine the validity of master curves generated by this horizontal and vertical shifting of frequency and temperature sweeps, we performed a longer term creep test for 24 h at 23°C. Figure 8 shows the creep master curve obtained by the two-dimensional shifting of creep curves (from different temperatures) and the actual creep data for 24 h. A relatively good agreement can be observed, but the two curves tend to deviate from each other at longer times. Such a phenomenon was reported by Marias and Villoutreix,[19]
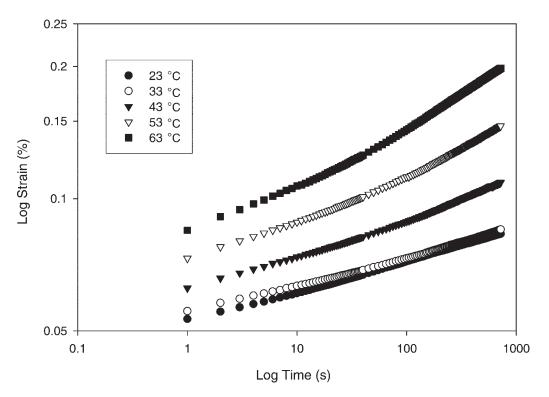
Figure 4   Creep strain versus time at five different temperatures.

who tried to shift creep compliance data of a PMR-15 polyimide along the time axis with the WLF equation [eq. (2)] to obtain a master curve. This indicates that the effect of temperature on the creep behavior is much more pronounced than the effect of time. That is

why the master curve deviates from the actual creep curve at longer times (higher temperatures).

Finally, the applicability of the primary creep [eq. (3)] was investigated. First, the short-term creep curve (12 min) was modeled with the primary creep strain
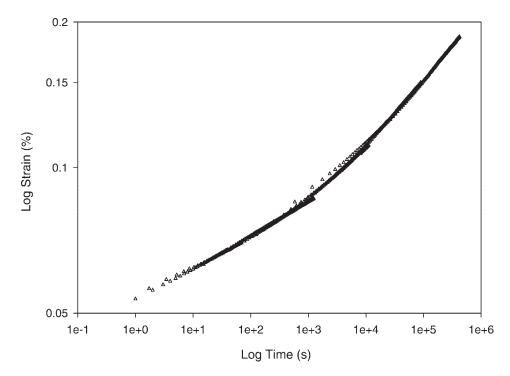

Figure 5   Master curve of the creep strain generated by the horizontal shifting of the creep data at different temperatures.
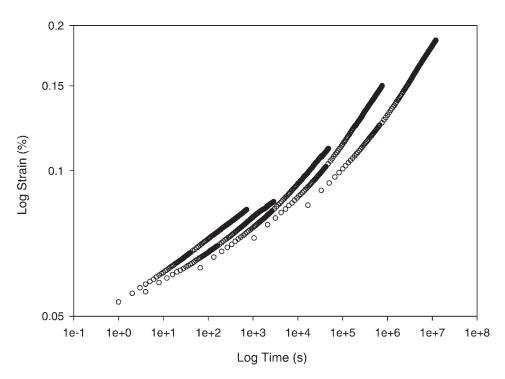
Figure 6 Curves of the creep strain superposed with the frequency sweep horizontal shift factors.

model [eq. (3)], and the governing equation was derived. This model was then used to extrapolate the creep behavior of the composite to 24 h. The resulting curve was then plotted together with the actual 24-h creep curve explained previously. This is presented in Figure 9. A very good agreement can be observed between the actual creep curve and the extrapolated curve. This clearly indicates that the power-law model is a very good method for predicting creep behavior at room temperature.

Figure 10 shows the creep master curve derived by the horizontal shifting of creep data and the actual
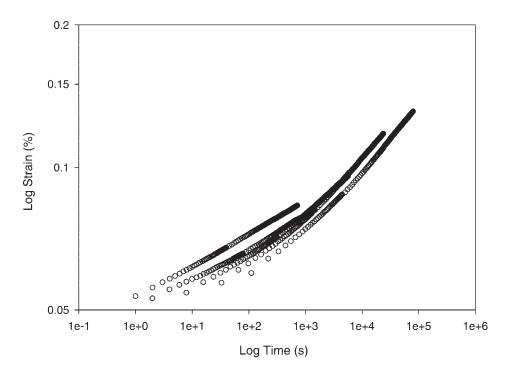

Figure 7 Curves of the creep strain superposed with the frequency sweep horizontal and vertical shift factors.
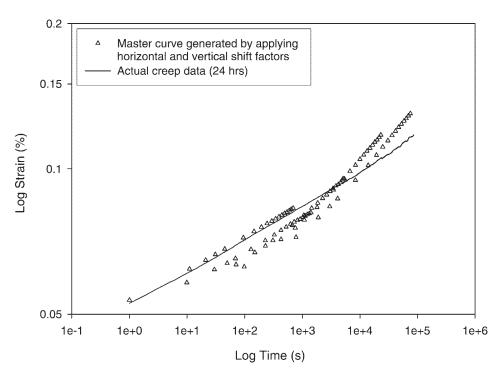
Figure 8 Master curve of TTS creep and actual creep data.

creep curve for 24 h. Again, the curves deviate from each other at longer times. The overall study of TTS performed on HDPE and kenaf-fiber composites indicates that these composites are not thermorheologically simple and that TTS can be applied only to such composites with caution. The base polymer (in this case HDPE) is itself reported to be thermorheologically complex, and the presence of fibers adds to the complexity. Thus, TTS can be expected to not work well for semicrystalline polymers and their composites. It was indicated earlier that the power-law model proved very satisfactory in predicting the long-term
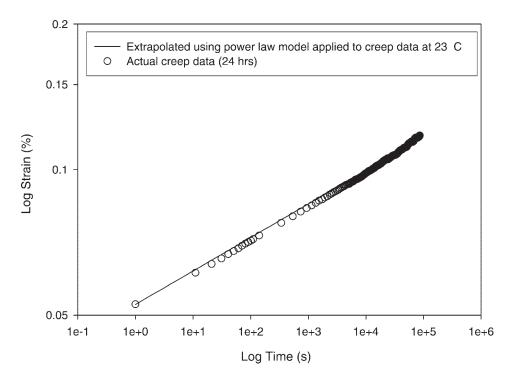

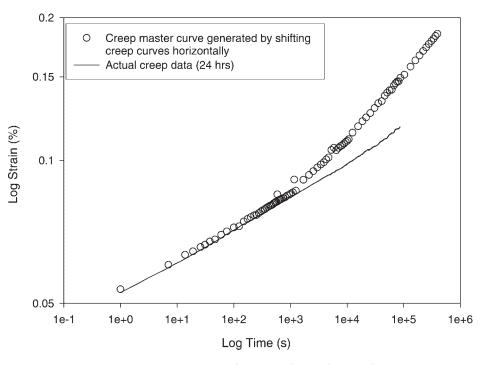**Figure 9** Power-law-extrapolated creep and actual creep data.

Figure 10 Master curve of creep and actual creep data.

creep behavior of such composites. However, the results of this study, too, must be used with caution because creep behavior is a complex phenomenon that is dependent on a variety of parameters, such as the stress level, temperature, and environmental conditions. In concurrence with the results of previous researchers[8,9,12,15] for semicrystalline polymers, an Arrhenius equation better explains the temperature dependence of the shift factors than the WLF equation for the kenaf-fiber/HDPE composite of this study. E in the Arrhenius equation [eq. (1)] determined by the two-dimensional minimization method is also closer to the values found in the literature for HDPE,[7] and this indicates that this is probably a better method for performing TTS for this composite. Although the superposition methods used here show some deviations at longer times, they all overestimate the creep strain. This implies that the master curves still could be used to give a conservative estimate for the creep behavior of composites for which no other long-term test results are available.

CONCLUSIONS

The following conclusions can be drawn from this discussion:

- Frequency sweep data were superimposed with single horizontal shifting and two-dimensional minimization methods to obtain master curves covering a higher range of frequencies. The two-dimensional minimization method was more satisfactory in terms of satisfying TTS requirements,

and kenaf-fiber/HDPE composites are clearly thermorheologically complex materials. Shift factors were found to conform to an Arrhenius equation for their temperature dependence.
- Shift factors obtained from frequency isotherm superposition were applied to creep strain isotherms at the same temperatures, and a single horizontal shift factor was not adequate to explain the temperature dependence of this parameter.
- TTS master curves generated with both methods were compared with actual 24-h creep test data. The TTS curves deviated from the experimental curve at longer times (higher temperatures). This indicates that the effect of temperature on the viscoelastic response of such materials is much more significant than the effect of time, and so the convenient TTS method would overestimate longer term creep.
- The primary creep strain model of eq. (3) was fitted to 12-min creep data. The resulting equation was then extrapolated to 24 h, and this compared well with the 24-h creep data. Thus, the creep strain model of eq. (3) can be successfully used to predict the long-term creep behavior of natural-fiber/thermoplastic composites.

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