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Equivalent Time Temperature Model for Physical Aging and Temperature Effects on Polymer Creep and Relaxation

The equivalent time temperature method (ETT) is a novel extension of the equivalent time method. ETT is developed in this work to deal with time-temperature shifting of long-term polymer and polymer composite creep data, including the effects of physical aging at nonuniform temperature. Modifications to classical testing methods and protocols are presented to obtain accurate and repeatable data that can support long-term predictions with nonuniform temperature conditions through time. These techniques are used to generate momentary Time temperature superposition (TTSP) master curves, temperature shift factor rates, and aging shift factor rates. Novel interpretation and techniques are presented to deal with the coupled age-temperature behavior over long times. Validation of predictions against over 20,000 Hr of long-term data in field conditions is presented. [DOI: 10.1115/1.1789956]

Introduction

From the point of view of structural analysis, creep is the most important feature of polymer behavior; it controls the design of most structures and provides the main motivation for the advent of fiber-reinforced polymers [1]. The effect of temperature on creep behavior has been extensively studied [2-6] but there seems to be some confusion as to the limitations of these studies in relation to physical aging. Specifically, the need to use only unaged data to construct the master curve seems to have been lost in the engineering community. On the other hand, physical aging of polymers [7-12] and composites [13-24] has been extensively studied, but the results of these studies have not found widespread application in the structural engineering practice. For example, Guerdoux et al. [8] measured the torsional viscoelastic properties of small cylindrical and rectangular specimens, demonstrating the need for an additional step to the horizontal shift proposed by Struik [7]. Guerdoux et al. [8] used the model proposed by Chai and McCrum [22], which implies that a vertical shift, a rotation, and a horizontal shift are needed to superimpose experimental aging data onto a master curve. Other researchers claim to have compared their predictions (based on short-term tests) with longterm data, but the later spans only days. In other words, previous work is limited in the duration of the long-term data used for validation. For example, Dean et al. [10] performed creep tests on specimens ($145 \times 12 \times 6$ mm) for approximately 12 days. On the other hand, short-term data is used in this work to predict and compare with long-term data up to 1800 days. Previous work was also limited in the span of the initial age t_e of the samples. While Dean et al. [10] used short-term data to predict long-term data, both with an initial age of 7.5 and 72 hours, an extrapolation from $t_e = 1$ Hr to $t_e = 3$ months is demonstrated in this work.

Another aspect is the type of geometry and loading of the specimens used in the comparisons. Previous work [10] compares predictions based on short-term data (e.g., a few hours) to long-term data (e.g., 12 days) with both sets of data obtained with the same small specimens (e.g., $145 \times 12 \times 6$ mm). The present study attempts to develop a test protocol to determine the required param-

eters in order to predict long-term creep data of an element used in an engineering application (e.g., pipes). The long-term data used for validation in this work was obtained from full-size samples $(1829 \times 304 \times 10 \text{ mm})$ under simulated field conditions (i.e., external pressure), which is markedly different from the short-term samples (i.e., small samples under bending). Therefore, the present research is an attempt to demonstrate that accurate longterm predictions of structural performance can be obtained by following certain rules for data gathering and data reduction.

Furthermore, we demonstrate that the classical numeemperature superposition method is not accurate unless aging effects are included using the methodology proposed herein. For example, in Fig. 1, 2 Hr. of data at 40°C with an initial age of $t_e = 1$ Hr shifted to 21°C by the classical method does not match the 21°C data, the TTSP master curve, or the ETT prediction at 21°C. In summary, a method is proposed to accurately perform temperature and age shifting of data, even of long-term data where the effects of temperature, creep, and age are coupled.

Finally, there is strong interest in testing longer than allowed by the snapshot assumption [7]. In fact, there is a plethora of invaluable studies in the literature that provide long-term data on many aspects of material behavior, including creep compliance D(t). However, most data available is not comparable because the temperature and/or initial age of the samples differ among them. In some cases, the test temperature varies throughout the duration of the test [21]. ETT allows any data containing agning and/or variable testing temperature effects to be shifted to any age and/or temperature, as demonstrated in this present work.

Experimental

Five different materials are tested, three of which are different formulations of Poly Vinyl Chloride (PVC), one is High Density Polyethylene (HDPE), and the other is polyester reinforced with polyester fibers (PRP), which are designated with the letters L, M, N, O, and P. ASTM E 1640-99 was used to obtain the glass transition temperature of the materials from Dynamic Mechanical Analysis.

Testing Fixture. The relationship between stress and strain depends on time due to creep [2] and physical aging [7]. Short-term creep and aging have been studied in the frequency domain using dynamic mechanical analysis (DMA) [8,18,24]. However,

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Fig. 1 Classical shift from 40°C to 21°C of data containing aging does not overlap actual data at 21°C having the same initial age and test duration, PVC

two drawbacks of DMA testing motivate the development of a new testing fixture: specimen size and test duration. While polymer specimens from structural applications are usually thick, on the order of 10 mm or more, DMA specimens are small, on the order of 10 mm×1.5 mm×15 mm. Therefore DMA specimens must be cut from structural-size samples. Such small specimens do not capture well the inhomogeneities encountered in polymers used in structural applications. A new creep bending testing (CBT) fixture is therefore proposed that can use specimens with the full thickness of the structural sample, with a maximum testing size of 50 mm×material thickness×231 mm. The larger size of the CBT specimens allows for a better representation of the material properties to be tested. In addition, DMA equipment is expensive and can accommodate only one sample. Running long-term tests on a DMA becomes costly. Therefore, the CBT fixture was designed to perform inexpensive, long-term creep testing in a configuration similar to ASTM D6272-98 four-point bending conditions inside an environmental chamber.

The CBT fixture (Fig. 2) uses two loading points with spacing of 64 mm, which is one third of the support span of 192 mm. Thanks to the low-cost design, eight fixtures were fabricated. Four fixtures support a specimen with a maximum width of 25 mm while four other fixtures support a specimen with a maximum width of 50 mm. All four-load points have a radius of 7.94 mm, which allows for a minimum specimen depth of 4.96 mm according to ASTM D6272-98 Section 6.2. Displacement is measured with a linear optical encoder with an accuracy of 0.005 mm and a







Fig. 3 Side view of CBT fixture during testing. Note the rubber band holding the specimen and, behind it, the knife with sparand-scale assembly.

maximum travel of 50 mm. The optical encoder, model LDK-4-4-B and spar and scale assembly, model B36679-4-0-50.0 are from Dynamics Research Corporation.

The majority of the fixture is constructed out of aluminum, except for the load supports and the vertical rods where stainless steel was used. The fixture is designed to be unaffected by thermal expansion and it does not require any type of temperature compensation even under large temperature fluctuations inside the environmental chamber. The deflection is measured with an optical encoder that does not require any temperature compensation, partially thanks to be mounted on CTE compatible materials.

The optical encoder consists of two parts, the spar and the scale. The spar has a series of lines etched at a precise distance from one another, like a ruler. The scale counts the lines as the spar moves in front of it, thus measuring the deformation optically. In the CBT fixture, the scale is mounted to the carriage and the spar is mounted to a knife that slides inside the carriage and rests on top of the specimen at center span (Fig. 3). Since the carriage rests on the specimen at the loading points and the knife at center span, the system measures the deflection between the loading points and the center span, exactly in the shear free zone (Fig. 4). This allows for simple computation of the axial compliance (modulus) without complications arising from the effects of shear deformation during bending. Linear bearings were used to allow the carriage to descend freely and apply the load to the specimen. Thus, the load is fixed and equal to the weight of the carriage, resulting in a true creep test.

Each specimen is held with rubber bands (Fig. 3), hanging from the loading arms, which allows the top of the specimen to remain in contact with the bottom of the loading arms, and the knife to remain in contact with the top of the specimen at the center span at all times prior to and during the test. This allows us to reset the initial deformation in the data acquisition software to zero with



Fig. 4 Creep Banding Testing (CBT) fixture schematic showing the four point bending configuration and the operation of the "knife"

the knife resting on the center span and no load applied. Therefore, this allows for an accurate measuring of the deflection, even if the specimen is not flat as a result of irreversible creep deformation from prior testing.

Prior to testing, the carriage is held up by a spacer (not shown) so that the bottom of the specimen does not touch the support arms, which are separated by the full span of 192 mm (Fig. 2). Loading is applied by removing the spacer, thus allowing the bottom of the specimen to load on the support arms, as shown in Fig. 2. Data is acquired from the testing fixtures using an ACS-Tech80 5312B ISA Encoder Interfacing card with four axes. An Intelbased computer running Windows 98 is used to read the card and store the data. Software drivers provided by the DAQ manufacturer were modified to write data to files in specific time increments using Visual Basic 6.0. All tests are performed in a Cincinnati Sub-Zero environmental chamber model Z-32 that uses a Chromalox 2030 microprocessor controller.

Testing Protocol. New samples are produced at the vendor facility or field installation of each material. All samples are cut perpendicular to the direction of extrusion and have a minimum length of 30 cm. The direction of extrusion is properly labeled. Thermoset polymer and polymer composite samples must be produced flat as they cannot be reformed after curing. Thermoplastic samples that are not flat are then flattened as follows. First, the samples are placed in an oven, concave side down on a piece of flat aluminum with a thickness of 12.7 cm and overall dimensions slightly greater than the sample. A second identical aluminum plate is placed on top of the sample and 20 Kg of additional weights are added. The samples, aluminum plates, and additional weights are then heated to the annealing temperature T_H and maintained at that temperature for not less than 48 hours. The specimen annealing temperature T_H is set to 15°C above the glass transition temperature T_g of the material, but below it's melting point T_m .

The flat samples are cut, using a band saw, into specimens having a minimum span-to-thickness aspect ratio of 16-to-1, a maximum width of 50 mm, and a minimum depth of 4.96 mm. The thickness and width of each specimen are measured at both ends and at the center of the span using a micrometer as per section 6.3 of ASTM D790 and then averaged. The specimens, except for HDPE, are annealed in an oven at temperature T_H for at least 30 min. HDPE is annealed at the temperature used to reform the material during field installation in order to mimic as close as possible the crystalline structure of the polymer as used in the actual structural application. Specimens are then quenched between steel plates for approximately 5 min. After the specimens are quenched, they are placed in the fixture and held in place with rubber bands wrapped around the inner loading nodes. Next, the scale assembly is placed in the carriage and resting onto the sample at the center span (Fig. 3). Using the data acquisition software, the readouts are then zeroed, the test filename and path are entered, and the data are then recorded.



Fig. 5 Compliance curves for various increasing aging times t_e , PVC

Specimens are annealed and quenched, then placed in the fixture at a specified temperature below T_g to let age. At each stage of the testing protocol, the specimen is aged for an aging time t_e , then creep tested for a time interval no longer than $t_e/10$ following the snapshot assumption [7] to avoid noticeable aging effects during creep testing.

The compliance D(t) is calculated from the deflection data. The equation for the compliance under four-point bending is derived using the following method. Referring to Fig. 4, the center deflection of a beam under four-point bending with 1/3 load span is [19]

$$d1 = \frac{-Pb(L^2 - b^2)^{3/2}}{18\sqrt{3}EIL} + \frac{-Pa(L^2 - a^2)^{3/2}}{18\sqrt{3}EIL}$$
(1)

where P is the load, L is the distance of the support span, E is the modulus of elasticity, I is the moment of inertia, a=L/3, and b=L/3. The deflection at the load points is [19]

$$d2 = \frac{Pa^2b^2}{6EIL} + \frac{Pb}{12EIL}[x^3 - (L^2 - b^2)x]$$
(2)

where a = L/3, b = 2L/3, and x = L/3. The deflection in the shear-free zone is

$$\delta = d1 - d2 \tag{3}$$

Thus the compliance is

$$D = \frac{243(64\sqrt{6} + 135)\,\delta wh^3}{2117PL^3} \tag{4}$$

where w is the width of the specimen, h is the thickness of the specimen, P is the load, and L is the support span.

Mechanical Conditioning. The need for annealing and quenching specimens is to rejuvenate the samples and be able to record the age, with age zero being at the time of quenching. As shown in Fig. 5, specimens tested at different ages have different compliance even when tested at the same temperature. As the material ages it gets stiffer, thus reducing the amount of deflection observed during an interval of time. Therefore, with each successive test without rejuvenation, the compliance curves in Fig. 5 should lie under one another. This was not observed within the first, and sometimes second tests. This is because an imperfect specimen must adjust and settle onto the load supports. In other words, specimens need to undergo mechanical conditioning after quenching. Therefore, the following is proposed as a means of mechanically conditioning the samples. In the aging study, the first two tests are discarded and the sample is never removed from the fixture as it undergoes creep, recovery, and aging, until the test is completed. Also, while constructing the TTSP master curve,

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two one-minute creep tests are performed, at $t_e = 20 \text{ min}$ and $t_e = 25 \text{ min}$, after every quenching, and their associated data is discarded.

Physical Aging

When a polymer is heated above its glass transition temperature T_g , into the rubbery state, it attains sufficient mobility to erase the effects of aging and residual stress carried over from the glassy state at lower temperatures. The process is called annealing and it requires certain time, which is referred to as annealing time. Quenching, i.e., rapidly cooling down below T_g , into the glassy state, sets the polymer into a state on thermodynamic inequilibrium. With time, the polymer evolves slowly towards the equilibrium condition in a process that is called physical aging. Thus, age zero ($t_e=0$) is the time at which quenching occurs, precisely the moment at which the material crosses T_g during cooling and/or curing, i.e., during quenching.

Creep testing is used to evaluate the creep compliance D(t) as a function of time. Since time implies aging, the true change of creep compliance due to time and the effects of aging are combined and seemingly inseparable. Thus, two creep tests performed for the same amount of testing time on two samples that have different age at the onset of the test yield different results. Aging studies attempt to resolve this dilemma by separating the compliance from the aging effects.

In order to test for compliance without noticeable aging effects, the testing time must be much shorter than the age of the sample at the onset of the test. This is called the snapshot assumption [7] because a test performed during such a short time $(\lambda < t_e/10)$ will exhibit negligible effects of aging. The time λ is the unaged time, that is, the time elapsed during a test while the effects of aging are not noticeable. The Greek letter λ is used in this study to differentiate it from the actual time t that is longer than that afforded by the snapshot assumption and therefore spans sufficient time for the effects of aging to be noticeable.

In order to model aging, tests at different ages are performed at a constant temperature. The testing schedule is set up to have equal increments of age in base-10 logarithmic scale

$$\log(\delta t_e) = \log(t_{e(i+1)} - t_{e(i)}) = \text{const}$$
(5)

A typical set of total compliance $D(\lambda)$ curves for different ages are shown in Fig. 5. The compliance $D(\lambda)$ is separated into an elastic component D_o and a creep component $D_{\alpha}(\lambda)$ and the later is modeled with a power law

$$D = D_o + D_a(\lambda) = D_o + D_1 \lambda^m \tag{6}$$

where D_o is the initial compliance, D_1 is the creep coefficient, λ is the time, and *m* is the power-law exponent. A master curve of creep compliance is constructed by rotating, then shifting all curves to a reference age t_{eR} . The reference age is defined as the curve with the greatest age when the test was started (highest value of t_e) [15,17]. The need for a slight rotation prior to shifting is evidenced by the curves in Fig. 5 having slightly different slopes, and it is explained in detail in [20,23]. The shift factors $a_e(t_e)$ used to shift the curves in Fig. 6 are plotted versus the corresponding ages in double logarithmic scale. The shift factor data can be fitted with a linear equation

$$\log(a_e) = \mu \log(t/t_{eR}) \tag{7}$$

where μ is the aging shift factor rate [7] with units [1/log(time)] (Table 1).

Given a curve $D(\lambda)$ obtained at a constant age t_e , it is a simple exercise to use it at any age by shifting it as $D(\lambda/a_e)$. However, samples tested need to be very old in order to yield a useful range of unaged time λ . The solution to this limitation is to use time-temperature superposition to generate the compliance curve.



Fig. 6 Set of rotated compliance curves for various ages and resulting master curve at $t_{eR}{=}\,4513$ Hr, PVC

Temperature Time Superposition Method

The effect of increasing temperature on polymer creep is to accelerate it. Therefore, long time creep behavior could be conceivably studied by testing at high temperature for a short period of time. We shall see that this is accurate as long as testing does not violate the snapshot assumption. Time-temperature superposition (TTSP) allows us to obtain a creep compliance master curve $D_{\alpha}(\lambda)$ over a range of time longer than afforded by either the patience of the operator or by the snapshot assumption, or both. Tests at the same temperature but different age result in different compliance curves, as shown in Figs. 5 and 6. It is clear then that individual tests at various temperatures must be done at constant age for then to be meaningful. Testing is performed at several temperatures so that the resulting data overlaps over a range in the compliance axis, as shown in Fig. 7. All curves are then shifted to a reference temperature T_R . The resulting shift factors $a_T(T)$ are then plotted versus temperature as shown in Fig. 8. The data is then fitted with a linear equation

$$\log(a_T) = \mu_T (T - T_R) \tag{8}$$

where μ_T is the temperature shift factor rate with units [1/°C].

Since all the individual tests at various temperatures are done at constant age t_e , and every test duration does not exceed the snapshot assumption $t_e/10$, the TTSP master curve represents the behavior of the polymer undisturbed by aging, even though it spans a longer time than $t_e/10$.

Using the master curve at other temperatures and/or ages is a trivial exercise since it can be simply shifted to a new time

λ

$$' = 1/(a_e a_T) \tag{9}$$

This is referred to as the classical shifting method. Equation (9) cannot be used if the compliance curve D(t) is obtained experimentally over a range of time longer than afforded by the snapshot assumption, as demonstrated in this study.

Three specimens of each material are tested to obtain a statistically significant master curve and shift factor plot (Table 1). Specimens are tested in a temperature range approximately 21°C

 Table 1
 Comparison of aging shift factor rate and temperature shift factor rate and goodness of curve fits for all materials.

| Material Type | μ | R^2 | μ_T | R ² |
|---------------|-------|-------|---|----------------|
| L | 0.715 | 0.941 | $\begin{array}{r} -0.109 \\ -0.0832 \\ -0.0774 \\ -0.157 \\ -0.113 \end{array}$ | 0.969 |
| M | 0.602 | 0.895 | | 0.998 |
| N | 0.177 | 0.936 | | 0.983 |
| O | 0.481 | 0.988 | | 0.961 |
| P | 0.720 | 0.999 | | 0.966 |



Fig. 7 Set of compliance curves for various temperatures and resulting master curve at T_R =21°C, PVC

to 57°C with a 5°C to 7°C interval between successive tests. The testing temperature should not exceed the T_g of the material.

The curves are shifted by minimizing the difference in shifted time $(t_R - t_i/a_{Ti})$, where t_R is the time on the reference curve at temperature T_R , t_i is the time of the curve being shifted, and a_{Ti} is the shift factor between the two curves on a base-10 log-log scale. Three specimens are tested at or near each nominal temperature in the testing schedule. The data sets are designated T_{1a} , T_{1b} , T_{1c} , through T_{ic} where a, b, c, denote the three specimens used per material, i=1...N, and N is the number of different temperatures tested. Then, each data set is shifted until they overlap with the data of the previous temperature, taking the lowest temperature as a reference temperature $(a_T=1)$. Due to material variability and experimental error, each data set at a particular temperature T_i do not lie on top of each other. In order to average the data and the shift factors simultaneously, the following method is proposed to shift the data:

1. The lowest tested temperatures T_{1a} , T_{1b} , and T_{1c} are used as temporary reference temperature $(a_T=1)$. Note that the actual testing temperatures of the three specimens T_{ia} , T_{ib} , and T_{ic} are very close to the nominal testing temperature T_i but not identical due to inherent variability of the environmental chamber from test to test.

2. One curve at the next (higher) temperature T_{ia} , where *i* is the number of the data set being shifted, is then shifted to each previous curve $T_{(i-1)a}$, $T_{(i-1)b}$, $T_{(i-1)c}$ producing three shift factors.

3. This process is repeated for the next two specimens T_{ib} and T_{ic} producing six more shift factors.

4. The nine shift factors are then averaged, resulting in a single shift factor $a_T(T_i)$ for the data at T_i .

5. Data for T_{ia} , T_{ib} , and T_{ic} are then shifted using the averaged shift factor, $a_T(T_i)$.

Several other shifting methods were examined. In one method, a power law was fit to each data set; then averaged the fitting parameters of each data set to produce an equation representing the material at a particular temperature. In another method, the compliance for each data set at each time increment were averaged yielding one set of data at that temperature. The shapes of the individual curves obtained from these methods did not overlap when shifted, so these methods were discarded.

Once the individual curves were shifted using the preferred method outlined above, the TTSP master curve and scatter are shown in Fig. 7. Next, the log-base-10 of the shift factors is plotted vs. temperature $(T-T_R)$ in Fig. 8, where T_R is the reference temperature. Linear regression of this data yields an equation representing the log-base-10 of the shift factor as a function of temperature (Table 1). This allows us to calculate a shift factors of a poly-



Fig. 8 Temperature shift factor plot, PVC

mer are determined they can be used to shift data from any type of mechanical response, i.e., stress relaxation, creep, or dynamic testing [6]. It is observed that TTSP master curves are difficult to fit with an equation if they span a long time. Several equations such as the Kohlrausch equation [15-17] and the power law have been used in the literature but the selection of the following equation

$$D(t) = D_o + \lambda/m + D_1 \lambda^{1/n}$$
⁽¹⁰⁾

fits the data well for all materials in this investigation. Note the use of λ , not *t*, since a TTSP master curve has no aging effects.

Equivalent Time Method

Aging makes the polymer stiffer and stiffer with time. All things being equal, the longer the age, the longer the time it takes to attain a unit increment of deformation under creep testing. In other words, the unaged time λ in the unaged compliance $D(\lambda)$ is stretched into real time t when aging takes place, to yield the aged compliance D(t). The time stretching is given by the equivalent time method [7]

$$t = t_e [(\alpha \lambda / t_e + 1)^{1/\alpha} - 1]$$
 (11)

where $\alpha = 1 - \mu$. Such process is valid only when the unaged compliance $D(\lambda)$ is obtained within the constraints of the snap-shot assumption.

Equivalent Time Temperature Method

Revisiting the example explained in the Introduction, note the use of t, not λ , for long-term data that includes the effects of aging. All these data cannot be shifted for age or temperature by using Eq. (9), since Eq. (9) applies only to unaged, snapshot-type data. For example in Fig. 1, note that 2 hr data at 21°C with initial age $t_e = 1$ hr matches the ETT prediction, but 2 hr of data at 40°C with $t_e = 1$ hr shifted to 21°C by the classical method (Eq. (9)) does not match the 21°C data and it does not match either the TTSP master curve nor the ETT prediction at 21°C. In contrast, the proposed ETT method is able to shift data containing aging effects.

The ETT method can be described succinctly as follows:

1. Transform the aged data (e.g., 2 hr data) to the unaged domain using the inverse of Eq. (11), that is

$$\lambda = \lfloor (t/t_e + 1)^{\alpha} - 1 \rfloor t_e / \alpha \tag{12}$$

- 2. Perform the shift (e.g., to 2160 hr) in the unaged domain using Eq. (9).
- 3. Back transform to the time domain using Eq. (11).

To validate the ETT method, 40° C long-term data (with aging effects) was shifted to 21° C by the ETT method described above and compared with the compliance predicted by stretching the time in the master curve (Eq. (10)) using Eq. (11). As shown in

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Fig. 9 TTSP master curve, prediction, and data at $t_e=1$ Hr, 21°C. PVC

Fig. 9, the prediction using Eqs. (10)-(12) results in excellent correlation with long-term data collected over time t larger than $t_e/10$ at 40°C, then shifted using ETT to 21°C.

For further validation, the result of applying classical shifting (i.e., Eq. (9)) from $t_e = 1$ hr to $t_e = 2,160$ hr on 2 hr of creep data (labeled as CBT data) is shown in Fig. 10. Obviously, 2 hr of data with age $t_e = 1$ hr at the onset of testing violates the snapshot assumption. Therefore, classical shifting results in a very poor comparison with actual data obtained with initial age t_e = 2160 hr. On the other hand, the same data compares well with the data at $t_e = 2160$ hr when shifted by the ETT method proposed herein.

Further application of this method is motivated by the need to effect temperature compensation of data collected over long periods of time. If, for practical reasons, such data cannot be collected at constant temperature, there will be considerable interest in reporting the data at constant temperature. For example, more than 10,000 hr creep data of full-size encased polymer liners are reported in [21] and shown in Fig. 10. Due to the large laboratory space occupied by the encased liners and the long duration of the tests, it is unpractical to perform such experiments under constant temperature conditions. The same is true for field experiments where the seasonal and daily temperature variations obviously affect the data. While temperature compensation of snapshot-type data is easily accomplished by classical shifting (Eq. (9)), such a procedure cannot be applied to 10,000 hr data unless, as per the snapshot assumption, the samples were 100,000 hr old to begin with. That is almost 12 years! The solution is to use the procedure



Fig. 10 Comparison of classical and ETT shifting of shortterm and long-term data (PVC, 21°C, t_e =2,160 Hr)

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proposed herein to transform all data to the unaged condition, perform the temperature compensation there, and transform the compensated data back to the time domain.

Conclusions

The constraint imposed on the time-temperature superposition method by physical aging, namely that applies only to unaged data, is reviewed and validated with experimental data. A method is proposed to use the equivalent time method in conjunction with time-temperature superposition to shift long-term data for both age and temperature. The procedure is demonstrated using experimental data. A standardized method for shifting momentary creep curves from several specimens in order to obtain a TTSP master curve is presented. Applications to practical situations are described.

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Nomenclature

- T_g = glass transition temperature T_H = annealing temperature

$$t = time$$

- t_e = aging time
- λ = unaged time
- a_e = aging shift factor
- μ = aging shift factor rate
- a_T = temperature shift factor
- μ_T = temperature shift factor rate
- D = creep compliance

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