Physical Aging of Amorphous PEN: Isothermal, Isochronal and Isostructural Results

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Received March 22, 1999; Revised Manuscript Received November 24, 1999

ABSTRACT: The sub-glass-transition viscoelastic and physical aging responses of an amorphous poly(ethylene naphthalate) (PEN) have been studied using uniaxial tension stress relaxation experiments. It is known that PEN exhibits a strong β relaxation that overlaps the α relaxation in the experimental time and temperature ranges studied. In prior work, we had shown that both amorphous and semicrystalline PEN exhibit thermorheologically complex behaviors in that neither time–temperature nor time–aging time superposition apply to the materials. Here we compare results from two-step aging experiments in which the material is first annealed at a temperature near the nominal glass transition temperature of 120 °C. In the second step, the viscoelastic response of the material is tested at a lower temperature, following classical sequential aging techniques. We find, for samples first annealed at 100 °C, that the amorphous PEN shows time–temperature superposition behavior for constant annealing times. The results are interpreted in terms of an isostructural or constant fictive temperature glass. When the responses are compared isothermally for different fictive temperatures, as found previously, thermorheological simplicity breaks down. Possible reasons for this behavior are discussed.

Introduction

The structural recovery and physical aging responses of polymers are important to understand because they bear both on the dimensional stability of the material during processing and upon the subsequent long-term performance of the finished product. In this work we describe experiments on an amorphous poly(ethylene naphthalate) (PEN) in which the physical aging response is examined under isostructural conditions. While, for many materials, whether one performs aging experiments isochronally or isostructurally makes no difference, our results show that for the PEN there is a difference. Because the differences, at least conceptually, are subtle, yet potentially fundamental, we first spend time defining what we mean by glassy structure and the definition that we use for isostructural experiments and how those differ from the isochronal experiments and isothermal experiments that are generally used in physical aging studies.

Structural Recovery in Glasses. Referring to Figure 1, when a glass-forming polymer is cooled from the melt state, there is a point in temperature at which the volume or enthalpy begins to depart from the equilibrium value. This temperature is referred to as the glass temperature $T_g$ or the glass transition temperature, $T_g$. When the material remains isothermal below $T_g$, a spontaneous decrease in the volume or enthalpy is observed that has come to be referred to as structural recovery or structural relaxation.1–5 Hence, for the purposes of this article, it becomes important to define the structural (or thermodynamic) state of the glass. This has been done historically in one of two ways. The most common, and that followed here, is to conceive of the glassy state as being defined by the absolute temperature $T$ and by a structural parameter referred6 to as the fictive temperature $T_F$. In Figure 1 we see that the fictive temperature is defined by taking a point in the glassy state (point B in the diagram) and drawing a line parallel to the glassy volume (v) or enthalpy (H) line until it intersects the equilibrium line. The point of intersection defines $T_F$ and the line defines an isostructural state with the appropriate fictive temperature.

The other definition of the isostructural state comes from the work of Kovacs et al.3,7 and is defined in terms of the departure from equilibrium $\delta$. $\delta$ is defined as $(v - v_\infty)/(v_\infty)$ or $(H - H_\infty)/H_\infty$ and is essentially a line parallel to the equilibrium line at a fixed normalized volume or normalized enthalpy from the equilibrium line. The subscript $\infty$ denotes infinite time or the equilibrium value of v or H. Clearly, the isostructural state defined by $T_F$ and that defined by $\delta$ are related but not identical.8 The distinction between them arises in models of the kinetics of glassy recovery, such as the Tool–Narayanaswamy–Moynihan (TNM) or the Kovacs–Aklonis–Hutchinson–Ramos (KAHR) models.
Figure 2. Fictive temperature vs logarithm of time after a quench from 125 °C (Tb) to the temperatures indicated. The plot shows the expected evolution of the glassy structure as a function of aging time based on the TNM model. See text for discussion.

Figure 2 shows the evolution of T$_F$ with time after a quench as calculated from the TNM model. Both the TNM and KAHR models of the structural recovery include a term that shifts the time scale of the response function just as one does the viscoelastic functions in classic time—temperature superposition. In the case of structural recovery, it is assumed that there is a shift factor a$_T$ for temperature T and one for the structure (either a$_T$ or a$_{aT}$). The two shift factors are usually assumed to be separable, and so, it arises that the product a$_T$ a$_{aT}$ in the fictive temperature (TNM) formulation is equal to the product of a$_{aT}$ a$_T$ in the KAHR formulation. However, a$_T$ = a$_{aT}$ and a$_{aT}$ = a$_T$. Even though the shift factors for the two models can be related, there is a fundamental importance to knowing which is the appropriate measure of the glassy structure—T$_F$ or T. We also note that separability of the structure and temperature shift factors is not always assumed. The reader is referred to the literature (refs 1–10) for more information concerning these models. Below we elaborate on the importance of how we describe the glassy structure and how it may affect the interpretation of viscoelastic data.

Classical Physical Aging. To understand a typical physical aging experiment, we refer to Figures 1 and 2. First, the material is quenched to a specified aging temperature T$_a$ and held isothermally while the structure recovers. During the structural recovery, the normal physical aging experiment is performed following a protocol originally proposed by Struik, in which a sequence of loading probes is applied to the material at different aging times t$_i$ after the quench. Two things are important. First, as shown in Figure 2, the thermodynamic state of the glass (T$_F$) changes with aging time after the temperature jump due to the structural recovery. Therefore, we expect that the mechanical response should change. Second, because the viscoelastic measurement requires some time to obtain the viscoelastic response, it is important that the measured response not be appreciably affected by the ongoing structural recovery. Struik established that probes whose duration was less than 10% of the aging time were short enough that the measured response was a reliable “snapshot” of the response at the particular glassy structure (T$_F$) being probed. Figure 3 shows schematically the typical loading sequence used in this type of aging experiment.

In Figure 4, we depict the results of a typical aging experiment for a polycarbonate glass in stress relaxation conditions. What we observe is that the relaxation curves obtained at different aging times shift along the time axis and can be superimposed using a time—aging time superposition principle, as first established by Struik. For many polymeric materials, and polycarbonate is one of them, Struik showed that there is a range of temperatures where time—aging time superposition is valid and that this is generally between the $\alpha$ (or glassy) and $\beta$ (sub-glass) transitions. Furthermore, if time—aging time superposition and time—temperature superposition are both valid, the total shift factor a$_1$ a$_{1T}$ (or a$_{1aT}$) has a physical meaning that is unmistakable. Figure 5 shows typical total shift factors vs temperature for polycarbonate for a range of aging times. An observation that both time—temperature and time—aging time superposition are valid, implies that temperature—structure superposition is valid either with T$_F$ or $\delta$ as the measure of structure. We refer to this as global thermorheological simplicity.

Aging of Materials with Overlapping $\alpha$ and $\beta$ Relaxations. Global thermorheological simplicity seems to be valid when the material in question has a very weak $\beta$ relaxation or in a range of temperatures where the $\beta$ and $\alpha$ relaxations do not overlap. However, and this is related to Struik’s original observation that aging principles are only valid above the $\beta$ relaxation,
it is now known that materials having strong $\beta$ relaxations that overlap with the $\alpha_1$ relaxation do not follow global thermorheological simplicity.\textsuperscript{15–20} In fact, it is generally observed that neither time–temperature superposition nor time–aging time superposition holds. Examples of this are shown in Figure 6 for creep experiments with PEN that we have reported previously.\textsuperscript{18} Figure 6a shows the data before attempted “shifting”, and Figure 6b shows the data shifted to superimpose at the shortest times. It is clear that time–aging time superposition does not hold for this isothermal aging experiment. In Figure 7 we show the 32 h isochronal results for different temperatures. Clearly, samples tested after constant aging time $t_a$ at different aging temperatures $T_a$ do not superimpose. Hence, isochronal time–temperature superposition does not hold either.

An important aspect of the behavior of the PEN, which we have addressed previously,\textsuperscript{18} is the nature of the $\alpha_1$ and $\beta$ processes. First, it is important to note that literature reports\textsuperscript{23} for the temperature change of the dynamic response for PEN shows that the $\beta$ process extends approximately from $-30$ to approximately $+100 ^\circ C$—hence it is very broad and is visibly overlapping with the $\alpha_1$ or glass transition process. In our prior creep work,\textsuperscript{18} we were able to fit the $\beta$ process with a Cole–Cole function and the $\alpha_1$ process with a Kohlrausch–Williams–Watts function. The different processes are clear in Figures 6 and 7. Such an analysis follows the original suggestion of Read et al.\textsuperscript{15–17} On the basis of a similar analysis of the current data, but now for stress relaxation, the relative contributions of the two processes can be estimated from the prefactors on the Cole–Cole and KWW functions. For aging times of 0.5 h: at $100 ^\circ C$, such an analysis implies that the $\beta$ process contributes approximately 88% of the relaxation while, at $30 ^\circ C$, it contributes only about 29% of the relaxation.

**Isothermal, Isochronal, and Isostructural Experiments.** It is not obvious that more can be learned about aging when one observes a violation of global thermorheological simplicity. However, in analyzing the two-step aging experiments performed in this study, we discovered, through serendipity, that simple thermorheological simplicity can be recovered by performing isostuctural aging experiments. Therefore, we define the isothermal, isochronal, and isostructural experiments that are to be considered in this work. Parts a–c of Figure 8 present schematics of the differences in struc-
ture for glasses subjected to the conditions typical of the isothermal experiment, isochronal experiment (time—temperature) and the isostructural experiment, respectively. Referring to Figure 8a we see that the isothermal experiment is performed by quenching from above the glass transition temperature to below it and then probing the isothermal aging response in the “classic” manner discussed above. In Figure 8b, we see that the isochronal experiment is obtained by performing single quenches to different temperatures and comparing the viscoelastic responses obtained at specific aging times $t_a$, i.e., isochrones. In Figure 8c we see that the isostructural experiment is performed by first annealing the sample at a high, but sub-$T_g$, temperature $T_a$ for different annealing times $t_a$. Then the sample is quenched to lower temperatures and the viscoelastic responses obtained. The resulting conditions are such that the viscoelastic results are compared at essentially constant fictive temperature. As we show subsequently, for amorphous PEN, isostructural experiments result in time—temperature superposition. However, time—structure superposition does not hold.

**Experimental Section**

**Material.** Amorphous PEN film specimens from the Eastman Kodak Co. were used in this study. The amorphous films had a nominal thickness of 140 $\mu$m. Samples for stress relaxation testing were prepared by cutting strips of material 55 mm long and 9.8 mm wide. The sample to sample variability of geometry in width and length was measured to be less than 1% based on the range of measurements. Each sample was measured with a micrometer which could be read to within 2.5 $\mu$m. This leads to an uncertainty in the thickness measurement of less than 2%, which is greater than the ability to measure the film thickness variability. The glass transition temperature for the amorphous material was obtained using differential scanning calorimetry (DSC) at a heating rate of 20 °C/min following a cooling at the same rate. The value of the glass transition was obtained from the midpoint of the heat capacity change and it was found to be 121 °C for the amorphous PEN. The midpoint $T_g$ obtained during 20 °C/min cooling run was found to be 114 °C. The reader is referred to Seyler for a discussion of the measurement uncertainties typical of DSC measurements as well as for a discussion of the differences in assignment of $T_g$ values based on different measurement techniques.

**Mechanical Testing.** All stress relaxation tests were performed on an MTS systems servohydraulic machine in a tensile mode. Because of the difficulty of testing thin films, new clamps were specially designed to accommodate the thin films used in this study. All experiments were performed at a strain of 0.5% to keep the measurements in the linear viscoelastic regime.

For the aging experiments, the samples were first heated to 125 ± 0.2 °C, a temperature above the nominal glass transition of amorphous PEN, for 30 min to erase the prior thermal history of the material (Figure 9a). The samples were then annealed in another oven at $T_a = 100 ± 0.1$ °C for different times $t_a = 1, 4, 32, \text{and} 100 \text{h}$. Finally, the specimens were removed to the testing chamber that had been preheated to the aging temperature $T_e$ where the physical aging experiments were carried out. Similar tests were also performed by

![Figure 8](image1.png)

![Figure 9](image2.png)
annealing at $T_a = 120 \pm 0.1 \, ^\circ\text{C}$ for $t_a = 1$ and 32 h, followed by the aging experiments.

After the sample was placed in the testing chamber at the aging test temperature $T_a$, sequential stress relaxation tests were performed to probe the aging response (see Figure 9b). The test procedure followed the sequential protocol described previously and proposed originally by Struik. Aging times considered were from 0.5 to 16 h. At a given annealing time at 100 °C and at a given aging temperature, the same specimen was used for the entire test. Loads of duration $t_l$ were applied at increasing aging times, $t_a$ such that the ratio $t_{a0}$ was maintained constant at 0.1. The applied loads are essentially probes into the material structure and are of a sufficiently short duration that the structural recovery (aging) does not significantly influence the measurements. By allowing the sample to recover for a time, $9t_l$, the material essentially forgets the effect of the previous loading cycle. Experiments were performed at temperatures $T_a$ of 30, 50, 70, and 90 °C. The temperature of the apparatus was measured to fluctuate about the mean temperature over a range of $\pm 0.1 \, ^\circ\text{C}$. 

Measurement Uncertainty. The experimental precision in the stress relaxation data, based on two standard deviations from multiple measurements, on different samples was less than 10% of the reported value. As mentioned above, the same specimen was used throughout each aging experiment. This minimizes the variation associated with material variability and sample misalignment within a single aging experiment. To estimate the precision of the multiple measurements in a single aging test, we measured the magnitudes of the vertical shifts required to superimpose the measurements at different aging times. The trends of the shifts with aging time were considered were from 0.5 to 16 h. At a given annealing time at 100 °C and at a given aging temperature, the same specimen was used for the entire test. Loads of duration $t_l$ were applied at increasing aging times, $t_a$ such that the ratio $t_{a0}$ was maintained constant at 0.1. The applied loads are essentially probes into the material structure and are of a sufficiently short duration that the structural recovery (aging) does not significantly influence the measurements. By allowing the sample to recover for a time, $9t_l$, the material essentially forgets the effect of the previous loading cycle. Experiments were performed at temperatures $T_a$ of 30, 50, 70, and 90 °C. The temperature of the apparatus was measured to fluctuate about the mean temperature over a range of $\pm 0.1 \, ^\circ\text{C}$. 

Estimation of the Fictive Temperature of the PEN

The experimental conditions chosen for the current study were partially determined by the parameters of interest to Eastman Kodak, who partially funded this work. As a result, they were not preselected to obtain an isostructural state. In fact, the experimental observations described in the next section are what led us to think of the material response in isostructural conditions and of the possible importance of isostructural experiments that we described in the introductory sections of this paper. To establish that the experimental conditions chosen for study do indeed lead to an isostructural state as measured by the fictive temperature, we used the Tool–Narayanaswamy–Moyvinian (TNM) model of structural recovery to estimate the value of $T_f$ for PEN. The fundamental equations needed for the TNM model are:

\[ \frac{dT_f}{dT} = 1 - \exp \left[ - \left( \int_0^t \frac{dT}{t_{e0}} \right)^\beta \right] \]  

The parameters in the equation are $t_{e0}$, a characteristic relaxation time in the stretched exponential response function, $\beta$, a shape parameter describing the stretching of the response function, $T$, absolute temperature, and $T_f$, the fictive temperature. This equation can be solved numerically and we did this using a computer program provided by S. L. Simon and W. Sobieski [12] of the University of Pittsburgh.

The temperature and structure dependencies of the characteristic time in eq 1 are given by:

\[ t_{0f}(T, T_f) = \alpha_t a_{1f} e^{\Delta h R (1/T - 1/T_f)} > (1-x) \Delta h R (1/T_f - 1/T) \]

\[ t_{0f} \]

where $x$ is a parameter that partitions the shifting of the time between temperature and structure. The value of $x$ lies between 0 and 1. When $x = 0$, the material shows no temperature dependence and when $x = 1$, the relaxation time depends only upon temperature and not on the structure of the glass. $R$ is the gas constant and $\Delta h$ is an activation energy. The parameter $t_{0f}$ is the value of the relaxation time at the reference temperature $T_r$. Often $T_r$ is taken to be the nominal glass transition temperature.

The parameter values for amorphous PEN were obtained by Dr. J. James, M. O'Reilly of Eastman Kodak company from differential scanning calorimetry measurements and are reported in Table 1. For the calculations here we assumed that the cooling rate for the step from 125 to 100 °C (or 120 °C) was 200 °C/min and that the subsequent cooling rate to the aging temperatures (300, 50, 70, 90 °C) was 10 °C/min. Table 2 presents a matrix of annealing and aging parameters used in this study along with the fictive temperatures calculated from the TNM model using the parameters for PEN given in Table 1. The original idea in thinking about the thermal treatments was that, for samples annealed at different times $t_a$ at $T_a$ and then tested at lower temperatures $T_a$, the primary determining factor in the fictive temperature would be the annealing time. From Table 2, this is the case except for short annealing times and a testing (aging) temperature of 90 °C. However, even here, the fictive temperature only changes by 1.9 °C upon aging from 1800 to 57,600 s (0.5–16 h). For the purposes of further discussion, consequently, we treat our results as isostructural for a given annealing time and temperature, recognizing that there may be some small variation from this condition.

Results

Isothermal Aging Experiments. Figure 10 displays the isothermal results in aging experiments at 100 °C (Figure 10a) and 120 °C (Figure 10b) performed in specimens treated at 125 °C, to erase prior aging, and subsequently measured at the two aging temperatures. These two temperatures were used as the annealing temperatures in the isothermal experiments, and the isothermal aging test results displayed in Figure 10 form a baseline for the expected material behavior in the isostructural experiments. In Figure 10a, it can be seen that physical aging influences the response of the material at 100 °C. Figure 10b shows that, at 120 °C, the PEN responses are nearly the same for all aging times.

Figures 11–14 show the isothermal results obtained at the different annealing times at 100 °C at aging temperatures $T_a = 30, 50, 70, and 90 ^\circ\text{C}$ and at different aging times as double logarithmic plots of the relaxation
Looking first to parts a and b of Figure 11, it can be seen that the logarithm of the relaxation modulus is quite linear in the logarithm of time over the whole aging time range investigated here for the
short annealing times (1 and 4 h) at 100 °C. We have previously referred to this behavior in PEN in isothermal aging experiments without an annealing pretreatment as "power law" behavior. (The effect of aging observed here is, however, less than in samples quenched directly from 125 to 30 °C). In addition, one can see in Figure 11 that the value of the relaxation modulus is higher as annealing time at 100 °C increases because the fictive temperature decreases with anneal-
ing and the material has moved closer to the equilibrium state. For the material annealed for 32 h at 100 °C, Figure 11d shows that, at the longest aging times, the power law relaxation behavior is no longer observed over the whole experimental time range.

Recalling that PEN has a very broad β relaxation23 which influences the viscoelastic responses measured by creep and stress relaxation, either in amorphous18,31 or semicrystalline31,32 PEN, we remark that the relaxation moduli observed at this low temperature, 30 °C, are mainly related to the contribution of the β relaxation process to the overall relaxation response.

Relaxations related to the α process become more evident as the aging temperature increases. Hence, we see that the curvature in the relaxation response apparent at the longer aging times at 30 °C and for the longest annealing times at 100 °C becomes more evident as aging temperature is increased to 50 °C (Figure 12). We have previously referred to this as an “exponential-like” process and it is related to the glass transition of PEN. The complexity found in the viscoelastic response18,23,31,32 of PEN is a consequence not only of the fact of two relaxation processes being close to each other but also because each mechanism exhibits different temperature and aging time dependencies. The annealing process at 100 °C does not change the fact that the two relaxation mechanisms overlap, but the partial evolution of the structure toward the equilibrium state during the annealing at 100 °C does change the behavior of the material. As shown in the insert entitled “without annealing” in Figure 12d, the specimen heated at 125 °C and directly quenched to and measured at 50 °C displays the two relaxation processes remain overlapped as aging time increased. However, the overlap in the two relaxation processes does not occur in the same manner as when the specimen is annealed at 100 °C prior to being measured at 50 °C. Consequently the shapes of the relaxation curves are seen to differ as depicted in this figure. It looks as though the annealing process has separated, somewhat, the two relaxation mechanisms, and there is a transition region where the overlap between the two relaxations is weaker with than without the annealing. Also, the aging response at 50 °C is less in the annealed samples than in specimens quenched directly to 50 °C. Interestingly, even though the fictive temperature does not change for the annealed samples upon aging at 50 °C (see Table 2), the material does still exhibit physical aging. This result is consistent with other observations5,29,33,34 in which different material processes exhibit different time scales to equilibration or, equivalently, to different fictive temperatures.

When the aging temperature is increased to 70 °C, as depicted in Figure 13, it is possible to observe the two mechanisms acting together. The “power law” behavior is displayed at the shortest experimental times while the “exponential-like” one is exhibited at the long experimental times. It is also seen that the aging effect at this temperature is larger than at either 30 or 50 °C. Additionally, we see again that, despite a nearly constant fictive temperature, the material undergoes physical aging.

When the aging experiments are performed at 90 °C, the α relaxation process dominates the relaxation response in the experimental time range (Figure 14). For all annealing times, it is observed that the material ages after being quenched to 90 °C. This is not surprising because the fictive temperature changes somewhat during the aging at this temperature (Table 2).

Time–Aging Time Reduction. It is common in the analysis of physical aging experiments to superimpose the data obtained at different aging times by shifting them along the time axis using time–aging time superposition2,13–20,24–26,31,32,35 in case of the PEN without the annealing process at 100 °C, it was found that time–aging time superposition did not work.18,31,32 The presence of the large β mechanism23 that interferes with the main α or glass transition in PEN makes superposition of the data difficult. In addition, physical aging is still occurring18,31,32 at temperatures lower than Tg as measured by dynamic mechanical analysis.23 This is somewhat at variance with what has become a common rule of thumb and that was originally put forth in Struik’s13 classic work that the temperature range in which the aging occurs in an amorphous polymer is between the glass transition temperature and its first secondary transition (the α and β relaxations in amorphous polymers, respectively). (Importantly, Struik’s subsequent work36 showed that aging can occur below Tg.)

In specimens annealed at 100 °C, both the α and the β mechanisms are apparent in the relaxation responses. Therefore, unless the two mechanisms were to have the same structural (or aging time) dependencies, we would expect to observe a breakdown of time–aging time superposition, as observed in the classical aging experiments reported previously18,31,32 for PEN. Manual shifting of the relaxation curves demonstrates the lack of time–aging time superposition for the amorphous PEN. The results are shown in Figure 15. In the figure, only one annealing time at 100 °C for each aging temperature is shown; the other 100 °C annealing conditions follow similar behavior. As seen, the shifting of the different aging curves results in a time–aging time master curve only when a single relaxation mechanism
dominates the viscoelastic response. For example, at 30 °C (where the power law mechanism dominates) and at 90 °C where the exponential-like process dominates) time–aging time superposition is valid. On the other hand, because of the proximity of the two relaxation mechanisms at the intermediate temperatures, the shifting process results in deviations from a single "master curve" at the longest times for the 50 °C data, whereas for the 70 °C data the deviations occur at the short times.

Time–Temperature Reduction. Because of the strong, and overlapping, α and β relaxation mechanisms and the breakdown of global rheological simplicity, it was anticipated that time–temperature superposition for samples annealed at the same conditions would also break down. We expected that the α and β mechanisms would each have different temperature and structure (aging time) dependencies and the material would be thermorheologically complex. Surprisingly, this was not the case. As shown in Figure 16, for samples annealed at $T_a = 100$ °C for 1 h and tested at the different aging temperatures, time–temperature reduction appears to hold. The reader is referred to Table 2 for the calculated fictive temperatures for each of the thermal conditions. While we have not obtained perfect isostructural conditions, apparently the annealing treatment is such that temperature superposition is valid for these data. Figure 17 shows the time–temperature master curves for each annealing time. What is interesting is that, although time–temperature superposition seems to be valid for each annealing time, the results for each annealing time do not superimpose with each other. This implies that time–structure superposition is not valid—hence, we seem to have obtained a simple thermorheological simplicity, but global thermorheological simplicity is not obtained.

Another result relevant to the concept of the isostructural state is that the sample quenched to 100 °C, aged for 1 h, and then tested, would have close to the same structure as the samples described above. The test results from Figure 10a for this 1 h aging time at 100 °C experiment are replotted in Figure 16d, and we see that the curve superimposes with the other data. The whole of these data seems to imply that the 100 °C annealing treatment leads to a family of isostructural states for which the time–temperature superposition holds. Although the fictive temperatures for the different aging times differ slightly, this does not seem to have a major effect on the results obtained here.

Finally, estimation of the apparent activation energies $\Delta E_a$ for the temperature shift factors from the experiments with different annealing times at 100 °C, i.e., along constant fictive temperature lines (see Figure 8c), can be made from Arrhenius plots of the data. This is shown in Figure 18. The apparent activation energies are shown in Table 3 along with values calculated from the temperature dependence of the times characteristic of the α and β relaxations obtained previously from isochronal aging time measurements at different temperatures. The table depicts two values for $\Delta E_a$ obtained for the α mechanism from the previous data because the plot was not a straight line Arrhenius representation. The higher of the values are obtained from data at 80 and 100 °C. What we observe is that the values fall between those for the α and the β mechanisms. The values are typical of such processes.
Experiments with 120 °C Annealing Treatment

The postulate that we have obtained an isostructural state by annealing at a high temperature, which was then tested at lower temperatures, can be further investigated by performing the annealing treatment at another temperature. We chose to examine a higher temperature of 120 °C and annealing times of 1 and 32 h. The calculations indicated by the TNM model indicated that the two treatments should have resulted in a cessation of structural recovery before the earliest aging time investigated (as indicated by the fact that the values of $T_F$ are independent of annealing time $t_a$) and this seems to be the case as the viscoelastic behavior that is different. See text for full discussion.

### Table 3. Apparent Activation Energies $\Delta E_a$ for Isostructural Temperature Shift Factors $a_T$ for Amorphous PEN Annealed at 100 °C for Times $t_a$ of 1, 4, 32, and 100 h

<table>
<thead>
<tr>
<th>Experiment Description</th>
<th>$\Delta E_a$ (J/K mol)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed at 100 °C, $t_a = 1$ h</td>
<td>$1.25 \times 10^5$</td>
<td>This work</td>
</tr>
<tr>
<td>Annealed at 100 °C, $t_a = 4$ h</td>
<td>$1.21 \times 10^5$</td>
<td>This work</td>
</tr>
<tr>
<td>Annealed at 100 °C, $t_a = 32$ h</td>
<td>$1.10 \times 10^5$</td>
<td>This work</td>
</tr>
<tr>
<td>Annealed at 100 °C, $t_a = 100$ h</td>
<td>$1.05 \times 10^5$</td>
<td>This work</td>
</tr>
<tr>
<td>$\alpha$ relaxation (all data)</td>
<td>$5.31 \times 10^4$</td>
<td>Data from ref 18</td>
</tr>
<tr>
<td>$\alpha$ relaxation (80 and 100 °C data)</td>
<td>$1.03 \times 10^5$</td>
<td>Data from ref 18</td>
</tr>
<tr>
<td>$\beta$ relaxation</td>
<td>$1.41 \times 10^5$</td>
<td>Data from ref 18</td>
</tr>
</tbody>
</table>

*Results are compared with the values from data in prior isochronal aging experiments in which the $\alpha$ and $\beta$ relaxations exhibited different activation energies. Aging time is 16 h.*

### Figure 17
Comparison of the isostructural master curves for PEN having different annealing treatments at 100 °C, as indicated in diagrams. Aging time is 16 h for all curves: (a) individual curves; (b) curves shifted showing that each isostructural state (annealing time), while showing time–temperature superposition, has a viscoelastic behavior that is different. See text for full discussion.

### Figure 18
Logarithm of the temperature shift factor $a_T$ vs $1/T$ for PEN annealed at 100 °C for the times $t_a$ indicated in legend. Activation energies are reported in Table 3. Aging time is 16 h. See text for discussion.

### Figure 19
Isostructural time–temperature reduction of the relaxation modulus of PEN with 90 °C as the reference temperature for 16 h aging time and annealing times of 1 and 32 h annealing times at 120 °C. Diagram a indicates reasonable time–temperature superposition after 1 h of annealing. However, curve b shows breakdown of time–temperature superposition after 32 h of annealing. See text for discussion.
posability is not as great as in classical experiments (recall parts a and b of Figure 6).

Discussion

The observations made here have multiple possible explanations. The data for the 100 °C annealing treatment suggest that, in fact, the structural state obtained in the annealing process is such that the behavior of the PEN follows an isostructural time–temperature superposition principle. If this is true, the implication is that the fictive temperature is a good measure of the isostructural state of the glassy and amorphous PEN. Furthermore, it suggests that the breakdown in thermorheological simplicity often observed below the glass temperature may result from the material responses being compared in different isostructural states, depending on the thermal treatment.

A caution here is that the data obtained after annealing at 120 °C for 32 h do not follow time–temperature superposition. It is unclear why the two annealing temperatures (100 and 120 °C) produce different results. It would be interesting to further explore the behavior by performing annealing treatments at other temperatures, measurements that were beyond the scope of this study.

Additionally, it is possible that the structural states produced during the annealing at 100 °C, result in the α and the β mechanisms being separated far enough to not interfere with one another in the limited time frame of the current experiments (less than 5 logarithmic decades in time). (We do note that similar questions have been raised for time–temperature superposition in polymer melts,37–42.) Why, though, 100 °C would be the “optimum” choice for such a thermal treatment for such an effect to occur, while it does not occur at 120 °C, is not clear. It is also not clear why the materials annealed at 120 °C for the two different times (1 and 32 h) gave different results since their fictive temperatures should have been the same. One possibility here is that the material annealed at 120 °C is in equilibrium and the experiments begin to look more as if the material had been quenched directly from 125 °C, i.e., close to isochronal, rather than truly isostructural. Further experiments on PEN at different annealing temperatures should be performed in the future. Also, it would seem that another polymer with a strong β relaxation such as poly(methyl methacrylate) (PMMA) should be studied in similar experiments.

It is worth noting again that the TNM parameters for the PEN would suggest that the material should not show very significant structural recovery at, e.g., 30 and 50 °C and after either thermal treatment. Yet, we observe measurable physical aging. Because the TNM model has been known to have flaws, the observation of the continued aging process far below the glass temperature may provide insights into ways in which to improve the model. In thinking of this issue, however, it is also important to note that there is no need for the relaxations (or fictive temperatures) for the different processes to be the same (see refs 5, 29, 33, and 34 and references therein). However, it is also true that generally the differences in relaxations are reported to be somewhat subtle whereas here the observed differences would imply rather dramatic differences between the enthalpic and the mechanical fictive temperatures or structural recovery times.

Finally, there is work in the literature on ionic glasses41,42 in which there is some evidence for what we report here, viz., a thermorheological simplicity in the isostructural or constant fictive temperature glass. However, in those studies, what was observed was a breakdown of thermorheological simplicity above the glass transition and a change to thermorheological simplicity below the glass transition. The suggestion in those cases was a freezing out of one mechanism below Tg, unlike the case here where the material is thermorheologically complex below the glass transition and, it appears, is thermorheologically simple in the isostructural case. Hence, there is no freezing of one mechanism, rather, in the isostructural case it is found that the apparent activation energies for both the α and β mechanisms become identical. Also, we remark further that for different structures the reduced curves are different, hence our dichotomy between global thermorheological simplicity and simple thermorheological simplicity. The latter holds for the isostructural PEN, but the former does not.

Summary

The viscoelastic and physical aging responses for an amorphous poly(ethylene naphthalate) (PEN) under uniaxial tension stress relaxation conditions have been investigated. It is found that, while classical physical aging in the PEN results in a breakdown of both time–temperature and time–aging time superposition which are attributable to the presence of a strong β relaxation that overlaps the α relaxation in the experimental time and temperature ranges studied. This is unlike materials such as polycarbonate which exhibit global thermorheological simplicity in their responses to aging treatments. Here we found that, upon annealing the PEN at 100 °C for different times, we could obtain a simple time–temperature superposition behavior, though the different annealing times had master curves that could not each be superimposed. We have proposed that the behavior may be consistent with the concept of an isostructural state characterized by the fictive temperature. Results from annealing treatments at 120 °C do not fit as well into the isostructural picture. Experiments to further study the implications of the current results for materials with strong β relaxations are suggested.

Acknowledgment. This work was supported, in part, by the Eastman Kodak Co. M.L.C. thanks the NIST for support as a Visiting Researcher in the Polymers Division. Both G.B.McK and M.L.C. are thankful to J. M. O'Reilly, J. Greener, and J. R. Gillmor of the Eastman Kodak Co. for stimulating discussions and encouragement in this work.

References and Notes

Assignment of the Glass Transition

(1) As calculated from the TNM model using a computer program supplied by Simon and Sobieski.  
(2) Simon, S. L.; Sobieski, W. University of Pittsburgh, unpublished work.  
(11) Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the product is the best available for the purpose.  
(15) Lee, A.; McKenna, G. B. Polymer 1988, 29, 1812.  
(20) O’Reilly, J. M. Eastman Kodak Co., unpublished data.  
(26) Struik, L. C. E. Polymer 1987, 28, 57.  
(42) Struik, L. C. E. Polymer 1987, 28, 57.