

STRESS RELAXATION OF POLY(ETHYLENE NAPHTHALATE): ISOTHERMAL, ISOCHRONAL AND ISOSTRUCTURAL RESPONSES

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Abstract

The physical aging response of polymers is generally examined in isothermal conditions by following the viscoelastic behavior as a function of aging time. It is then often asked if time-aging time superposition applies at a single temperature. If so, it can then be ascertained if time-temperature superposition applies to the aging time reduced curves obtained at different temperatures.

In prior work from this laboratory we showed that isothermal time-aging time superposition did not apply to amorphous PEN. In this work we describe the surprising result that samples aged at 100 °C and then tested at 30 °C, 50 °C, 70 ° and 90 °C, that is isostructurally (constant fictive temperature) seem to follow time-temperature superposition.

Introduction

In the following paragraphs we refer to the Volume or Enthalpy vs Temperature schematics presented in Figures 1 a-c. It is important to consider the path dependence of the thermodynamic (or structural) state of a polymeric glass when it is tested mechanically. In Figure 1 a we show the *isothermal* experiment in which a glass is quenched to an aging temperature T_e from above the glass transition temperature T_g and then tested sequentially at increasing aging times after the temperature-jump. The response expected here is that observed in normal physical aging experiments [1]. In materials with a response that is dominated by a single viscoelastic process (α process), it is found that the principles of time-aging time superposition can be used to describe the material behavior. Furthermore, referring to Fig. 1 b, if samples are tested at different temperatures, responses at constant aging times, but different temperatures can be compared and *isochronal* responses are found to obey time-temperature superposition for the same materials [1-4]. However, there is now a considerable body of work [1, 4-10] in which materials that exhibit two strong relaxations (α and β processes) have been examined in the typical aging experiment and the findings have generally shown that, for isothermal aging experiments time-aging time superposition fails and there is a breakdown of time-temperature superposition for the isochronal experiments at different temperatures. While there has been some success in applying the time-aging time and time-temperature superposition principles to each mechanism individually, the results presented in this paper suggest another way of looking at the behavior of

such materials.

Referring to Figure 1 c, one can grasp an important idea in the physics of glasses: the so-called isostructural state which is based on the idea of a constant fictive temperature T_f . From the figure we see that the T_f is defined as the temperature of intersection between the equilibrium liquid line and a line parallel to the glassy volume or enthalpy line extrapolated to the liquid line from the glassy state. In the case of an *isostructural* aging experiment, one performs a quench to an annealing temperature T_i and anneals the sample for some time t_i . The sample is then rapidly cooled to an aging temperature $T_{e,i}$ where mechanical tests can be performed. As described in the following, it is found that for poly(ethylene naphthalate) (PEN) which is a material having a strong β relaxation close to the α process, that time-temperature superposition is followed for the isostructural glass. To our knowledge, such results have not been reported previously.

Experimental [11]

Amorphous PEN films from Eastman Kodak Company were used in this study. The films had a nominal thickness of 140 μm . 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. Measurements were made with a micrometer which could be read to within 2.5 μm . This leads to an uncertainty in the thickness measurement of 1.8 %, which is greater than the ability to measure the variability in the film thickness. The glass transition temperature was obtained using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. The T_g from the midpoint in the heat capacity change was estimated to be 120 °C. The reader is referred to Reference 12 for a discussion of the uncertainties in the measurement of T_g using DSC.

All stress relaxation tests were performed on an MTS Systems servo-hydraulic machine in a tensile mode. Special grips were designed to accommodate the thin films used in the study. All experiments were performed at a strain of 0.005 to keep the measurements in the linear viscoelastic regime [13].

Figure 2 shows the thermal and mechanical histories applied to the samples. The specimens were first heated to 125 ± 0.2 °C--a temperature above the nominal T_g of the PEN--for 30 minutes in order to thermally erase prior aging in the material.

The samples were then **annealed** in another oven at 100 ± 0.1 °C for different times t_a : 1 h, 4 h, 32 h and 100 h. Finally, the specimens were removed to the testing chamber on the MTS machine. This chamber had been pre-heated to the aging temperature where the physical **aging** experiments were performed.

Subsequent to placing a sample in the testing chamber, sequential stress relaxation tests were performed to probe the aging response. The test protocol, depicted in [Figure 2b](#), followed that originally proposed by Struik [1]. Aging times t_e considered ranged from 0.5 h to 16 h. Experiments were performed at aging temperatures of $T_e=30$ °C, 50 °C, 70 °C and 90 °C. The temperature of the apparatus was measured to fluctuate about the mean temperature over a range of ± 0.1 °C.

The measurement uncertainties have been described elsewhere [14] and are estimated to be less than ± 10 % of the measured values based on two standard deviations from multiple measurements on different samples. The variability in the measured relaxation modulus within a given aging experiment has been estimated to be less than 0.5 %.

Results

Isothermal: Time-Aging Time Reduction

[Figure 3](#) shows the results of our previous study in which isothermal aging experiments on amorphous PEN were performed in creep conditions. As can be seen, perhaps with the exception of the 100 °C experiments, time-aging time superposition does not apply to these data.

Isochronal: Time-Temperature Reduction

It was also found previously, as shown in [Figure 4](#), that time-temperature reduction of the creep data for amorphous PEN did not apply. As seen in the figure, superposition of the data for samples quenched to different aging temperatures and then aged for the same amount of time does not superimpose.

Isostructural: Time-Temperature Reduction

In the work presented here, we obtained isostructural specimens by annealing the material at 100 °C after the initial treatment at 125 °C to erase the prior thermal history. The samples were then subjected to a second thermal step and aged at the relevant values of T_e as discussed previously and depicted in [Figure 2](#). [Figures 5](#) show the results of a series of tests in which the samples were annealed at 100 °C and then aged for 1, 4 and 16 h at each of the aging temperatures. The curves show that for each aging time the time-temperature reduction works successfully to make a master curve at a reference temperature of 90 °C. We interpret these results to imply that time-temperature superposition of the isostructural PEN seems to apply. [Figure 6](#) shows a composite figure in which the master curves for different

isostructural materials are compared. Clearly, for aging times of 16 hours, while time-temperature superposition seems to apply, the individual master curves for the different annealing times do not superimpose. We interpret this result to imply that the different isostructural states affect the α and β relaxation mechanisms differently and, therefore, time-structure superposition does not apply to the amorphous PEN.

Discussion

In general, research scientists and engineers use time-temperature and time-aging time superposition procedures to provide a means of estimating long time performance in their materials. These procedures become tedious when the material does not exhibit thermo-rheological simplicity due to the existence, as in PEN of two different relaxation processes that can overlap. As noted in the introduction, it is often possible to separate the mechanisms and treat the data as if each mechanism follows thermo-rheological simplicity. And we had found previously that such an approach applies to aging data for PEN.

In attempting to understand the impact of structural recovery on the response of materials, however, simply noting that the β process has a different temperature and structure (aging time) dependence than does the α process may not be particularly informative. The findings of this paper, that isostructural data for the stress relaxation results in PEN follow time-temperature superposition are surprising. The implications of these results are not currently clear. However, we can comment that it is interesting that, at approximately constant fictive temperature (constant structure) the β and α processes follow the same temperature dependences. Does this imply a fortuitous traversing of the complex time-aging time surface? Or does it imply a more fundamental meaning to the isostructural state? Clearly further work to perform isostructural experiments rather than isochronal experiments in the aging of materials which exhibit apparent thermo-rheological complexity below the glass transition will provide further insight into the current observations.

Conclusions

Normal isothermal and isochronal aging experiments show thermo-rheological complexity in the behavior of amorphous PEN. Isostructural experiments demonstrate that PEN may be thermorheologically simple: that is the α and β processes exhibit the same temperature dependencies when the sample has been annealed to create an isostructural or iso-fictive temperature glass. The shape of the master curve depends on the structure of the glass, i.e., its fictive temperature.

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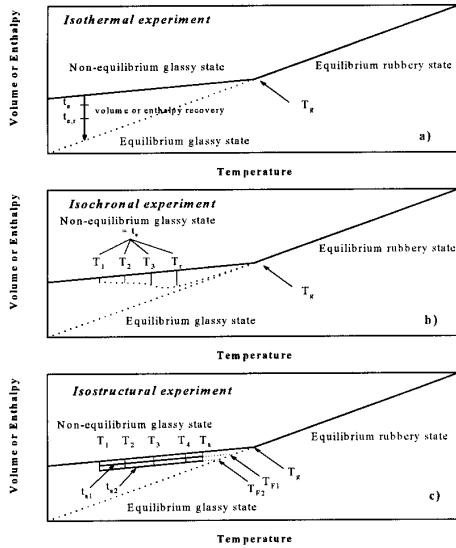


Figure 1. Schematic representation of the volume (enthalpy)- temperature behavior of a glass forming material: a) isothermal experiments; b) isochronal experiments; c) isostructural experiments.

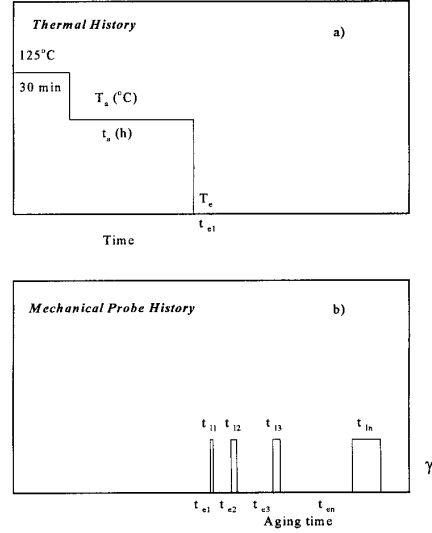


Figure 2. Schematic of temperature (a) and mechanical (b) histories used in experiments to obtain isostructural glasses. Sample quenched from above T_g to the annealing temperature T_e and then to the aging temperature T_e .

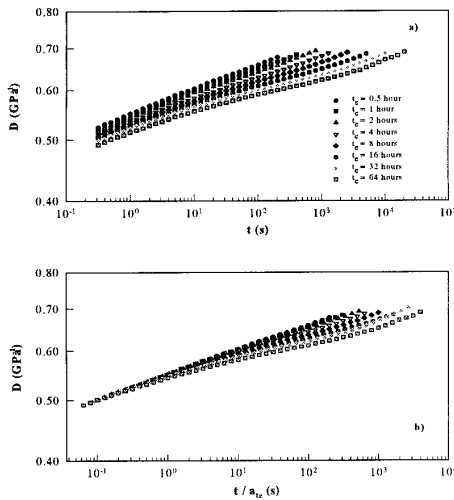


Figure 3. Isothermal experiments: a) Double logarithmic representation of amorphous PEN creep compliance at different aging times at 50 °C. b) Manual time-aging time reduction of curves in (a) showing lack of superposition. (After Reference 8.)

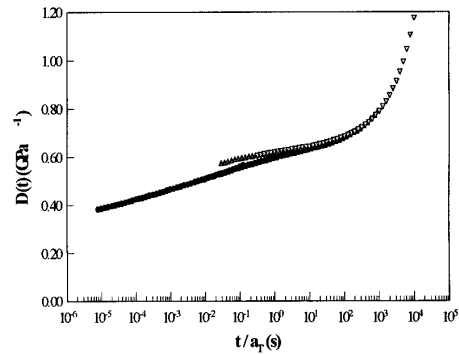


Figure 4. Isochronal experiments: reduced creep compliance curves for amorphous PEN for an aging time of 32 h. Curves shifted manually and demonstrate lack of time-temperature superposition. (●) 30 °C; (■) 50 °C; (Δ) 80 °C; (∇) 100 °C. (After Reference 8.)

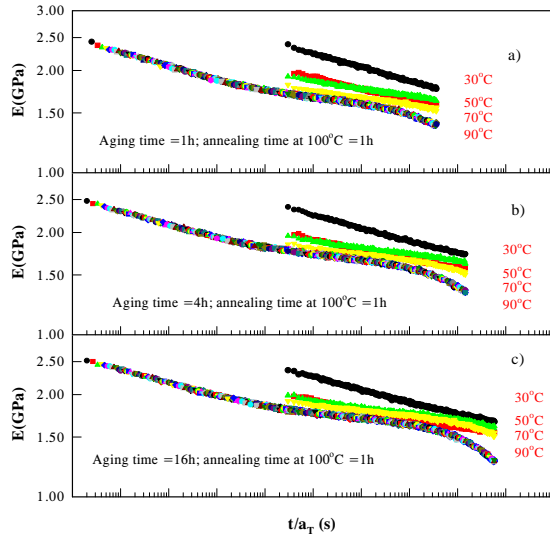


Figure 5. Isostructural mastercurves for PEN: Samples annealed at 100 °C for 1 h and tested at indicated temperatures for the indicated aging times. Reference temperature for master curves is 90 °C. The master curves for the different isostructural states (different aging times) are not superimposable. See text for discussion.

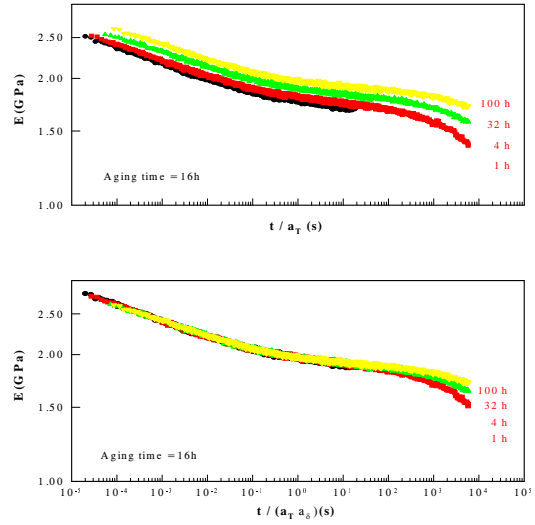


Figure 6. Comparison of master curves obtained at different isostructural states. Samples annealed at 100 °C for times indicated and aged at testing temperatures of 30 °C, 50 °C, 70 °C and 90 °C. Reference temperature for master curves is 90 °C. Curves shifted manually to indicate lack of time-structure superposition.