

PHYSICAL AGING AND CREEP CHARACTERIZATION OF A CARBON/POLYIMIDE COMPOSITE

I. M. Daniel¹, J. J. Luo², and Z. Sun³

¹*Walter P. Murphy Professor, Departments of Civil and Mechanical Engineering,
Robert R. McCormick School of Engineering and Applied Science, Northwestern University
2137 Sheridan Road, Evanston, IL 60208 USA*

²*Research Assistant, Department of Mechanical Engineering,
Robert R. McCormick School of Engineering and Applied Science, Northwestern University,
2137 Sheridan Road, Evanston, IL 60208 USA*

³*Research Assistant, Department of Civil Engineering,
Robert R. McCormick School of Engineering and Applied Science, Northwestern University,
2137 Sheridan Road, Evanston, IL 60208*

SUMMARY: The objective of this study was to characterize the long term behavior of a typical carbon/polyimide composite proposed for high temperature applications. The material investigated was IM7/K3B, a carbon-fiber reinforced thermoplastic polyimide. This material undergoes physical aging below its glass transition temperature of $T_g = 240^\circ \text{C}$. Physical aging was measured at various temperatures as a function of time. The aging strain was modeled by an exponential form in terms of the current temperature, the glass transition temperature, the equilibrium value of the aging strain and a constant determined experimentally. Experimental results corroborated the proposed model. The effects of aging were separated from those of creep by using two specimens instrumented with strain gages, one loaded under constant stress and one unloaded. Isothermal and nonisothermal creep tests were conducted. It was found that under a cyclic temperature condition creep can be higher than under isothermal conditions at the mean cyclic temperature.

KEYWORDS: physical aging, creep, modeling, carbon/polyimide composite, temperature effects.

INTRODUCTION

High temperature polymer composites are receiving special attention because of their potential applications to high speed transport airframe structures and aircraft engine components exposed to elevated temperatures. Typical composites considered for these applications are carbon/polyimide composites such as IM7/K3B. The long term durability of these materials is of great concern. It is related to and affected by physical aging of the polymeric matrix, viscoelastic deformation (creep) and hygrothermomechanical degradation. It is therefore important to investigate the processes involved and any accelerated test methodologies that will yield valid predictions of long term behavior.

It has been known that amorphous materials and especially polymers are not in thermodynamic equilibrium below their glass transition temperature (T_g). Over a temperature range below T_g they tend to approach the equilibrium state in a process called *physical aging*. During this process the material becomes more glasslike with accompanying increase in density, brittleness and stiffness and a decrease in creep compliance. Whereas physical changes may be small, the effects of aging on time dependent behavior, such as creep, can be very pronounced. Extensive research has been reported on the nature and effects of physical aging of polymers starting with the pioneering works of Kovacs [1] and Struik [2]. The latter determined the effects of aging on viscoelastic behavior by conducting a sequence of short-time (momentary) creep tests during the aging process. He introduced the concept of an aging-induced shift factor and produced creep master curves. The effects of physical aging on creep of thermoplastic composites were studied more recently by Nichols et al [3], Sullivan [4], Hastie and Morris [5], Skontorp and Wang [6] and Gates and Feldman [7].

Although the interaction of physical aging and viscoelastic behavior seems to be well understood and can be determined under isothermal conditions, it is difficult to apply results to prediction of long term behavior of composites undergoing environmental and loading fluctuations. Given a material of unknown aging history it would be desirable to assess its age and its effect on future behavior. It would be helpful if the "degree" of aging, instead of just chronological age, were quantified and then related to viscoelastic effects. The known physical change in a polymer during physical aging is a reduction in free volume which results in volumetric shrinkage. The objective of this work is to measure directly this aging-induced volumetric shrinkage and propose a model to quantify physical aging. Techniques were used for direct measurement of aging strains and separation of creep and aging effects.

MEASUREMENT AND MODELING OF PHYSICAL AGING

The material investigated was IM7/K3B, a carbon fiber reinforced thermoplastic polyimide. This material undergoes physical aging below its glass transition temperature of $T_g=240^\circ\text{C}$. The material was available in the form of 24-ply, 3.15 mm thick unidirectional plates. Unidirectional coupons 11.4 cm long and 1.27 cm wide were prepared and instrumented with high temperature strain gages oriented in the transverse to the fiber direction (WK-00-250BG-350, Micromeasurements) as shown in Fig. 1.

The volumetric shrinkage experienced by the composite due to aging of the matrix is directly related to the aging strain in the transverse direction. The total volumetric change of the composite is

$$\frac{dV_c}{V_c} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (1)$$

where $\varepsilon_1, \varepsilon_2, \varepsilon_3$ = strains along the three principal material axes. Since it is not expected for the carbon fiber to undergo aging and since the 2-3 plane can be assumed to be a plane of isotropy for the material,

$$\frac{dV_c}{V_c} \cong \varepsilon_2 + \varepsilon_3 \cong 2\varepsilon_2 \quad (2)$$

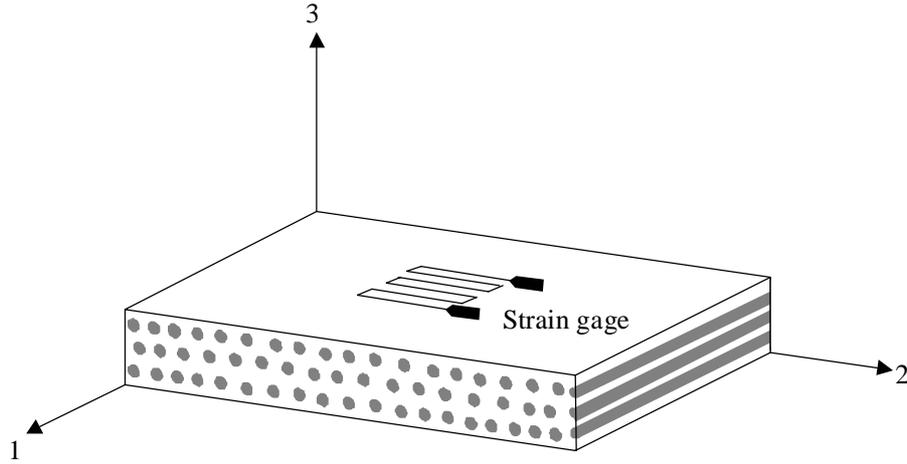


Fig. 1 Unidirectional composite specimen with strain gage in the transverse (2) direction

thus, the aging strain in the transverse (2) direction is one-half the volumetric change of the composite. Furthermore, since only the matrix undergoes aging, the volumetric change of the matrix is related to the measured strain as

$$\frac{dV_m}{V_m} = \frac{dV_c}{(1 - V_f)V_c} = \frac{2}{(1 - V_f)} \epsilon_2$$

or

$$\epsilon_2 = \frac{(1 - V_f)}{2} \left(\frac{dV_m}{V_m} \right) \quad (3)$$

where V_m = matrix volume
 V_f = fiber volume ratio

In order to correct for the temperature effects on the gage reading, a titanium silicate specimen instrumented with a similar gage was used as a reference [8]. The composite specimen was heated above $T_g=240^\circ\text{F}$ to "erase" any prior memory and then quenched down to the selected test temperature inside a thermal chamber. Recording of strain readings from the composite and reference specimens began as soon as temperature equilibrium was reached. Tests were conducted at various temperatures in the range 160-190°C. Typical aging strains in the composite in the transverse direction were obtained as a function of time at various temperatures (Fig. 2). As can be seen the magnitude of the aging strain at any given aging time increases with temperature at least in the time range investigated. Furthermore, all aging curves appear to reach asymptotic values which increase with temperature. This appears to be contrary to the concept of free volume where the ultimate reduction in free volume, thereby aging strain, should be higher at lower temperatures farther removed from T_g [9]. However, as observed by Struik [2], the slopes of volume versus temperature curves at fixed aging times are lower than that of the as quenched material (zero aging) and decrease with increasing aging time (Fig. 3). This is attributed to "freezing" of processes contributing to volume relaxation below T_g [1] and is consistent with the present experimental results. Similar trends for the initial stage of aging have been observed by Kung et al. [10] who also found a change in T_g with aging time.

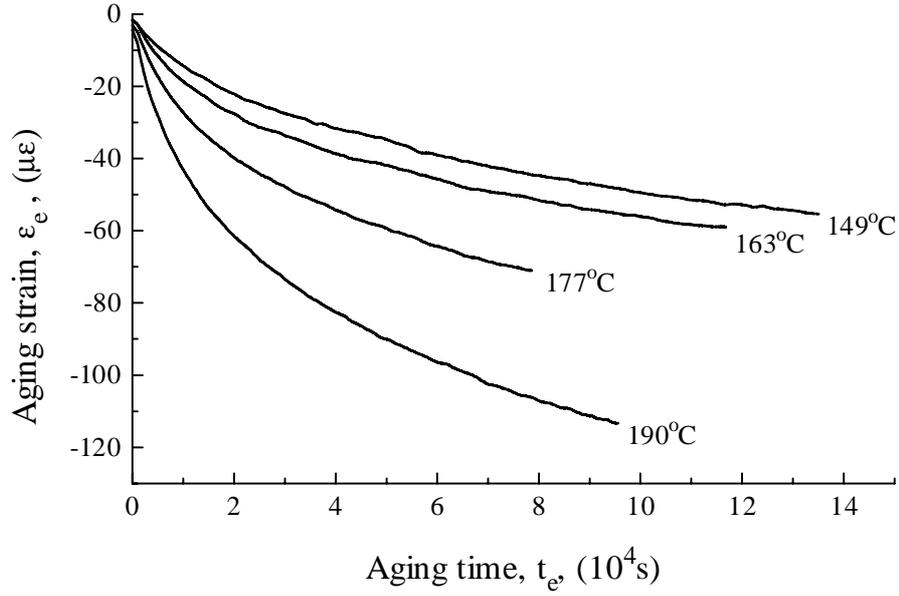


Fig. 2 Transverse aging strains in unidirectional carbon/polyimide at various temperatures as a function of time

The typical aging strain curve shown in Fig. 4 was modeled by the following exponential form

$$\frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = e^{-(t_e - t_0)/\tau(T)} \quad (4)$$

where $\epsilon = \epsilon(T, t_e)$ = current aging strain at time t_e and temperature T

ϵ_0 = reference strain at time t_0

$\epsilon_{\infty} = \epsilon_{\infty}(T)$ = equilibrium aging strain at temperature T

$\tau(T)$ = relaxation time at temperature T

This form was corroborated by plotting results of Fig. 2 on semi-log scale where $\log[(\epsilon - \epsilon_{\infty})/(\epsilon_0 - \epsilon_{\infty})]$ seems to vary nearly linearly with aging time (Fig. 5). The apparent deviations occur at long aging times where aging strain changes are small and of the order of experimental resolution.

The aging rate obtained from eq. (4) is

$$\frac{d\epsilon}{dt_e} = -\frac{1}{\tau}(\epsilon - \epsilon_{\infty}) \quad (5)$$

This model is very similar to the one proposed by Kovacs for isothermal volume relaxation [1]. The main difference is that in Kovacs' model the relaxation time, τ , is also a function of aging state, in this case aging strain, as $\tau(\epsilon, T)$. However, the structural relaxation time τ need not be affected by aging in the same way as the viscoelastic relaxation time.

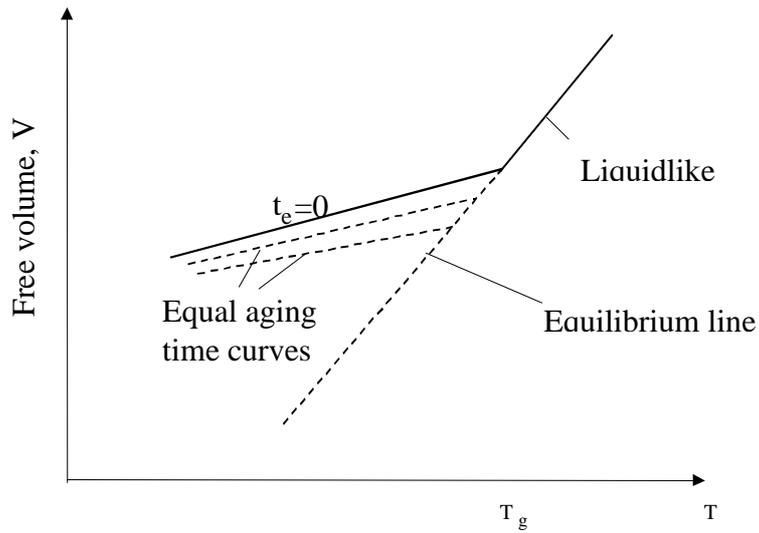


Fig. 3 Schematic curves of volume versus temperature showing slope reduction with increasing aging time

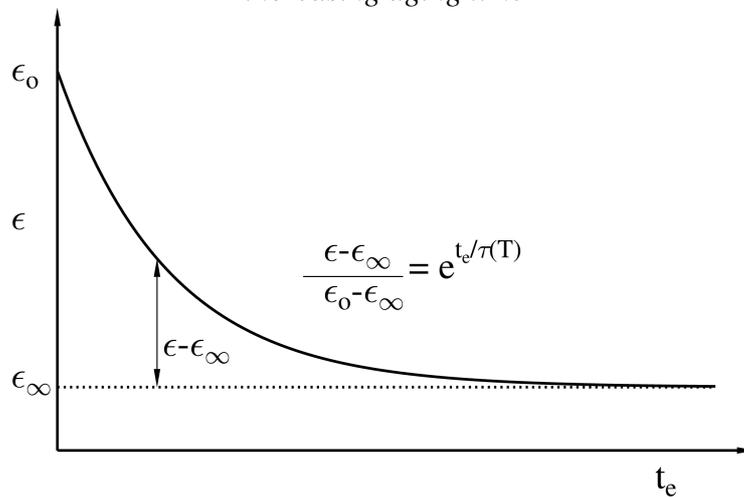


Fig. 4 Exponential modeling of physical aging of IM7/K3B carbon/polyimide composite

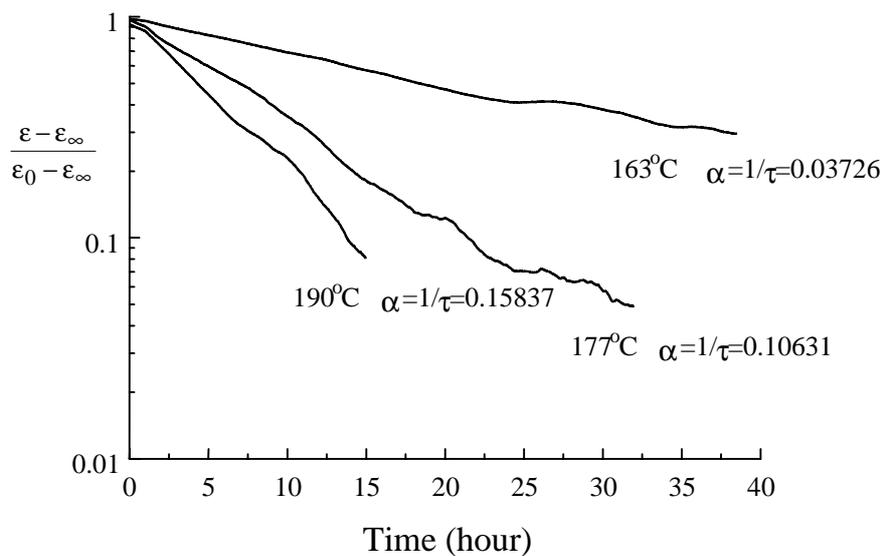


Fig. 5 Aging strains versus time at three different temperatures

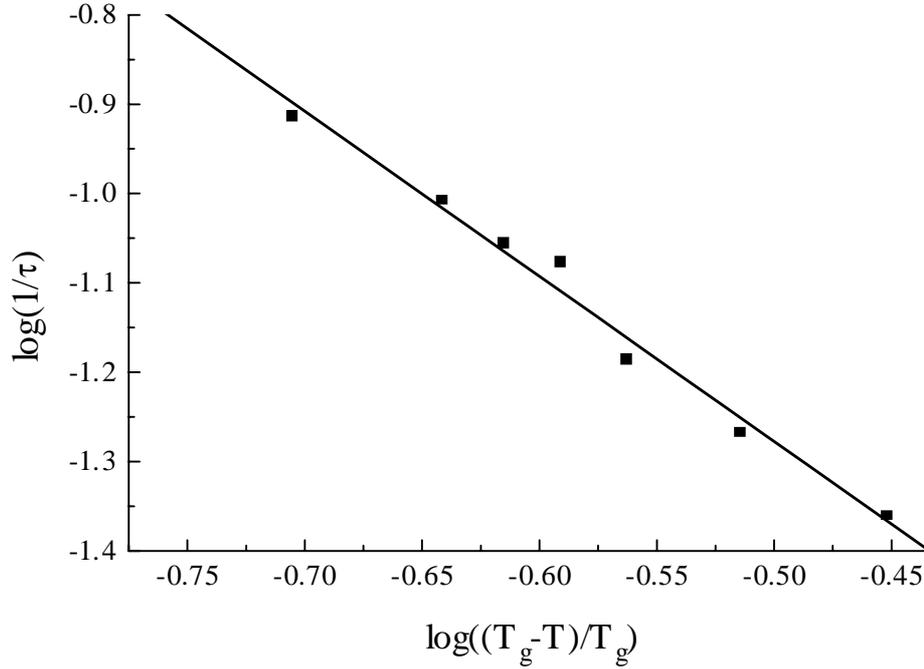


Fig. 6 Power law fit for relaxation time

The dependence of τ on temperature alone was modeled as

$$\tau = C \left(\frac{T_g - T}{T_g} \right)^\beta \quad (6)$$

where C and β are constants. A good fit of this form to experimental results is shown in Fig. 6. It was determined that $\beta = 1.85$ for the material studied here.

Assuming the model described above to be valid, it would be possible to describe aging under nonisothermal conditions. For a given temperature history $T(t_e)$ the resulting aging can be calculated from the rate relation (5)

$$\frac{d\varepsilon}{dt_e} + \frac{\varepsilon}{\tau} = \frac{\varepsilon_\infty}{\tau} \quad (7)$$

where the relaxation time $\tau[T(t_e)]$ and equilibrium aging strain $\varepsilon_\infty[T(t_\infty)]$ are functions of temperature and thereby functions of time. The solution of the differential eq. (7) is

$$\varepsilon = \frac{1}{p} \left[\int_{t_0}^{t_e} p \frac{\varepsilon_\infty}{\tau} dt_e + \varepsilon_0 \right] \quad (8)$$

where $p = \exp \left[\int_{t_0}^{t_e} \frac{1}{\tau} dt_e \right]$

The analysis above can be applied to the specific case illustrated in Fig. 7, where the sample was first aged at 177°C for a certain period of time, then cooled down to 149°C and aged for another period of time and then aged at 177°C for another time period. An isothermal aging curve for 177°C was constructed as follows. The segment corresponding to 149°C was

transformed on the time axis and shifted to fit the curve of 177°C aging. The last segment at 177°C needs only to be shifted on the time axis.

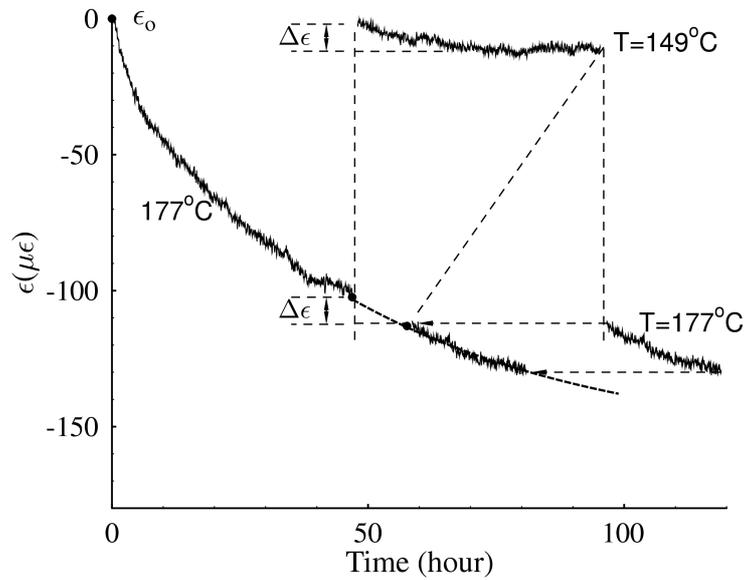


Fig. 7 Construction of master isothermal aging curve from segments of isothermal aging curves

CREEP BEHAVIOR

Creep tests were conducted on the same type of specimen used for measurement of aging. The specimens were 24-ply unidirectional IM7/K3B coupons instrumented with the same type of strain gages (WK-00-250BG-350) and a thermocouple. They were loaded under a transverse tensile stress of approximately 30% of the transverse strength of the specimen at the test temperature. The creep specimen was placed in an environmental chamber along with a similarly instrumented dummy specimen (Fig. 8). The strain readings from the dummy specimen, representing aging, were subtracted from the total readings from the active specimen to obtain the pure creep strain (Fig. 9).

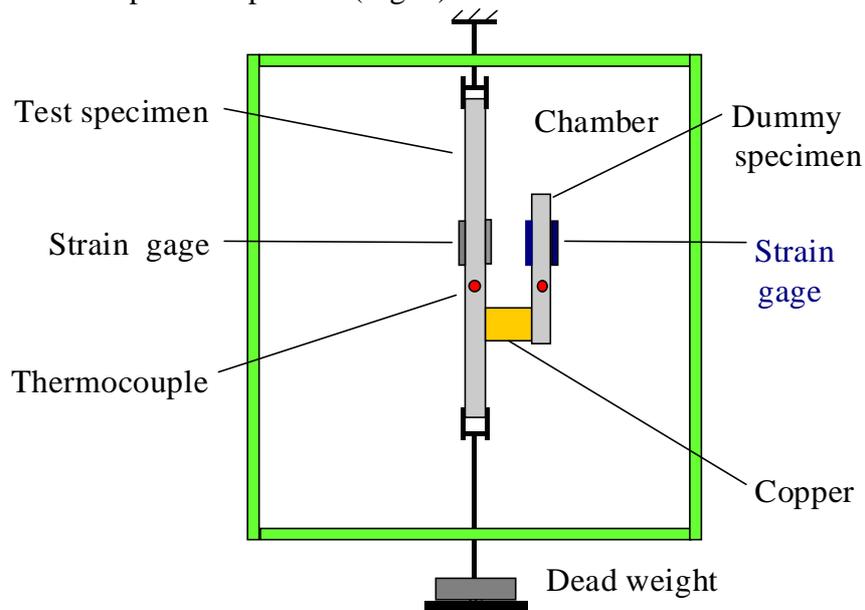


Fig. 8 Creep testing setup in environmental chamber

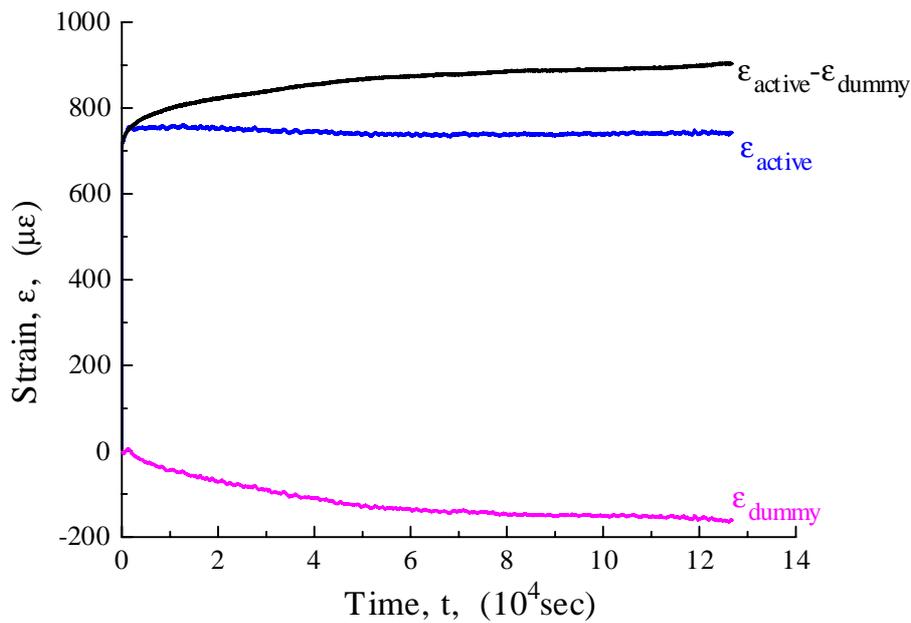


Fig. 9 Isothermal creep test of IM7/K3B at elevated temperature (350°F)

The effect of aging on creep was checked at one temperature only, 149°C, by means of short time creep tests at different aging times. No noticeable effects were detected, primarily due to the small amount of creep and small degree of aging. Despite the low creep recorded, it was noticed that the material experienced some degradation with time. The streaks shown in Fig. 10 did not cause failure but appear to be precursors of transverse matrix cracks.

Nonisothermal creep behavior was briefly investigated in a qualitative manner. The average creep compliance was determined under cyclic thermal conditions with the temperature cycled between 163 and 190°C and compared with isothermal creep compliances at 177 and 190°C (Fig. 11). Creep under cyclic thermal conditions is higher than isothermal creep at the mean cyclic temperature (177°C). This phenomenon could become more pronounced at higher temperatures and under higher loads.

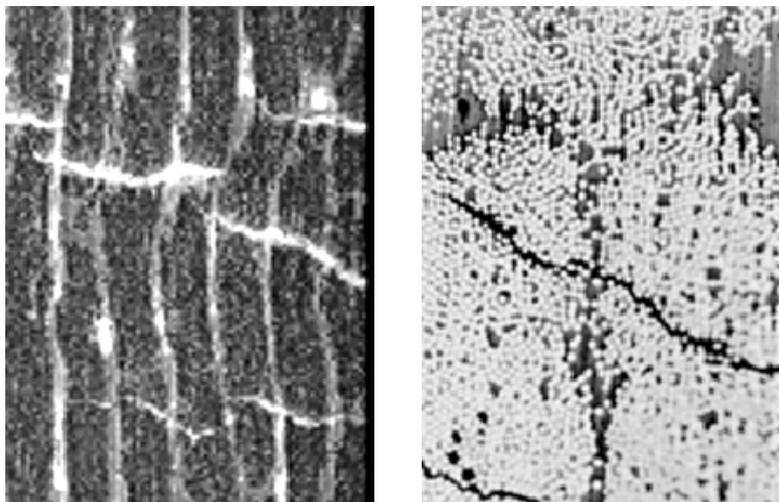


Fig. 10 Damage mechanisms during creep

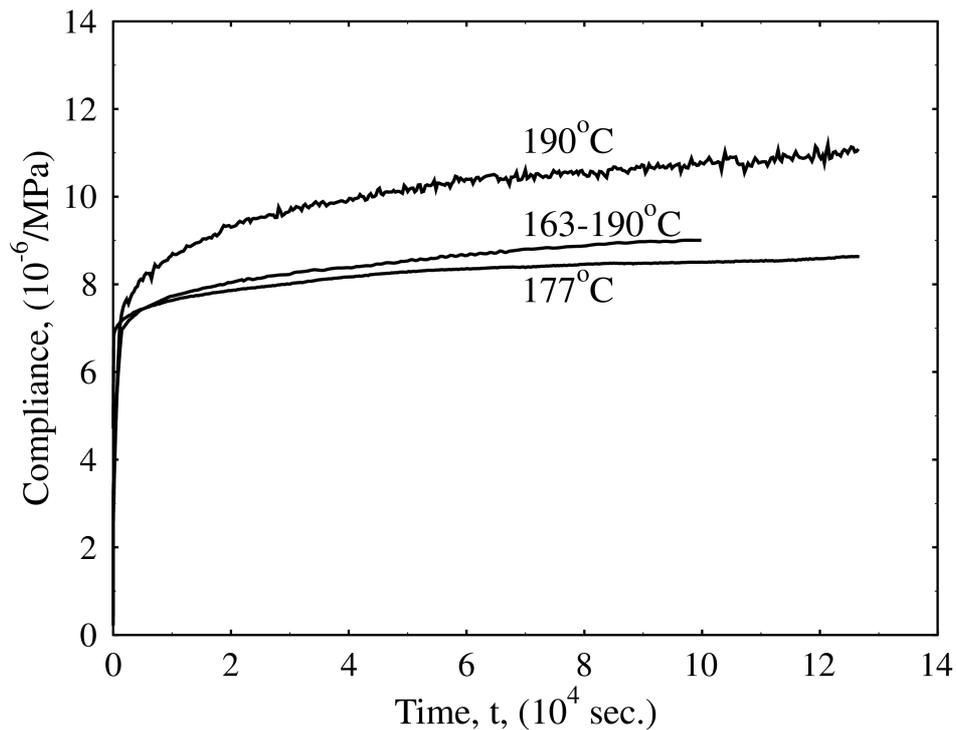


Fig. 11 Comparison of isothermal and thermal cycling creep tests of IM7/K3B

CONCLUSIONS

Techniques were developed for direct quantitative measurement of aging strain, thereby volumetric shrinkage due to aging. It might be questioned whether the aging strains recorded might be affected or even overshadowed by other effects, such as relaxation of residual stresses. Such effects, however, would have produced positive strains instead of negative and would be higher at lower temperatures where the residual stresses are higher.

The aging strains measured are negative and are higher at higher temperatures. The latter trend appears to be contrary to the concept of free volume, according to which the ultimate volumetric reduction should be higher at lower temperatures. There is no experimental evidence for this trend and explanations have been offered for the opposite trend, i.e., the one observed here [1].

Techniques were developed for separating aging and creep effects. The effect of aging time on creep was found to be small. Under cyclic temperature conditions creep can be higher than under isothermal conditions at the mean cyclic temperature.

ACKNOWLEDGEMENTS

The work described here was sponsored by the Air Force Office of Scientific Research (AFOSR) under grant number F49620-98-1-0056. We are grateful to Dr. Ozden O. Ochoa of the AFOSR for her encouragement and co-operation and to Mrs. Yolande Mallian for typing the manuscript. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

REFERENCES

1. Kovacs, A. J., *Fortschr. Hochpolym. Forschung*, Vol. 34, 1964, p. 394.
2. Struik, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, New York, 1978.
3. Nichols, M. E., Wang, S. S. and Geil, P. H., "Creep and Physical Aging in a Polyamideimide Carbon Fiber Composite," *Journal of Macromolecular Science - Part B: Physics*, Vol. 29, 1990, pp. 303-336.
4. Sullivan, J. L., "Creep and Physical Aging in Composites," *Composites Science and Technology*, Vol. 39, 1990, pp. 207-232.
5. Hastie, R. L. Jr. and Morris, D. H., "The Effects of Physical Aging on the Creep Response of a Thermoplastic Composite," *High Temperature and Environmental Effects on Polymeric Composites*, ASTM STP 1174, C. E. Harris and T. S. Gates, Eds., American Society for Testing and Materials, Philadelphia, PA, 1993, pp. 163-185.
6. Skontorp, A. and Wang, S. S., "High-Temperature Creep with Physical and Chemical Aging, and Associated Viscoelastic Constitutive Equations of Polyimide-Matrix Composites," in *Recent Advances in Composite Materials*, 1995 ASME Applied Mechanics and Materials Meeting, Los Angeles, MD Vol. 56, 1995, pp. 57-69.
7. Gates, T. S. and Feldman, M., "Effects of Physical Aging at Elevated Temperatures on Viscoelastic Creep of IM7/K3B," *Composite Materials: Testing and Design (Twelfth Volume)*, ASTM STP 1274, R. B. Deo and C. R. Saff, Eds., American Society for Testing and Materials, 1996, pp. 7-36.
8. Daniel, I. M. and Ishai, O., *Engineering Mechanics of Composite Materials*, Oxford University Press, New York, 1994, p. 310.
9. Struik, L. C. E., "Physical Aging in Plastics and Other Glassy Materials," *Polymer Engineering and Science*, Vol. 17, No. 3, March 1977, pp. 165-173.
10. Kung, H. K., Skontorp, A. and Wang, S. S., "High-Temperature Physical and Chemical Aging in Carbon-Fiber Reinforced Polyimide Composites: Experiment and Theory," in *Recent Advances in Composite Materials*, 1995 ASME Applied Mechanics and Materials Meeting, Los Angeles, MD Vol. 56, 1995, pp. 193-202.