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EFFECTS OF PHYSICAL AGING ON LONG-TERM BEHAVIOR OF COMPOSITES

by
Professor L. Catherine Brinson
Mechanical Engineering Department
Northwestern University
Evanston, IL 60202-3111

Abstract

The HSCT plane, envisioned to have a lifetime of over 60,000 flight hours and to travel at speeds in excess of Mach 2, is the source of intensive study at NASA. In particular, polymer matrix composites are being strongly considered for use in primary and secondary structures due to their high strength to weight ratio and the options of property tailoring. However, an added difficulty in the use of polymer based materials is that their properties change significantly over time (especially at the elevated temperatures that will be experienced during flight) and prediction of properties based on irregular thermal and mechanical loading is extremely difficult.

This study focused on one aspect of long-term polymer composite behavior: physical aging. When a polymer is cooled to below its glass transition temperature, the material is not in thermodynamic equilibrium and the free volume and enthalpy evolve over time to approach their equilibrium values. During this time, the mechanical properties change significantly and this change is termed *physical aging*. This work begins with a review of the concepts of physical aging on a pure polymer system. The effective time theory, which can be used to predict long term behavior based on short term data, is mathematically formalized. The effects of aging to equilibrium are proven and discussed. The theory developed for polymers is then applied to first to a unidirectional composite, then to a general laminate. Comparison to experimental data is excellent. It is shown that the effects of aging on the long-term properties of composites can be counter-intuitive, stressing the importance of the development and use of a predictive theory to analyze structures.

Physical Aging of Polymers

The traditional means to explore the effects of physical aging on mechanical properties is through a series of sequenced creep and recovery tests. In these tests, the specimen is initially quenched from above the glass transition to a temperature below T_g. The time the material exists below its glass transition is referred to as the aging time, t_e. As aging time progresses, a series of short (in comparison to the elapsed aging time) creep tests are run to extract the momentary creep compliance of the material. A creep test is one in which the load is held constant and the strain is measured as a function of time. Aging proceeds on a log-time scale, as can be seen in Figure 1. The momentary curves are all identical in shape, shifted only across the log-time scale from one another with a shift factor, a_{t_e}. Note that the material gets stiffer (or less compliant) as aging time progresses. If the shift factor is plotted as a function of aging time on a double-log scale, it is found to map a straight line with a slope of μ as shown in Figure 2. The shift rate, μ, can then be considered to be a material constant.

The momentary material properties can then be shown to vary with aging time according to

$$S(t) = S_0 e^{(t/\tau(t_e))^\beta}$$

$$\tau(t_e) = \tau(t_{eref}) \cdot \left(\frac{t_e}{t_{eref}}\right)^\mu \tag{1}$$

where S_0, is the initial compliance, β a shape parameter, τ the relaxation time, t_{eref} the reference aging time.

Effective Time Theory

If the loading time of a material is not short in comparison to the previous aging time, then aging proceeds even as the test progresses. Thus, if the beginning aging time is t_e, at some time later during the test the aging time is $t + t_e$, where t is the test time. Taking the initial aging time t_e to be the reference aging time, the shift factor, a, at any instant in time can be defined based on μ. Thus in any time increment dt at time t, all relaxation times are $1/a$ slower and the time increment is $1/a$ less eventful than if aging time had not been increasing. The "effective" time increment can then be defined

$$d\lambda = a(t)dt, \quad a(t) = \left(\frac{t_e}{t_e + t}\right)^\mu \tag{2}$$

and the total test time can be reduced to the "effective time", λ

$$\lambda = \int_0^t a(\xi)d\xi. \tag{3}$$

Using the effective time in place of real time in Equation (1) results in prediction of long-term material response based only on material parameters determined from short term tests. Figure 3 illustrates the effective time theory prediction of long-term material response. Note that the compliance deviates sharply from the exponential momentary curve as the test time approaches and exceeds the initial aging time. Figure 4 illustrates the role of the shift rate, μ, in the long-term response of a material. Note that the larger values of μ lead to a stiffer response at longer times. Thus the shift rate can be used as a screening parameter for selection of materials, higher shift rates being preferable for structural applications.

Aging to Equilibrium

If the material is being loaded at temperatures close to its glass transition, the material can age into equilibrium during a relatively short time frame. According to experimental evidence on a polymer by McKenna and preliminary evidence by Gates on a composite, when the equilibrium aging time, t_e^*, is exceeded the shift rate does not become zero but decreases by an order of magnitude. In general, $\mu \approx 1$ before t_e^* and $\mu \approx 0.1$ after t_e^*. In this study the basic concepts of aging and effective time were mathematically formalized to handle this case. The specific formulae will be published elsewhere. Figure 5 shows the results of the long-term predictions along with short-term data from McKenna. Note that if the material is loaded with an initial aging time less than t_e^*, the response initially follows the momentary curve; then begins to deviate (becoming much stiffer than the momentary curve predicts) as the test time approaches initial aging time; then as the test time and initial aging time combined exceed t_e^*, the material has "aged into equilibrium" and the response follows parallel to the momentary curve once again. Since the material is aging at a much reduced rate after t_e^*, accumulating time no longer has the effect of causing the material to remain much stiffer than the momentary response. In the long term response of a material aged into equilibrium, the compliance increases in an exponential manner. Further experiments to verify these results are planned on composites. The implication here is that in a structural situation the material should never be permitted to reach temperatures close enough to T_g such that aging into equilibrium is possible.

Aging and Long Term Response of a Lamina

In an off-axis lamina, the properties in the loading direction can be determined from the properties in the fiber direction, S_{ij}, through the traditional transformation

$$\{\varepsilon\} = [\bar{S}(t)]\{\sigma\}; \; \bar{S}_{ij}(t) = f(\theta, S_{ij}). \tag{4}$$

The transverse compliance, S_{22}, and the shear compliance, S_{66}, are the only terms of the compliance matrix that are matrix dominated and therefore subject to physical aging. Note that each of these compliance terms will have its own set of defining material parameters $(S_0, \beta, \tau(t_{eref}), \mu)$. Consequently, due to the complex interaction of all these terms, the long-term compliance of a lamina with a given fiber angle cannot be intuitively predicted.

The long-term response of a lamina can, however, be determined by applying physical aging concepts to update the relaxation time and effective time individually for the shear and transverse compliance, then performing the transformations of equation (4). Note that equation (4) holds only for the case of constant loading. A future extension to this work will be implementation of the theory into a convolution integral form constitutive law for viscoelasticity. To illustrate the complexity of long term lamina response, consider Figure 6, where the long term load-direction compliance is plotted for a variety of fiber angles. The results coincide precisely with experimental data (not shown) up to 10^6 seconds, after which there are no further experimental data points. Note that at short times, the 90° lamina is the most compliant as would be expected, but as time progresses the 45° lamina becomes actually more compliant than the 90°. This occurs because even though the shift rates of the transverse and shear compliance were taken to be the same for this illustration (in fact, they differ) and thus the effective time for both terms is identical, the S_{66} term which dominates the 45° response is more compliant in the long term than the S_{22} term.

Aging of a Laminate

The last portion of this work examined the response of composite laminates to physical aging. This was accomplished by incorporating the process of physical aging of a lamina (from the previous section) into standard lamination theory. This work is still ongoing, but a sample result is shown in Figure 7. Here the change in compliance of a quasi-isotropic laminate, $[0/\pm 45/90]_s$, is given over a long time range. Note that the compliance is now plotted on a semi-log scale since the changes in compliance are not as dramatic with fiber domi-

nated lay-ups. Notice, however, that the stiffnesses change by 8%-12% over a 10 year period, which is certainly significant for most structural applications, HSCT not excluded. Continuing work will examine sensitivity of the composite response to small changes of angle in the 0° lamina and investigate the effects of temperature on long-term aging of composites. Stress level dependencies will also be examined.

References

Gates, T. S. and Feldman, M., "The Effects of Stress and Physical Aging on the Creep Compliance of a Polymeric Composite," *34th AIAA SDM Conference*, **vol. AIAA-93-1575-CP, Part 4**, April 19-22, 1993, pp. 2348-2356.

Halpin, J. C., *Primer on Composite Materials Analysis*. Technomic Publishing Co., Lancaster. 2nd Edition, 1992.

Hastie, R. L. J., *The Effect of Physical Aging on the Creep Response of a Thermoplastic Composite*. Ph.D., Virginia Tech, 1991.
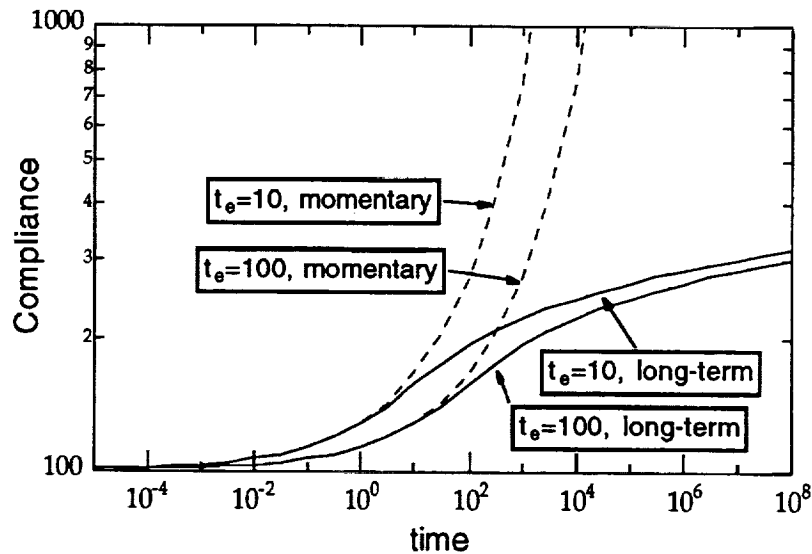
Lee, A. and McKenna, G. B., "The Physical Ageing Response of an Epoxy Glass Subjected to Large Stresses," *Polymer* **31**, 1990, pp. 423-430.

Struik, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*. Elsevier Scientific Publishing Co., New York. 1978.
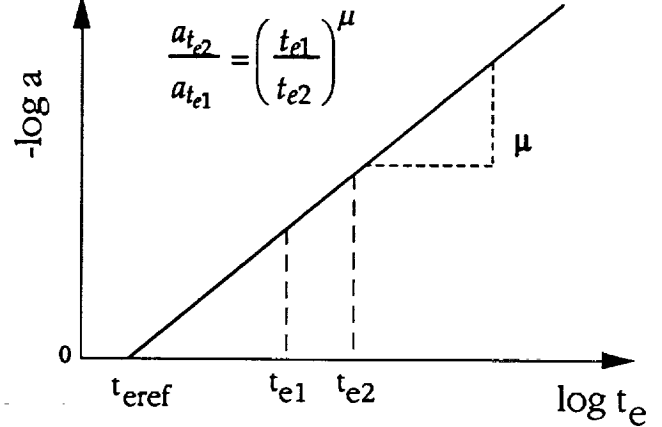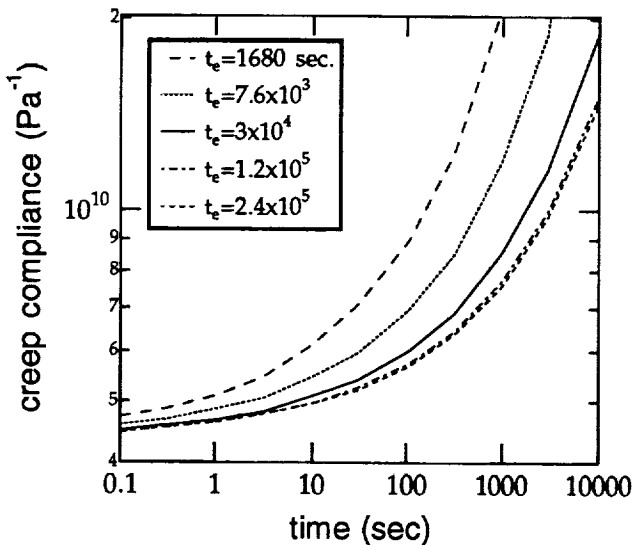
Figure 1: Momentary creep curves with progressing aging time; McKenna data on epoxy.

Figure 2: Definition of Shift Rate

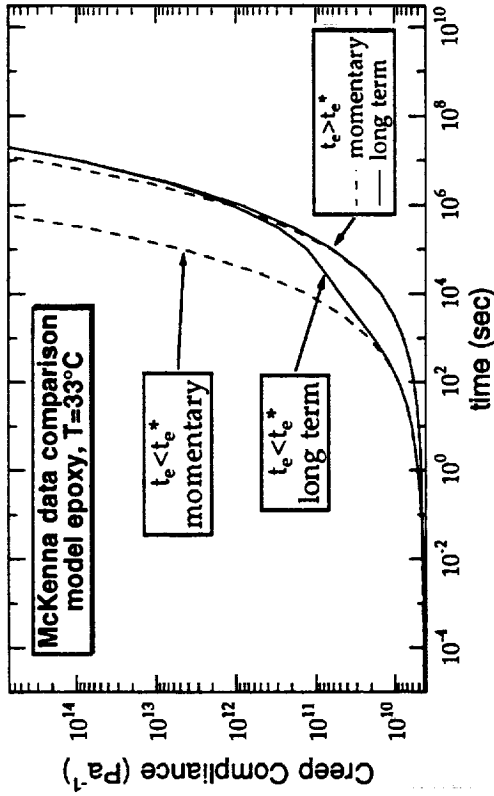**Figure 3:** Comparison of long-term and momentary response

Figure 4: Effect of different shift rates on the long-term material response

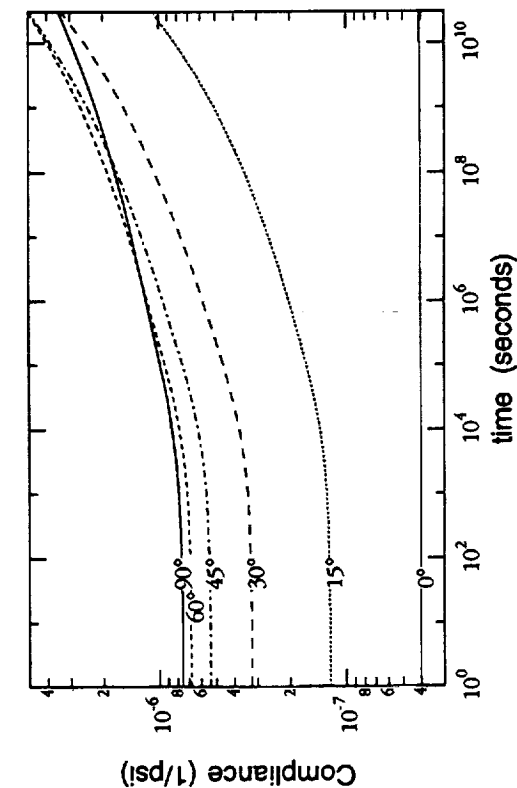**Figure 5:** Momentary and long term response when aged to equilibrium

Figure 6: Comparison of the effect of aging on the long term compliance for varying fiber angles. Hastie data, on IM7/8320 with $\mu_{66}=\mu_{22}=0.77$.

Figure 7: Change in compliance of quasi-isotropic laminate of IM7/8320.

77