Final Report for
NASA-Langley Research Grant, NCC1-271,
*Synergistic Effects of Physical Aging and Damage on Long-term Behavior of Polymer Matrix Composites*,
Principal Investigator, L. Cate Brinson
Project Dates: 11/1/97-11/1/99

Summary:

The research consisted of two major parts, first modeling and simulation of the combined effects of aging and damage on polymer composites and secondly an experimental phase examining composite response at elevated temperatures, again activating both aging and damage. For the simulation, a damage model for polymeric composite laminates operating at elevated temperatures was developed. Viscoelastic behavior of the material is accounted for via the correspondence principle and a variational approach is adopted to compute the temporal stresses within the laminate. Also, the effect of physical aging on ply level stress and on overall laminate behavior is included. An important feature of the model is that damage evolution predictions for viscoelastic laminates can be made. This allows us to track the mechanical response of the laminate up to large load levels though within the confines of linear viscoelastic constitutive behavior.

An experimental investigation of microcracking and physical aging effects in polymer matrix composites was also pursued. The goal of the study was to assess the impact of aging on damage accumulation, in terms of microcracking, and the impact of damage on aging and viscoelastic behavior. The testing was performed both at room and elevated temperatures on $[\pm 45/90_3]$ and $[0_2/90_3]$ laminates, both containing a set of $90^\circ$ plies centrally located to facilitate investigation of microcracking. Edge replication and x-ray-radiography were utilized to quantify damage. Sequenced creep tests were performed to characterize viscoelastic and aging parameters. Results indicate that while the aging times studied have limited influence on damage evolution, elevated temperature and viscoelastic effects have a profound effect on the damage mode seen. Some results are counterintuitive, including the lower strain to failure for elevated temperature tests and the catastrophic failure mode observed for the $[\pm 45/90_3]$ specimens. The fracture toughness for transverse cracks increases with increasing temperature for both systems: transverse cracking was completely absent prior to failure in $[\pm 45/90_3]$, and was suppressed for $[0_2/90_3]$. No significant effect of damage on aging or viscoelastic parameters was observed.

Publications:

The major contributions of this work are outlined in two publications:


The following will briefly describe the work, but explicit details will be omitted for brevity. Additional information can be found in the papers.

**Presentations:**
The research has been presented in several major conferences:

- **Poster session: Gordon Conference, Santa Barbara, CA, 9-14 January 2000, “Aging and Damage in Polymeric Composites”**
- **University of Massachusetts - Amherst, 25 February 1999, “Aging and Damage in Viscoelastic Composites”**
- **The Boeing Company, High Speed Research Workshop, 15 September 1998, “Physical Aging and Damage in Polymer Composites”**
- **ASTM Conference, Atlanta, 4 May 1998, “Aging During Elevated Temperature Stress Relaxation of IM7/K3B Composite”**

**Introduction**

Composite laminates are known to sustain multiple damage modes which by themselves are not critical to the final failure but which lead to other mechanisms causing failure. Extensive work has been done in understanding the damage and failure of composites at room temperature (Highsmith and Reifsnider, 1982; Kim and Mai, 1991). Room temperature tests were performed by Nairn (1995) on cross-ply laminates to investigate the effect of physically aging the laminates at high temperature on the micro-cracking fracture energy. It was seen that for carbon/polyimide (IM7/K3B) laminates, aging did not affect the fracture energy for very long times while for carbon(AS4)/polysulfone laminates, there was a sharp drop for relatively short aging times.

With respect to modeling, much has been done to understand and model the micro-structural damage processes in polymeric composites and their effect on thermo-mechanical response. However, damage studies on such heterogeneous, anisotropic materials have been restricted, until recently, to linear elastic constitutive behavior. The effects of viscoelasticity, viscoplasticity, aging and micro-structural damage on each other as well as on the global response have yet to be addressed. Before predictive models can be developed, these issues must be understood and various questions need to be addressed: for example, how does damage evolve for viscoelastic composites? Does aging affect the damage behavior of composites and to what degree and how does temperature affect damage evolution?
This work begins to answer some of the above questions. A mechanistic model evaluating the stress fields and stiffness properties of damaged viscoelastic cross-ply laminates is first developed and then extended to include damage evolution. Residual modulus computations and physical aging effects on laminate behavior are detailed. Some simplifying assumptions are made with respect to the critical stress for crack initiation and the magnitude of the stress drop with new crack formation. Linear viscoelasticity is used along with the correspondence principle. What results is a model that can therefore predict a good first approximation for the mechanical behavior of a damaged and aged viscoelastic laminate subjected to any given (simple) applied load history.

Concurrently with the modeling, an attempt is made to experimentally characterize the influence of damage on the material properties of thermoplastic composite laminates. The influence of temperature on the damage and failure of two different laminate systems are also studied. Interesting new results are reported which show that a laminate fails like a monolithic material at temperatures close to the matrix glass transition temperature.

**Damage Evolution Model for Viscoelastic Composites**

In this section, a viscoelastic damage model for cross-ply laminates of the type $[0°/90°]_s$ is developed. Aging is included in the analysis and property changes of the laminate are predicted for different applied stress rates. The model is based upon previous work on linear elastic cross-ply laminates by Hashin (1985) where we modify the mathematical framework to apply to linear viscoelastic composites through the elastic-viscoelastic correspondence principle (Schapery, 1967; Tschoegl, 1989). The model is restricted to linear viscoelastic composites because the correspondence principle as used here does not hold for non-linear viscoelastic constitutive behavior. It is noted that laminates with outer off-axis plies instead of $0°$ plies can be treated approximately by assuming equivalent unidirectional properties for the off-axis plies (Nairn and Hu, 1994). Hashin’s model was selected because of the reasonably accurate representation of the stress state between interacting transverse cracks with regard to damage evolution calculations (Akshantala and Talreja, 1998) and also because of the ease of extending it to the viscoelastic case via the correspondence principle. Nonetheless, the essential features of the present method and results should hold regardless of the damage model under consideration.

The constitutive equation for a linear viscoelastic material is given in integral form as,

$$\varepsilon_{ij} = \int_0^t S_{ijkl}(t-\tau) \frac{\partial \sigma_{kl}}{\partial \tau} d\tau$$  \hspace{1cm} (1)

Taking the Laplace transform of equation (1) and noting that the right hand side is a convolution integral, gives,

$$\tilde{\varepsilon}_{ij}(s) = \tilde{S}_{ijkl}(s) \tilde{\sigma}_{kl}(s)$$ \hspace{1cm} (2)

where the bar on top denotes Laplace transformed quantities and the tilde denotes the Carson transform ($s$ multiplied transform). Note that equation (2) is obtained by assuming that the material is stress free at $t=0$. The Laplace transformed viscoelastic
The constitutive equation is identical to the linear elastic constitutive equation. The equilibrium and compatibility equations are also identical to their elastic counterparts with the stress and strain terms written as transformed quantities. Therefore, the viscoelastic problem is equivalent to solving an elastic problem in the Laplace domain. It is often simpler to solve such an associated elastic problem and invert the resulting solutions to obtain the time dependent viscoelastic solution. In what follows, explicit dependence of the transformed quantities on the transform variable is not shown.

Figure 1a shows a cross-ply laminate with transverse cracks in the 90° layer due to a uniform tensile membrane force, $N_{xx}$, applied to the laminate. The unit cell used for the analysis is shown in Figure 1b. The analysis follows the procedure outlined by Hashin (1985), with necessary modifications for viscoelastic materials. Specifically, the problem is solved in the Laplace domain via the correspondence principle.

Here we delineate the mathematical steps. Detailed equations may be found in the journal paper. First, we assume that $\sigma_{xx}$ is a function of $x$ only

$$\bar{\sigma}^{L(1)}_{xx}(x) = \bar{\sigma}_1[1 - \phi_1(x)]$$
$$\bar{\sigma}^{L(2)}_{xx}(x) = \bar{\sigma}_2[1 - \phi_2(x)]$$

(3)
where superscript \( L \) indicate total stresses for the laminate, bars indicate the axial stresses in the undamaged laminate, and (1) and (2) denote 90° and 0° layers of the laminate. Then we use equilibrium equations

\[
\frac{\partial \sigma_{x}^{(m)}}{\partial x} + \frac{\partial \sigma_{zz}^{(m)}}{\partial z} = 0
\]

and boundary conditions

\[
\overline{\sigma}_{xz}^{(1)}(x,0) = 0
\]

\[
\overline{\sigma}_{xz}^{(1)}(x,t_1) = \overline{\sigma}_{xz}^{(2)}(x,h)
\]

\[
\overline{\sigma}_{zz}^{(2)}(x,0) = 0 \quad \overline{\sigma}_{xx}^{(1)}(\pm a) = 0
\]

Substituting \( \sigma_{xx}(\phi) \) into equilibrium and boundary conditions provides an admissible stress system, which is then used to express the complementary energy. Via a standard minimization procedure the proper \( \phi \) is found.

To examine the issue of damage evolution, we consider the constitutive law again and subdivide the time into what happens before a new crack forms (\( t < t_1^* \)) and what happens after (\( t > t_1^* \))

\[
\epsilon_{ij}(t) = \int_{0}^{t_1} S_{ijkl}(t - \tau) \frac{\partial \sigma_{kl}}{\partial \tau} d\tau + \int_{t_1}^{t_1^*} S_{ijkl}(t - \tau) \frac{\partial \sigma_{kl}}{\partial \tau} d\tau + \int_{t_1^*}^{1} S_{ijkl}(t - \tau) \frac{\partial \sigma_{kl}}{\partial \tau} d\tau
\]

The second term represents an instantaneous change in stress as the new crack forms. We assume a maximum stress failure criterion for the formation of a new transverse crack, at which point the crack spacing changes from 2a to a. Again, the correspondence principle is used to transform the problem to the Laplace domain and two cases are considered: the initial case of crack spacing 2a and the case of crack spacing a. Since these are solved as separate boundary value problems individually, application of the correspondence principle is still valid. The major assumption in this portion of the work is that the change in crack spacing is instantaneous and that the stresses with the new crack spacing of a are identical to the previous solution if initial spacing of a was assumed. This is a reasonable assumption as the process should be so fast as to avoid history effects and all boundary conditions for the new problem are satisfied. This process is illustrated schematically in Figure 2. With this assumption the stress and strain fields for new crack spacing are found sequentially in the Laplace domain. To transform solutions back to the time domain, ter Haar's approximation is used

\[
f(t) = \left[ \tilde{f}(s) \right]_{s=1/t}
\]
Stress increases until $\sigma_{xx}(x=0) = \sigma_{crit}$

New crack at $x = 0$

$\sigma_{xx}(x=a/2)$ drops to known value

--- Repeat analysis with new crack spacing

Figure 2: Schematic showing stress variation at a particular point in unit cell. Solid line is stress variation as move from crack spacing of 2a to crack spacing of a. Dashed line is stress variation for problem with initial crack spacing of a.

Some results of the analysis are presented below, where the laminate Young's modulus is defined to be the quasielastic form

$$E_{x}(t) = \frac{\sigma_{0}(t)}{\varepsilon_{x_{avg}}(t)}$$

and aging effects are included via appropriate modification of the time dependent modulus properties with an aging shift rate (Brinson and Bradshaw, 1995; Brinson and Gates, 1995). Figure 3 shows the axial stress at the midpoint of the unit cell and demonstrates that it takes longer to reach the critical stress at the lower loading rate nonproportionally with the higher loading rate. The reason for nonproportionality is that the 90° layer has longer to relax at the lower loading rate and consequently is incapable of carrying the same stress as before: it sheds the additional load onto the 0° layer. This fact is clearly observed in Figure 4 where the change in the laminate Young's modulus is plotted against time. Normalization for modulus is done using the initial modulus of the laminate ($t=0$) and the time is normalized with respect to the time it takes to reach $\sigma_{crit}$.

The Young's modulus of the laminate at the 0.1 MPa/sec stress rate is lower than that at 1.0 MPa/sec because the average laminate strain is greater for the reasons mentioned above. Laminate modulus with aging increases (not shown) such that the curves in Figure...
4 could represent moduli at the same loading rate with the triangles being aged longer. In the limit of very long aging times, elastic response (constant stress) is observed.

\[
\text{IM7/K3B, \([02/903]\_s)\]
\]

\[
\sigma_{xx} \quad 0.4 \quad 0.2 \quad 0.1 \quad 0.0 \quad 1.0 \quad 0.9 \quad 0.8 \quad 0.7 \quad 0.6 \quad 0.5 \quad 0.4 \quad 0.3 \quad 0.2 \quad 0.1 \quad 0.0
\]

\[
\text{Time (seconds)}
\]

**Figure 3:** variation of stress in the 90° ply with time at two applied stress rates; \(\sigma_{\text{crit}} = 12.9\text{MPa}\)

\[
\text{Aging time=6hr}
\]

\[
\text{Normalized Time}
\]

**Figure 4:** Comparison of laminate longitudinal modulus change with time at two different applied stress rates

\[
\text{Aging time=6hr}
\]

\[
\text{Normalized Time}
\]
Figure 5 plots the change in crack density with applied stress. Results for different initial aging times are compared. All curves are sigmoidal shaped and the tendency of crack saturation is clearly seen. It is also observed that longer aging times result in a larger crack density at a given applied stress. Or, in other words, for longer aging times, transverse cracks form sooner at the same applied stress rate. It is however noted that the effect of aging on the critical stress of 90° plies is not known and in the present analysis the same stress was applied for all aging times. Following Arnold’s (1995) work on the effect of aging on crazing of neat resins, it is guessed that longer aging times might delay transverse crack formation. This would cause the crack density curves with aging in Figure 9 to shift to the right.

Figure 6 plots the longitudinal Young's modulus of the [0₂/90₃]₄ laminate with increasing damage. Once again the elastic case is shown for comparison. Note that for the viscoelastic case, the modulus decay for shorter aging times is greater prior to the formation of a new crack but the instantaneous drop due to change in crack density is smaller. The smaller instantaneous drop is due to the more compliant material shedding more of its load over time to the 0° plies before the formation of a new crack. The combined effect of relaxation and stress drop with crack formation ultimately leads to residual laminate Young’s modulus that quickly tends to the same value for all aging cases.

IM7/K3B, [0₂/90₃]₄

Figure 5: Damage evolution with applied stress for varying aging times. The evolution curve for the elastic case is shown for comparison.
In summary, a micromechanics based damage model was used to predict the stress fields in a damaged viscoelastic cross-ply laminate. Elastic-viscoelastic correspondence principle involving Laplace transforms was used to obtain the time dependent stresses. The influence of physical aging on the viscoelastic material properties was also included in the model. To account for damage evolution, the correspondence principle is extended for changing transverse crack spacing through an assumption relating to instantaneous change in stresses. To the knowledge of the authors, this paper represents the first micromechanics based damage evolution model for viscoelastic laminates. The predictions of damage evolution and damage modulus of a laminate have presented interesting trends. First, due to the viscoelastic relaxation in the 90° plies:

- we see a loading rate dependence for damage evolution. For example, the applied stress for transverse crack formation is larger at a lower loading rate than that at a higher rate.
- the laminate residual secant modulus is smaller at slow loading rates due to the continual shedding of stress on to the adjacent 0° plies.
- the residual modulus change of a laminate is a combination of changing crack density and viscoelastic stress relaxation. However, a larger change in modulus due to relaxation leads to a smaller instantaneous drop due to new crack formation.

Figure 6: Variation in Young's modulus for a laminate aged to different times. The combined effect of viscoelasticity and damage on the modulus is clearly seen and indicated explicitly for the 12 hour aging case. Elastic case shown for comparison.
Also, due to aging of the laminate the damage characteristics were modified as follows.

- Longer aging times resulted in stiffer 90° plies and hence shorter times for crack formation compared to shorter aging times. For the same reason, a laminate aged for long times sees greater damage at the same applied stress levels.
- The residual modulus change due to viscoelastic relaxation is smaller at longer aging times compared to that for shorter aging times while the modulus change due to crack formation is larger.

While both of these latter points indicate a trend toward the elastic response of the laminate as the laminate ages, it is noted that the important influence of temperature and physical aging on the critical stress for transverse cracking needs to be studied. Significant changes in $\sigma_{\text{crit}}$ will alter the nature of these results. Some of these issues are examined in the experimental work in the next section.

**Experimental Characterization of Aging, Temperature and Damage**

In the experimental work, polymer composite specimens were tested to investigate impact of aging and temperature on microstructural damage. Sequence testing provides a measure of the aging rate of the material system and the impact of material damage on this aging rate is determined. Damage is induced in specimens by monotonic tension loading to predesignated strain levels. The effect of temperature and aging state is also investigated as to its effect on damage accumulation and damage mode of the material.

The material system being considered is a polyimide matrix, Avimid K3B (Du Pont), reinforced with continuous IM7 carbon fibers. [±45/90]s and [0/90]s laminate configurations were studied. Test coupons with dimensions of 254 mm X 25.4 mm were cut from panels and stored in a dessicator to minimize moisture absorption. Isothermal aging of all specimens was done in a resistance type oven at 225°C. The specimens were initially rejuvenated at 15°C above the glass transition temperature of the K3B matrix (240°C) for one half hour to erase the effects of prior temperature and loading history. They were then quenched inside the oven using compressed air to 225°C and maintained at that temperature for the desired aging time. Below is first listed experimental procedures, followed by results. Again, further details can be found in the paper.

**Sequenced creep tests** to characterize aging were performed to laminates with and without damage. Axial strain data using high temperature strain gages bonded to the front and back of the specimen was continuously recorded with the data acquisition software, LabVIEW. The strain gages were of the type WK-00-125AD-350 (Micro-Measurements). The aging times at which the creep compliance curves were recorded were, 0.375, 0.75, 1.5, 3, 6, 12, 24 and 48 hours. A constant load step was applied for 10% of the aging time so that only the momentary response was measured and the aging effects during the load portion are insignificant.

**Monotonic tension tests** were performed in both displacement control and load control. All strain controlled room temperature tests were performed on a computer controlled
Sintec 20/G screw-driven testing machine. Axial strain was measured using an extensometer with gage length of 1.0 in. The crosshead speed was adjusted to correspond to a strain rate of 0.4 %/min as measured by the extensometer. The applied strain rate on the specimen as calculated from the crosshead rate differs from the extensometer calculated strain rate by about 100% especially at high temperatures. High temperature tests were done on an Instron 8500 servo-hydraulic testing machine. The specimen is enclosed in a high temperature convection oven. The specimen was heated at the rate of 3°C per minute. The grips are water cooled and the load cell is thermally insulated and cooled using a fan to prevent the transducer from being influenced by temperature. High temperature long gage length strain gages of the type WK-00-375BG-350 (Micro-Measurements) were attached to the specimen.

To make quantitative evaluation of damage occurring inside the laminate, surface replication technique was used. The specimen edge was first polished using silicon carbide grinding paper with grit sizes of 400, 600 and P2400 (Buehler). Next, a thick replicating tape (11340, Ernest F. Fullam, Inc.) made of cellulose acetate was softened using a drop of acetone and pressed over the damaged laminate for over one minute. The test was stopped at the desired strain levels and replication done while the specimen was still in the testing machine. The tape is then observed under a microscope and the damage quantified by itemizing density of edge cracks.

X-ray radiography is another non-destructive technique that can detect damage within the laminate. Since surface replication gives only edge information of the laminate, the extent of transverse crack inside the laminate is not obtained. For the present material system, it was seen that transverse cracks initiate readily but they do not propagate as easily. Such information can be gathered using X-ray radiography. The process entails introducing a solution of Zinc Iodide into the laminate. As the solution is opaque to X-rays, the damaged areas in the laminate where the solution has penetrated are seen as dark regions on film. A cabinet type X-ray unit, Faxitron series 4855B (Hewlett Packard) was used. The applied voltage was 30 KVP and the exposure time was 30 seconds. The source to film (object) distance was maintained at 24 inches.

The first item investigated was the effect of microstructural damage on aging. Specimens were taken to strain levels of 0.4%, 0.6% and 0.8% and surface replication performed to determine the amount of damage at each strain level. Also, after each strain level, the specimen was rejuvenated and a standard sequence creep test was performed (it was noted that cracks did not heal due to the elevated temperatures in rejuvenation). It was observed that apart from a slight increase in initial compliance due to damage, there is no significant change in the shape of the creep curves. This implies that microstructural damage has no effect on the retardation times of the viscoelastic laminate for the aging times investigated. Also, the computed shift factors did not change measurably indicating that the aging behavior is not affected due to micromechanical damage in the laminate. These results show that the high stresses around the microcracks have an effect on the initial compliance of the structure but do not influence the global viscoelastic behavior.
To examine the impact of aging on damage accumulation, damage tests (monotonic tension tests) were performed on specimens with varying degrees of aging. The damage tests were performed first at room temperature and then at elevated temperature. The room temperature tests showed no significant trend with aging as illustrated by the x-ray radiography results in Figure 7. Since very long term aging was not possible in this research, no data is available on aging time on the order of a year. It is certainly possible that significantly longer aging times would result in a noticeable impact on microstructural damage progression, even for room temperature damage testing.

Figure 7: Specimens aged for time periods shown prior to room temperature damage tests. Xray shows microcracking in 90° plies.

The second set of tests involved aging and testing the laminates at the same elevated temperature. There is very little information available on the effects of temperature on microstructural damage and failure. This segment of the work led to surprising results. The specimens tested at room temperature demonstrated a typical failure pattern: significant transverse microcracking in the 90° plies, followed by final fracture of the specimen with a complete transverse crack in the 90° plies, scissoring of fibers in the 45° plies and ultimately fiber breakage. In contrast, the specimens tested at elevated temperature show almost no microcracking at the same strain levels, and a sudden catastrophic failure mode demonstrated in Figure 8. The gross shear failure occurs at a lower strain level than the failure for specimens at room temperature and a post-mortem analysis of the laminate (peeling back the outer 45° plies) shows that while some portion of the failure is a transverse crack in the 90° plies, a substantial fraction is fiber breakage in the 90°'s along a 45° shear direction.
Multiple specimens were tested at several elevated temperatures and varying aging times. The angle crack/catastrophic failure mode was repeatable and consistently observed for temperatures above 210°C, while failure similar to the room temperature failure occurred below this temperature. Aging did not impact the damage mode for the aging times used, nor did strain rate affect the results. The results in Figures 7 and 8 clearly show that while the toughness of the material for transverse crack formation increases with elevated temperature (hence no transverse cracking at .8% or 1% strain), the energy required for global failure is lower. This result has implications for modeling microcracking of viscoelastic laminates: as discussed in the previous section the value for $\sigma_{crit}$ will need to be determined quite differently as a function of temperature and for temperatures high enough the microcracking model is inappropriate as another failure mechanism is active.

The final tests performed were on cross-ply laminates, with x-ray radiography results in Figure 9. It is observed that at high temperature, the transverse cracks are few and partial whereas at room temperature they are relatively complete and the crack density was measured to be 0.65 cracks/mm using surface replication. This result indicates an increase in fracture energy for microcrack formation especially since the stress-strain curves at 225°C and room temperature were identical up to the 0.8% strain level. The final failure strain was 1.2% for both cases and the failure modes are also identical which essentially highlights the fact that the 0 plies are unaffected by temperature, unlike the 45° plies in the earlier tests. The longer aging time again was seen to have no significant impact on failure stress/strain or microstructural damage evolution.
The following conclusions are drawn:

- Increasing damage levels within the laminate did not change the viscoelastic response of the laminate. The aging shift rate was also unaffected by damage.
- Material aging had little impact on evolution of damage in the material for the aging times examined.
- Monotonic tests on \([\pm 45/90_3]_s\) laminates showed that the initial modulus of the laminate was not influenced by temperature, except for a small change at the highest temperature tested. However, nonlinear behavior commenced sooner at higher temperatures.
- For the \([\pm 45/90_3]_s\) laminates distributed damage within the laminate decreases with increasing temperature and above 210°C the laminate fails in shear. The shear failure is along the 45 plies and is accompanied by failure of the fibers within the 90 layer. No multiple cracks observed within the laminate at high temperatures.
- Strain to failure is similar for specimens at room and elevated temperatures at 1.5% and 1.2% respectively for the \([\pm 45/90_3]_s\) laminate.
- There is no effect of temperature on the failure mode of cross-ply laminates. The stress-strain curves at room temperature and 225°C are almost identical because the 0 plies are relatively unaffected by temperature.
- The fracture toughness for transverse cracks increases with increasing temperature for both laminates tested.
References