LONG TERM DURABILITY OF UNIDIRECTIONAL CFRP USING TOUGHENED MATRIX RESIN

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1 Introduction

The mechanical behavior of polymer resins exhibits time and temperature dependence, called viscoelastic behavior, not only above the glass-transition temperature $T_g$ but also below $T_g$. Thus, it can be presumed that the mechanical behavior of FRP using polymer resins as matrices also depends on time and temperature even below $T_g$ which is within the normal operating temperature range. Therefore, it is strongly expected that the accelerated testing methodology for the long-term life prediction of composite structures exposed under the actual environments of temperature and others is established.

In our previous papers, the time and temperature dependence of the static, creep and fatigue strengths for various directions of CFRP laminates with various combinations of fiber and matrix were measured. The master curves of these static, creep and fatigue strengths of CFRP laminates were constructed by using measured data based on the time-temperature superposition principle (TTSP) to be held for the viscoelastic behavior of matrix resin. As results, it was cleared experimentally that the long-term static, creep and fatigue strengths of CFRP laminates can be predicted by using the short-term strengths measured based on TTSP for the viscoelastic behavior of matrix resin. We have proposed a general and rigorous advanced accelerated testing methodology (ATM-2) which can be applied to the life prediction of CFRP exposed to an actual load and environment history based on the three conditions. One of these conditions is the fact that the time and temperature dependence on the strength of CFRP is controlled by the viscoelasticity of matrix resin [1]. The formulations of creep compliance and time-temperature shift factors of matrix resin are carried out based on the time-temperature superposition principle (TTSP). The formulations of long-term life of CFRP under an actual loading are carried out based on the three conditions.

In this paper, the tensile and compressive strengths in the longitudinal and transverse directions of unidirectional CFRP with toughend matrix resin are evaluated under various temperatures. The time and temperature dependence of these static strengths is discussed based on the TTSP which holds for the viscoelastic behavior of matrix resin.

2 ATM-2

ATM-2 is established with following three conditions: (A) the failure probability is independent of time, temperature and load history [2]; (B) the time and temperature dependence of strength of CFRP is controlled by the viscoelasticity of matrix resin. Therefore, the TTSP for the viscoelasticity of matrix resin holds for the strength of CFRP; (C) the strength degradation of CFRP holds the linear cumulative damage law as the cumulative damage under cyclic loading.

The long-term fatigue strength exposed to the actual loading where the temperature and load change with time can be shown by the following equation based on the conditions (A), (B) and (C).

$$\log \sigma_f (t', T_0, N_f, R, P_t)$$

$$= \log \sigma_0 (t' \theta_0, T_0) + \frac{1}{\alpha} \log [-\ln (1 - P_t)]$$

$$- n_f \log \left[ \frac{D^* (t', T_0)}{D (t' \theta_0, T_0)} \right]$$

$$- \left( \frac{1 - R}{2} \right) n_f \log (2N_f) + n_f^* \log (1 - k_D)$$

(1)
The first term of right part shows the reference strength (scale parameter for the static strength) at reduced reference time \( t_0' \) under the reference temperature \( T_0 \).
The second term shows the scatter of static strength as a function of failure probability \( P_i \) based on condition (A). \( \alpha \) is the shape parameter for the strength.
The third term shows the variation by the viscoelastic compliance of matrix resin which depend on temperature and load histories. \( n_t \) is the material parameter. The viscoelastic compliance \( D^* \) in (1) can be shown by the following equation:

\[
D^*(t', T_0) = \frac{\sigma(t', T_0)}{\sigma(t', T_0)} = \int_0^t D_c(t' - \tau, T_0) \frac{d\sigma(\tau)}{d\tau} d\tau'
\]

\( t' = \int_0^t \frac{d\tau}{\alpha_c(T(\tau))} \)  

where \( D_c \) shows the creep compliance of matrix resin and \( \sigma(\tau') \) shows the stress history. \( t' \) is the reduced time at \( T_0 \), \( \alpha_{f0} \) shows the time-temperature shift factor of matrix resin and \( T(\tau) \) shows the temperature history.
The fourth and fifth terms show the degradation by the cumulative damage under cyclic load. The \( N_i \) and \( R \) show the number of cycles to failure and the stress ratio at the final step, respectively. \( n_t \) and \( n'_t \) are the material parameters. The \( k_0 \) shows the accumulation index of damage defined as the following equation based on the condition (C).

\[
k_0 = \sum_{i=1}^* \frac{n_t}{N_i} < 1
\]

where \( n_t \) and \( N_i \) are the number of cycles and the number of cycles to failure at the loading of step \( i \), respectively.
The procedure for determining the materials parameters in the formulation is illustrated in Fig. 1. In this paper, we conduct the viscoelastic tests for matrix resin and the static tests for unidirectional CFRP. The master curves of static strengths can be shown by simplifying (1) as

\[
\log \sigma(t', T_0, N_i, R, P_i) = \log \sigma(t_0', T_0) + \frac{1}{\alpha} \log [-\ln(1 - P_i)]
\]

\[ n_t \log \left( \frac{D^*(t', T_0)}{D_c(t_0', T_0)} \right) \]

where the viscoelastic compliance \( D^* \) in (4) can be shown by the following equation.

\[
D^*(t', T_0) \approx D_c(t'/2, T_0)
\]

\[ \log \sigma(t_0', T_0, N_i, R, P_i) \]

\[ n_t \log \left( \frac{D^*(t', T_0)}{D_c(t_0', T_0)} \right) \]

3 Experimental procedures

Unidirectional CFRP laminate (T800S/EP) consists of carbon fiber T800 and epoxy resin. For T800S/EP(HT), the core-shell rubber particles (diameter 100nm, weight fraction 4%) are added to the matrix resin.
The dynamic viscoelastic tests for the transverse direction of unidirectional CFRP were carried out at various frequencies and temperatures to construct the master curve of creep compliance for matrix resin.
The static tests for typical four directions of unidirectional CFRP were carried out at various temperatures to construct the master curves of static strength for unidirectional CFRP. Longitudinal tension tests were carried out according with SACMA 4R-94. Longitudinal bending tests were carried out according with ISO 14125 to get the longitudinal compressive static strengths. Transverse bending tests were carried out according with ISO 14125 to get the transverse tensile static strengths. Transverse compression tests were carried out according with SACMA 1R-94. Test
specimen dimension were shown in Fig. 2. Test conditions were shown in Table 1.

(a) Longitudinal tension

(b) Longitudinal bending

(c) Transverse bending

(d) Transverse compression

Fig. 2 Test specimen dimension

Table 1 Test conditions

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Test temperature</th>
<th>Test speed</th>
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</thead>
<tbody>
<tr>
<td>Longitudinal tension</td>
<td>25, 50, 120, 180°C</td>
<td>1 mm/min</td>
</tr>
<tr>
<td>Longitudinal bending</td>
<td>190, 180°C</td>
<td>1 mm/min</td>
</tr>
<tr>
<td>Transverse bending</td>
<td></td>
<td>2 mm/min</td>
</tr>
<tr>
<td>Transverse compression</td>
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</table>

4 Results and discussion

4.1 Viscoelastic behaviour of matrix resin

The left side of Fig. 3(a) shows the loss tangent $\tan \delta$ for the transverse direction of unidirectional CFRP (T800S/EP) versus time $t$, where time $t$ is the inverse of frequency. The right side shows the master curve of $\tan \delta$ which is constructed by shifting $\tan \delta$ at various constant temperatures along the logarithmic scale of $t$ until they overlapped each other, for the reduced time $t'$ at $T_0=25°C$. Since $\tan \delta$ at various constant temperatures can be superimposed so that a smooth curve is constructed, the TTSP is applicable for $\tan \delta$ for the transverse direction of unidirectional CFRP. The master curve of $\tan \delta$ for T800S/EP(HT) can also be constructed as shown in Fig. 3(b).

The left side of Fig. 4(a) shows the storage modulus $E'$ for the transverse direction of unidirectional CFRP (T800S/EP) versus time $t$. The right side shows the master curve of $E'$ which is constructed by shifting $E'$ at various constant temperatures along the logarithmic scale of $t$ using the same shift amount for $\tan \delta$ and logarithmic scale of $E'$ until they overlapped each other, for the reduced time $t'$ at the reference temperature $T_0=25°C$. Since $E'$ at various constant temperatures can be superimposed so that a smooth curve is constructed, the TTSP is applicable for $E'$ for the transverse direction of unidirectional CFRP. The master curve of $E'$ for T800S/EP(HT) can also be constructed as shown in Fig. 4(b).

The time-temperature shift factor $a_{T_0}(T)$ which is the horizontal shift amount shown in Fig. 5(a) can be formulated by the following equation:

$$
\log a_{T_0}(T) = \frac{-\Delta H_1}{2.303G} \left( \frac{1}{T} - \frac{1}{T_0} \right) \text{He}(T_g - T)
+ \left[ \frac{-\Delta H_1}{2.303G} \left( \frac{1}{T_g} - \frac{1}{T_0} \right) + \frac{-\Delta H_2}{2.303G} \left( \frac{1}{T} - \frac{1}{T_g} \right) \right] \text{He}(T_g - T) + b_{T_0}(T)
$$

(6)

where $G$ is the gas constant, $8.314 \times 10^{-3}$ [kJ/(K•mol)], $\Delta H_1$ and $\Delta H_2$ are the activation energies below and above the glass transition temperature $T_g$, respectively. $H$ is the Heaviside step function.

The temperature shift factor $b_{T_0}(T)$ which is the amount of vertical shift shown in Fig. 5(b) can be fit with the following equation:
\[
\log b_g(T) = \left[ \sum_{i=1}^{5} b_{i}(T-T_0)^{-1} \right] H(T_0-T) \\
+ \left[ \sum_{i=1}^{5} b_{i}(T_0-T)^{-1} + \log \frac{T_0}{T} \right] \left[ 1 - H(T_0-T) \right]
\]  

(7)

where \( b_{0}, b_{1}, b_{2}, b_{3} \) and \( b_{4} \) are the fitting parameters.

The creep compliance \( D_c \) of matrix resin was back-calculated from the storage modulus \( E' \) for the transverse direction of unidirectional CFRP using [3]

\[
E(t) \equiv E'(\omega) \mid_{\omega \rightarrow \infty} \\
D_c(t) \sim 1/E(t)
\]

and approximate averaging method by Uemura [4].

The master curve of back-calculated \( D_c \) of matrix resin is shown in Fig.6. The master curve of \( D_c \) can be formulated by the following equation:

\[
\log D_c = \log D_{c,0}(t'_0, T_0) + \log \left[ \left( \frac{t}{t'_0} \right)^{m_g} + \left( \frac{t}{t'_r} \right)^{m_r} \right]
\]

(9)

where \( D_{c,0} \) is the creep compliance at reduced reference time \( t'_0 \) and reference temperature \( T_0 \), and \( t'_r \) is the glassy reduced time on \( t'_0 \), and \( m_g \) and \( m_r \) are the gradients in glassy and rubbery regions of \( D_c \) master curve. Parameters obtained from the formulations for \( a_{T_0}(T) \), \( b_{T_0}(T) \), and \( D_c \) are listed in Table 2.

The influence of rubber particles on the viscoelastic behavior of matrix resin can not be confirmed.

Fig.3 Master curves of loss tangent for transverse direction of unidirectional CFRP

Fig.4 Master curves of storage modulus for transverse direction of unidirectional CFRP
Table 2 Parameters for master curve and shift factors of creep compliance for matrix resin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EP</th>
<th>EP(HT)</th>
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<tr>
<td>$T_0[^\circ C]$</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$T_1[^\circ C]$</td>
<td>221</td>
<td>223</td>
</tr>
<tr>
<td>$D_{c,0}[1/GPa]$</td>
<td>0.282</td>
<td>0.278</td>
</tr>
<tr>
<td>$f_a[\text{min}]$</td>
<td>$8.53 \times 10^{12}$</td>
<td>$8.71 \times 10^{13}$</td>
</tr>
<tr>
<td>$m_9$</td>
<td>0.0218</td>
<td>0.0189</td>
</tr>
<tr>
<td>$m_9'$</td>
<td>0.391</td>
<td>0.309</td>
</tr>
<tr>
<td>$\Delta H_1 [\text{kJ/mol}]$</td>
<td>154</td>
<td>153</td>
</tr>
<tr>
<td>$\Delta H_2 [\text{kJ/mol}]$</td>
<td>585</td>
<td>638</td>
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<tr>
<td>$b_0$</td>
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<td>$1.35 \times 10^{-3}$</td>
</tr>
<tr>
<td>$b_1$</td>
<td>$-1.34 \times 10^{-3}$</td>
<td>$-6.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>$b_2$</td>
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<td>$1.89 \times 10^{-6}$</td>
</tr>
<tr>
<td>$b_3$</td>
<td>$-2.49 \times 10^{-7}$</td>
<td>$-1.44 \times 10^{-8}$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>$6.24 \times 10^{-10}$</td>
<td>$3.89 \times 10^{-11}$</td>
</tr>
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4.2 Master curves of static strengths for unidirectional CFRP

Figure 7 shows the relationship between the static strengths and temperature for longitudinal tension, longitudinal compression, transverse tension and transverse compression for T800S/EP and T800S/EP(HT) of unidirectional CFRP. Figure 8 shows the relationship between the static strength of unidirectional CFRP and the viscoelastic compliance of matrix resin. The slope of this relation corresponds to the parameter $n_r$ in Table 3. Figure 9 shows the master curves of unidirectional CFRP obtained from the strength data at various temperatures by using the time-temperature shift factors $a_{T0}$ shown in Fig. 5(a). The solid and dotted curves in these figures show the fitting curves by Eq.(4) using the master curves of creep compliance of matrix resin in Fig. 6. The parameters obtained by formulation are shown in Table 3. For longitudinal tension, the test data for $T=25[^\circ C]$, $80[^\circ C]$ and $120[^\circ C]$ are used for formulation. The influence of toughened matrix resin on the static strengths can be confirmed only for longitudinal tension at the region of high temperature.

Figure 10 shows the fracture appearances of tensile test specimen after longitudinal tensile test. The tensile fracture occurs in relatively lower
temperature, while the longitudinal large cracks occur in the high temperature. Figure 11 shows the SEM images of fracture surface of carbon fiber after the longitudinal tensile test. The cohesive fracture of matrix resin can be observed at the room temperature, while the surface of carbon fiber can be clearly observed at high temperature. It is considered that the fracture mechanism for longitudinal tension changes with temperature.

5 Conclusion
A general and rigorous advanced accelerated testing methodology (ATM-2) for the long-term life prediction of polymer composites exposed to an actual loading having general stress and temperature history has been proposed. The tensile and compressive static strengths in the longitudinal and transverse directions of unidirectional CFRP are evaluated using ATM-2. The applicability of ATM-2 can be confirmed for these static strengths. The time and temperature dependence of static strength in four directions of unidirectional CFRP are uniquely determined by the viscoelastic behavior of matrix resin. The influence of toughened matrix resin on the static strengths for the longitudinal tension can be confirmed.

References

Fig.7 Static strength of unidirectional CFRP versus temperature
Fig. 8 Static strength of unidirectional CFRP versus viscoelastic compliance $D^*$ of matrix resin

Fig. 9 Master curve of static strength for unidirectional CFRP
Table 3 Parameters for master curve of static strength of unidirectional CFRP

<table>
<thead>
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<th>LT</th>
<th>LB</th>
<th>LB</th>
<th>TC</th>
</tr>
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<tr>
<td>T800S/EP</td>
<td>3161</td>
<td>2695</td>
<td>109</td>
<td>204</td>
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<tr>
<td></td>
<td>15.3</td>
<td>20.0</td>
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<td>10.2</td>
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<tr>
<td></td>
<td>0.50</td>
<td>1.43</td>
<td>1.30</td>
<td>1.57</td>
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<tr>
<td>T800S/EP(HT)</td>
<td>3272</td>
<td>2433</td>
<td>116</td>
<td>194</td>
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<tr>
<td></td>
<td>11.5</td>
<td>21.6</td>
<td>14.8</td>
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<tr>
<td></td>
<td>0.71</td>
<td>1.50</td>
<td>2.14</td>
<td>2.05</td>
</tr>
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</table>

Fig. 10 Fracture appearances after the test of longitudinal tension

Fig. 11 SEM image of fracture surface of carbon fiber after the longitudinal tension test