Time and Temperature Dependence on Flexural Strength of Heat-resistant CFRP Laminates*

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The flexural fracture behavior of four kinds of CFRP laminates with the combination of heat-resistant thermosetting resin and PAN-based carbon fiber were investigated by three-point bending tests over a wide range of temperature and deflection rate. The flexural fracture behavior by the fractographs as well as the flexural strength strongly depend on the testing rate and temperature. The master curves for these strengths can be produced based on the time-temperature superposition principle. The time-temperature shift factor for the flexural strength of each laminate is quantitatively in good agreement with that for the stress-strain relation of the corresponding matrix resin. Therefore, it is cleared that the time and temperature dependence of flexural fracture behavior of heat-resistant CFRP laminates are mainly controlled by the viscoelastic behavior of matrix resin.

Key Words: CFRP, Heat-resistant Thermosetting Resin, Bending Test, Time-temperature Dependence

1. Introduction

As structural materials, fiber reinforced plastic (FRP) has excellent advantages that have light weight, high strength and high stiffness. The various mechanical properties are realizable with the combination of fiber and matrix resin. Therefore, it is used in the high reliable structure including aircraft, spacecraft, ships, trains, buildings, etc.

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 polymer composites also depends significantly on time and temperature even below $T_g$ which is within the normal operating temperature range.

In our previous papers the time-temperature dependence of the flexural strengths under constant strain-rate (CSR) for various kinds of FRP has been studied. The master curves of these strengths were obtained based on the time-temperature superposition principle\(^{(1)-(4)}\).

In this paper, the time-temperature dependent flexural CSR strength of four kinds of CFRP laminates with the combination of heat-resistant thermosetting resin and PAN-based carbon fiber were investigated by three-point bending tests over wide ranges of temperature and deflection rate. The time-temperature dependence of flexural CSR strength for these CFRP laminates was discussed based on the time-temperature superposition principle.

2. Experimental Procedure

The curing and testing condition of four types of CFRP laminates, A, B, C and D, are shown in Table 1.
Table 1  Curing and testing conditions of four types of CFRP laminates

<table>
<thead>
<tr>
<th>Fiber/Resin</th>
<th>Cure condition</th>
<th>t (mm)</th>
<th>b (mm)</th>
<th>l (mm)</th>
<th>s (mm)</th>
<th>Weaving</th>
<th>V (mm/min)</th>
<th>Test temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>G40-800/5260</td>
<td>190°C×120min + 215°C×240min</td>
<td>2</td>
<td>15</td>
<td>100</td>
<td>80</td>
<td>[45/0/90/−45]</td>
<td>0.02, 2, 200</td>
</tr>
<tr>
<td>B</td>
<td>IM600/PIXAM</td>
<td>360°C×10min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>MR600/PEFI-5</td>
<td>250°C×120min + 285°C×40min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[45/0/90/−45]</td>
<td>0.02, 2, 200</td>
</tr>
<tr>
<td>D</td>
<td>T400/3601</td>
<td>190°C×90min + 230°C×120min</td>
<td>2.7</td>
<td>15</td>
<td>82</td>
<td>60</td>
<td>satin woven fabric</td>
<td>0.2, 2, 200</td>
</tr>
</tbody>
</table>

t: Thickness  b: Width  l: Length  s: Span  V: Deflection

Fig. 1  Master curves of flexural CSR strengths for four types of CFRP laminates

Fig. 2  Flexural CSR strengths at T=230°C for various curing conditions

3. Results and Discussion

The each left side of Fig. 1 shows the flexural CSR strength $\sigma_f$ versus time to failure $t_f$ at various temperatures $T$ where $t_f$ is the time period from initial loading to maximum load during testing. The master curves of $\sigma_f$ were constructed by shifting at various constant temperatures along the log scale of $t_f$ so that they overlap on $\sigma_f$ at the reference temperature $T_0$ or on each other to form a single smooth curve as shown in the right side of each graph. The smooth master curves of $\sigma_f$ for types B, C and D can be obtained and the time-temperature superposition principle holds for these strengths. The smooth master curve of $\sigma_f$ for type A can be also obtained if the data at deflection rate $V=0.02$ mm/min over $T=150°C$ are ignored. It can be presumed that the reason why the data at $V=2$ mm/min over $T=150°C$ vary from the solid master curve is to be insufficient cure during molding process. Therefore, the additional curing at 230°C for 8 hours was given to the specimen of type A and then the flexural CSR strength at $V=2$ mm/min and $T=230°C$ was measured. Figure 2 shows the comparison of the flexural CSR strengths at $T=230°C$ for various curing condition. The strengths at $V=2$ mm/min clearly increase due to additional curing and slightly exceed the strength at $V=0.02$ mm/min in which the specimen is cured sufficiently during loading time in testing chamber. Therefore, it is clear that the master curve for type A moves from the solid curve to the dotted curve due to sufficient curing.
Time-temperature shift factor $\alpha_T(T)$ is defined by

$$\alpha_T(T) = \frac{t_f}{t'_0}$$

where $t'_0$ is the reduced time to failure.

The $\alpha_T(T)$ obtained experimentally are shown in Fig. 3. These $\alpha_T(T)$ agree with those for the storage modulus of the matrix resin for CFRP laminates indicated by dotted lines, which are given by two Arrhenius' equations with different activation energies $\Delta H$,

$$\log \alpha_T(T) = \frac{\Delta H}{2.303G} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

where $G$ is gas constant $8.314 \times 10^{-3}[\text{kJ/(K} \cdot \text{mol})]$. The activation energies for four types of matrix resin are widely different from each other.

Figure 4 shows the flexural CSR strength normalized to $T_b=150^\circ C$ against temperature at $V=2$ mm/min. Figure 5 shows the flexural CSR strength normalized to $T_b=150^\circ C$ and $t_{90}=1$ min against reduced time to failure. These figures can be constructed based on the time-temperature superposition principle. It is clear from these figures that the flexural CSR strength for all CFRP laminates at $T=$

![Fig. 4 Normalized flexural CSR strength at $V=2$ mm/min versus temperature for four types of CFRP laminates](image)

![Fig. 5 Normalized flexural CSR strength versus reduced time to failure for four types of CFRP laminates](image)
200°C keeps over 80% of those at $T=150^\circ$C (Fig. 4). Furthermore, these strengths at $T=150^\circ$C decrease remarkably with increasing of time to failure and decrease to 20–50% of those at $t_{w}=1$ min after 20 years (Fig. 5). Therefore, the time-temperature superposition principle is useful to evaluate the long-term strength for materials design.

4. Conclusion

The time-temperature dependent flexural CSR strengths for four kinds of CFRP laminates using heat resistant thermosetting resin were studied experimentally.

1. The smooth master curves of flexural CSR strength for four kinds of CFRP laminates can be obtained and the time-temperature superposition principle holds for these strengths.

2. Each time-temperature shift factor agrees well with that of the storage modulus of corresponding matrix resin.

3. The time-temperature superposition principle is useful to evaluate the long-term strength for materials design.

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References


