Modified Time-temperature Superposition Principle for Viscoelasticity of Thermosetting Resins

by

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October 18, 2010

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Background

The most important hypothesis used in our accelerated testing for the prediction of long-term life of CFRP is the time-temperature superposition principle (TTSP).

The time-temperature shift factor for the viscoelasticity of matrix resin, that is the accelerating rate, should be determined accurately based on TTSP.

The modified time-temperature superposition was proposed, in which the master curves of viscoelastic models are constructed by shifting vertically as well as horizontally viscoelastic modulus at various temperatures.

Objectives

The reliability of time-temperature shift factor determined for the creep compliance of the thermosetting resin by applying the modified TTSP is experimentally confirmed.

The applicability of simplified method using the dynamic mechanical analysis (DMA) test to get the reliable time-temperature shift factor is discussed and confirmed experimentally.

The formulation of master curve of creep compliance for matrix resin is introduced, and automatic determination of formulation parameters is introduced.
The master curve is constructed by shifting vertically as well as horizontally the creep compliances measured at various temperatures $T$ to superimpose smoothly to that at the reference temperature $T_0$. 
Adjust $a$ and $b$, the data plots at $T_2$ moves horizontally and vertically until a smoothest curve is got with the data plots at $T_1$. The maximal 6th order polynomial is used to fit the master curve.
Auto shifting method for creep compliance master curve

Time-temperature and temperature shift factors:

\[
\log a(T) = \frac{\Delta H_1}{2.303G} \left( \frac{1}{T} - \frac{1}{T_0} \right) H(T_g - T)
\]

\[
+ \left[ \frac{\Delta H_2}{2.303G} \left( \frac{1}{T_g} - \frac{1}{T_0} \right) + \frac{\Delta H_3}{2.303G} \left( \frac{1}{T} - \frac{1}{T_g} \right) \right] \left( 1 - H(T_g - T) \right)
\]

\[
\log b(T) = \left[ b_4 (T - T_0)^4 + b_3 (T - T_0)^3 + b_2 (T - T_0)^2 + b_1 (T - T_0) + b_0 \right] H(T_g - T)
\]

\[
+ \left[ b_4 (T_g - T_0)^4 + b_3 (T_g - T_0)^3 + b_2 (T_g - T_0)^2 + b_1 (T_g - T_0) + b_0 + \log \frac{T_g}{T} \right] \left( 1 - H(T_g - T) \right)
\]

Parameter determination:

\(T_g\) is determined by TMA test, \(\Delta H_1, \Delta H_2, b_{i(i=0,4)}\) are determined by auto shifting method.

\(G\): gas constant \(\Delta H\): activation energy \(T_g\): glass transition temp.
Composition and curing condition of creep specimen

Composition and curing condition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy : DGEBA (EPIKOTE 828, YUKA SHELL EPOXY)</td>
<td>100</td>
</tr>
<tr>
<td>Hardener : MNA (Methyl himic anhidride, Hitachi Chemical)</td>
<td>103.6</td>
</tr>
<tr>
<td>Cure accelerator : 2-Ethyl-4-methylimidazole (SHIKOKU CHEMIKALS)</td>
<td>1</td>
</tr>
</tbody>
</table>

Cure schedule

70°C × 12h+150°C × 4h+190°C × 2h+ (-0.5°C/min)

<table>
<thead>
<tr>
<th>Test type</th>
<th>Test period t</th>
<th>Temperature T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short term</td>
<td>10s.-3hr</td>
<td>50,60,70,80,90,100,110</td>
</tr>
<tr>
<td>Medium term</td>
<td>10s.-24hr</td>
<td>50,60,70,80,90,100,110</td>
</tr>
<tr>
<td>Long term</td>
<td>10s.-1000hr</td>
<td>50,80,100</td>
</tr>
</tbody>
</table>
Creep compliances measured in the long term

The smooth master curve is obtained by vertical and horizontal shifting.
Creep compliances measured in the medium term and short term

Medium term

Short term

The master curves coincide with the creep compliance measured in the long term at $T=50^\circ C$ by vertical and horizontal shifting.
Comparison of shift amount obtained from master curves by both methods

Same horizontal shift amounts and vertical shift amounts can be obtained by vertical and horizontal shifting regardless of test period.
Measurement of creep compliance of epoxy resin using DMA test

Comparison of test periods

If same time-temperature shift factor can be obtained by the creep test as DMA test, the long-term creep compliance can be predicted by DMA test.
Same horizontal shift amounts and vertical shift amounts can be obtained by vertical and horizontal shifting regardless of test period and test methods.
The master curves of compliance obtained from the creep test and DMA test agree well with each other.
Measuring of the storage modulus for the transverse direction of unidirectional CFRP (MR60H/1053)

Time-temperature and temperature shift factors:

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

\[
\log b_{T_0}(T) = \left[ b_4 (T - T_0)^4 + b_3 (T - T_0)^3 + b_2 (T - T_0)^2 + b_1 (T - T_0) + b_0 \right] \Delta H(T_g - T) \\
\quad + \left[ b_4 (T_g - T_0)^4 + b_3 (T_g - T_0)^3 + b_2 (T_g - T_0)^2 + b_1 (T_g - T_0) + b_0 + \log \frac{T_0}{T} \right] (1 - \Delta H(T_g - T))
\]

*G*: gas constant  \(\Delta H\): activation energy  \(T_g\): glass transition temp.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_0)</td>
<td>25 [°C]</td>
</tr>
<tr>
<td>(T_g)</td>
<td>162 [°C]</td>
</tr>
<tr>
<td>(\Delta H_1)</td>
<td>101 [kJ/mol]</td>
</tr>
<tr>
<td>(\Delta H_2)</td>
<td>760 [kJ/mol]</td>
</tr>
<tr>
<td>(b_0)</td>
<td>1.13E-02 [-]</td>
</tr>
<tr>
<td>(b_1)</td>
<td>-9.85E-04 [-]</td>
</tr>
<tr>
<td>(b_2)</td>
<td>2.43E-05 [-]</td>
</tr>
<tr>
<td>(b_3)</td>
<td>-2.23E-07 [-]</td>
</tr>
<tr>
<td>(b_4)</td>
<td>6.98E-10 [-]</td>
</tr>
</tbody>
</table>
Formulation of creep compliance

\[ \log D_c = \log D_c \left( t'_o, T_o \right) + \log \left[ \left( \frac{t'}{t'_o} \right)^{m_g} + \left( \frac{t'}{t'_{tg}} \right)^{m_r} \right] \]

where

- \( D_c \): creep compliance
- \( T_o \): reference temperature
- \( t' \): reduced time at \( T_o \)
- \( t'_o \): reference reduced time at \( T_o \)
- \( t'_{tg} \): glassy reduced time at \( T_o \)

Rule of mixture

Creep compliance of matrix resin:

\[ D_c(t') = \frac{1}{E_m(t')} \]

Back-calculation of \( E_m \)

\[ \frac{1}{E_m} = \frac{1}{V_y} \left[ \frac{1}{E_T} + \frac{1}{E_{ff}} - \frac{1}{V_y} \frac{V_m}{V_f} \right], \quad V_y = 0.516 \frac{V_m}{V_f} \]

- \( E_m \): storage modulus of matrix rein
- \( V_f, V_m \): volume fractions of fiber and matrix
- \( E_T, E_{ff} \): storage moduli in the transverse direction of CFRP and carbon fiber

| \( D_c(t'_o, T_o) \) | 0.347 | [1/GPa] |
| \( t'_o \) | 1 | [min] |
| \( t'_{tg} \) | \( 4.23 \times 10^{10} \) | [min] |
| \( m_g \) | 0.0116 | [-] |
| \( m_r \) | 0.2876 | [-] |
The reliability of time-temperature shift factor determined for the creep compliance of the thermosetting resin by applying the modified TTSP was experimentally confirmed.

The applicability of simplified method using the dynamic mechanical analysis (DMA) test to get the reliable time-temperature shift factor was confirmed experimentally.

The autoshift method is applicable to get smooth master curve of creep compliance and reliable time-temperature dependent shift factor master curve.

The master curve of creep compliance for matrix resin was formulated, and formulation parameters were determined automatically.

Thank you for your attention!