INFLUENCE OF MATRIX RESIN ON TIME-TEMPERATURE DEPENDENT STRENGTH OF UNIDIRECTIONAL CFRP

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Keywords: Unidirectional CFRP, Durability, Time-temperature dependent strength

Abstract
The tensile and compressive strengths in the longitudinal and transverse directions of three types of unidirectional CFRP which consist of same carbon fiber and different types of matrix resin are evaluated under various temperatures. The time and temperature dependence of these static strengths is discussed based on the time-temperature superposition principle which holds for the viscoelastic behavior of matrix resin. As results, the time and temperature dependence of static strength in four directions of unidirectional CFRP are uniquely determined by the viscoelastic behavior of matrix resin.

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 CFRP 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 CFRP structures exposed under the actual environments of temperature and others is established.

In our previous paper [1], 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 accelerated testing methodology (ATM) 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 viscoelastic compliance of matrix resin. The formulations of creep compliance and time-temperature shift factors of matrix resin are carried out based on 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 three types of unidirectional CFRP which consist of same carbon fiber and deferent types of 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. Accelerated testing methodology (ATM)

ATM 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).

$$\log\sigma_{\mathrm{f}}(t',T_0,N_{\mathrm{f}},R,P_{\mathrm{f}}) = \log\sigma_{\mathrm{f0}}(t_0',T_0) + \frac{1}{\alpha}\log\left[-\ln(1-P_{\mathrm{f}})\right] - n_{\mathrm{r}}\log\left[\frac{D^*(t',T_0)}{D_{\mathrm{c}}(t_0',T_0)}\right] \\ - \frac{(1-R)}{2}n_{\mathrm{f}}\log(2N_{\mathrm{f}}) + n_{\mathrm{f}}^*\log(1-k_{\mathrm{D}}) \tag{1}$$

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 the function of failure probability P_{f} based on condition (A). α is the shape parameter for the strength. The third term shows the variation by the viscoelastic compliance of matrix resin which depends on temperature and load histories. n_{r} is the material parameter. The viscoelastic compliance D^* in (1) can be shown by the following equation:

$$D^*(t',T_0) = \frac{\varepsilon(t',T_0)}{\sigma(t',T_0)} = \frac{\int_0^{t'} D_{\mathrm{c}}(t'-\tau',T_0)\frac{d\sigma(\tau')}{d\tau'}d\tau'}{\sigma(t',T_0)}, \quad t' = \int_0^t \frac{d\tau}{a_{T_0}(T(\tau))}, \tag{2}$$

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, a_{T0} 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. N_{f} and R show the number of cycles to failure and the stress ratio at the final step, respectively. n_{f} and n_{f}^* are the material parameters. k_{D} shows the accumulation index of damage defined as the following equation based on the condition (C).

$$k_{\mathrm{D}} = \sum_{i=1}^{n}\frac{n_i}{N_{\mathrm{f}i}} < 1 \tag{3}$$

where n_i and N_{fi} 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

$$\log \sigma_{\mathrm{f}}(t',T_0,N_{\mathrm{f}},R,P_{\mathrm{f}}) = \log \sigma_{\mathrm{f0}}(t_0',T_0) + \frac{1}{\alpha}\log[-\ln(1-P_{\mathrm{f}})] - n_{\mathrm{r}} \log\left[\frac{D^*(t',T_0)}{D_{\mathrm{c}}(t_0',T_0)}\right] \tag{4}$$

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

$$D^*(t',T_0) = D_{\mathrm{c}}(t'/2,T_0) \tag{5}$$

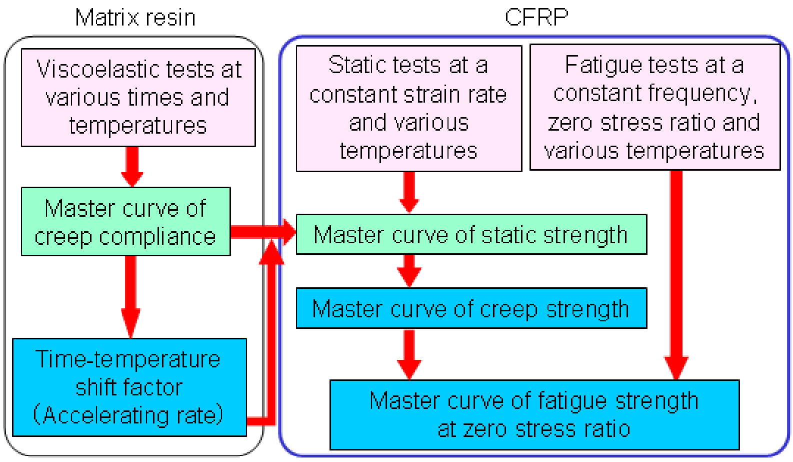


Figure 1. Procedure of accelerated testing

3. Experimental procedures

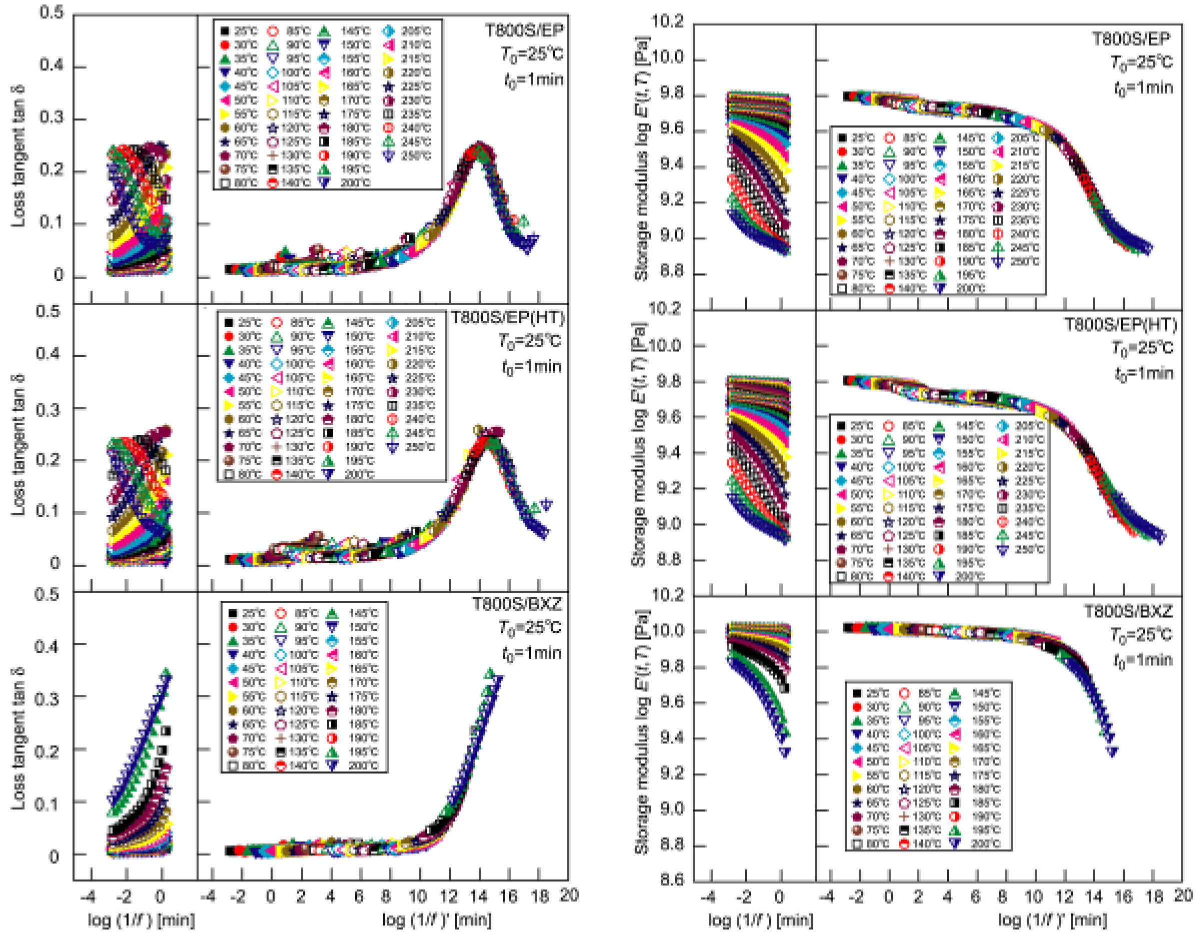
Three types of unidirectional CFRP which consist of same carbon fiber and deferent types of matrix resin are employed. T800S/EP consists of carbon fiber T800S and conventional epoxy resin. For T800S/EP (HT), core-shell rubber particles (diameter 100nm, weight fraction 4%) are added to the matrix epoxy resin. T800S/BXZ consists of carbon fiber T800S and flame resistant benzoxazine 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 temperatures, 25°C, 80°C, 120°C, 150°C (180°C) to construct the master curves of static strength for unidirectional CFRP. Longitudinal tension tests were carried out according to SACMA 4R-94. Longitudinal bending tests were carried out according to ISO 14125 to get the longitudinal compressive static strengths. Transverse bending tests were carried out according to ISO 14125 to get the transverse tensile static strengths. Transverse compression tests were carried out according to SACMA 1R-94.

4. Results and discussion

4.1. Viscoelastic behaviour of matrix resin

The left side of Fig.2(a) shows the loss tangent tan δ for the transverse direction of unidirectional CFRP versus time *t*, where time *t* is the inverse of frequency. The right side shows the master curve of tan δ which is constructed by shifting tan δ 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 δ at various constant temperatures can be superimposed so that a smooth curve is constructed, the TTSP is applicable for tan δ for the transverse direction of unidirectional CFRP.

The left side of Fig.2(b) shows the storage modulus *E'* for the transverse direction of unidirectional CFRP 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 δ 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 also applicable for *E'* for the transverse direction of unidirectional CFRP.



(a) Loss tangent tan δ

(b) Storage modulus *E*'

Figure 2. Master curves of loss tangent and storage modulus for transverse direction of unidirectional CFRP

The time-temperature shift factor $a_{T0}(T)$ which is the horizontal shift amount shown in Fig.3(a) can be formulated by the following equation:

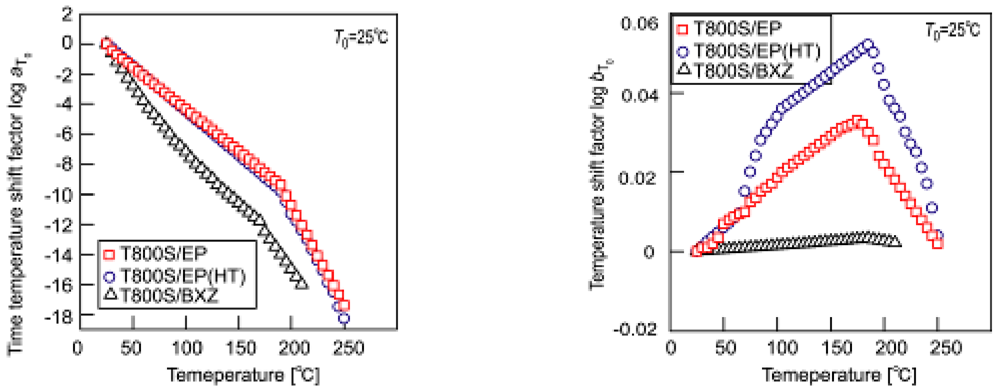
$$\log a_{T_0}(T) = \frac{\Delta H_1}{2.303G}\left(\frac{1}{T}-\frac{1}{T_0}\right)H(T_g - T) + \left[\frac{\Delta H_1}{2.303G}\left(\frac{1}{T_g}-\frac{1}{T_0}\right) + \frac{\Delta H_2}{2.303G}\left(\frac{1}{T}-\frac{1}{T_g}\right)\right](1 - H(T_g - T)) \quad (6)$$

where G is the gas constant, 8.314×10^{-3} [kJ/(K•mol)], ΔH_1 and ΔH_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 $b_{T0}(T)$ which is the amount of vertical shift shown in Fig.3(b) can be fit with the following equation:

$$\log b_{T_0}(T) = \log b_{T_0}(T) = [\sum_{i=0}^{n} b_i (T - T_0)^i]H(T_g - T) + [\sum_{i=0}^{n} b_i (T_g - T)^i + \log\frac{T_g}{T}](1 - H(T_g - T)) \quad (7)$$

where b_i is the fitting parameters.



(a)Time-temperature shift factor (b)Temperature shift factor

Figure 3. Shift factors of storage modulus for transverse direction of unidirectional CFRP

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]

$$D_c(t) \sim 1/E(t), \qquad E(t) \cong E'(\omega)|_{\omega\to 2/\pi t} \quad (8)$$

and approximate averaging method by Uemura [4].

The master curve of back-calculated D_c of matrix resin is shown in Fig.4. The master curve of D_c can be formulated by the following equation:

$$\log D_c = \log D_{c,0}(t'_0, T_0) + \log\left[\left(\frac{t'}{t'_0}\right)^{m_g} + \left(\frac{t'}{t'_g}\right)^{m_r}\right] \quad (9)$$

where $D_{c,0}$ is the creep compliance at reduced reference time t'_0 and reference temperature T_0, and t'_g 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 $a_{T0}(T)$, $b_{T0}(T)$, and D_c are listed in Table 1.

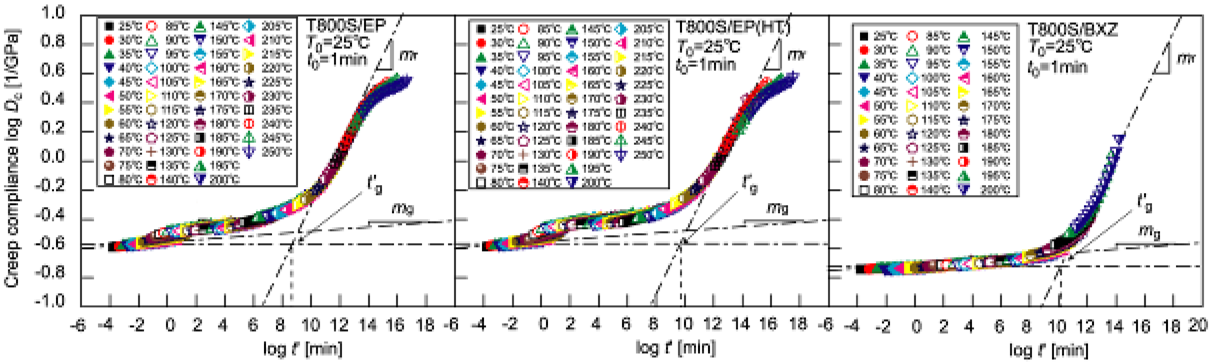


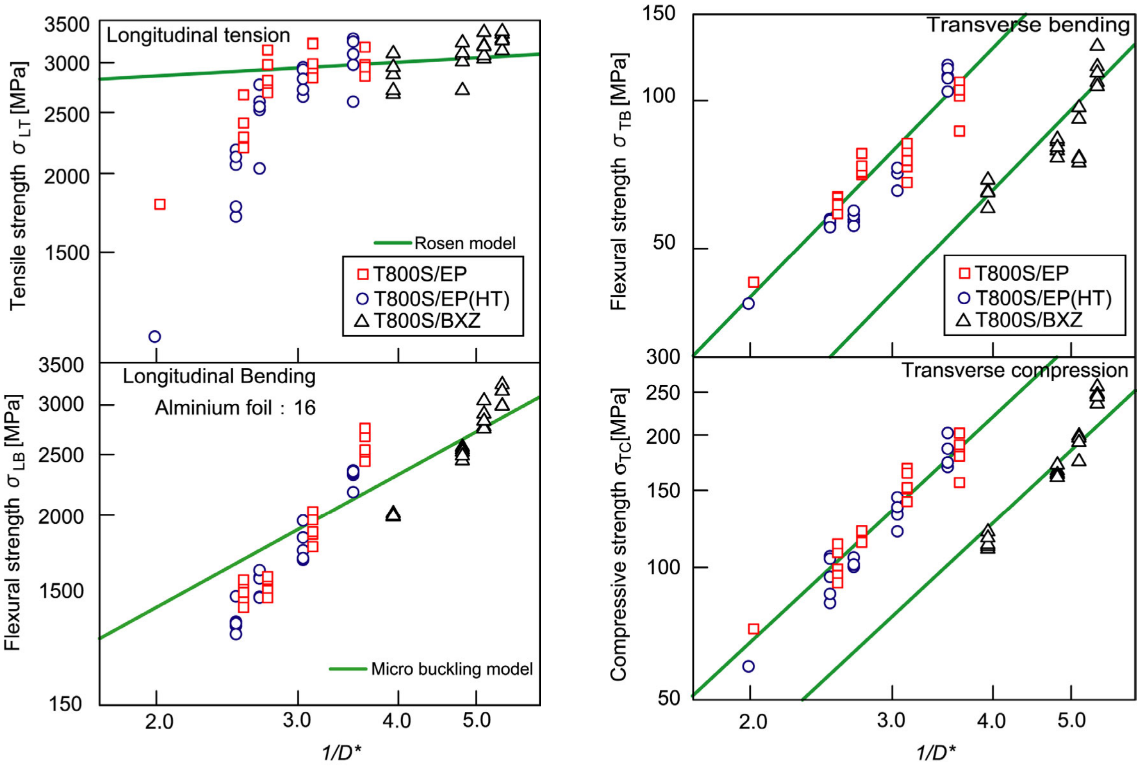
Figure 4. Master curves of creep compliance for matrix resin calculated from the storage modulus for the transverse direction of unidirectional CFRP

4.2. Master curves of static strengths for unidirectional CFRP

Figure 5 shows the relationship between the static strengths of unidirectional CFRP measured at various temperatures and the inverse of viscoelastic compliance D^* of matrix resin at the same conditions of time and temperature. Time and temperature dependence for these static strengths is uniquely determined by D^* for matrix resin, because each of the relationships between the static strength for unidirectional CFRP and D^* for matrix resin makes a straight line.

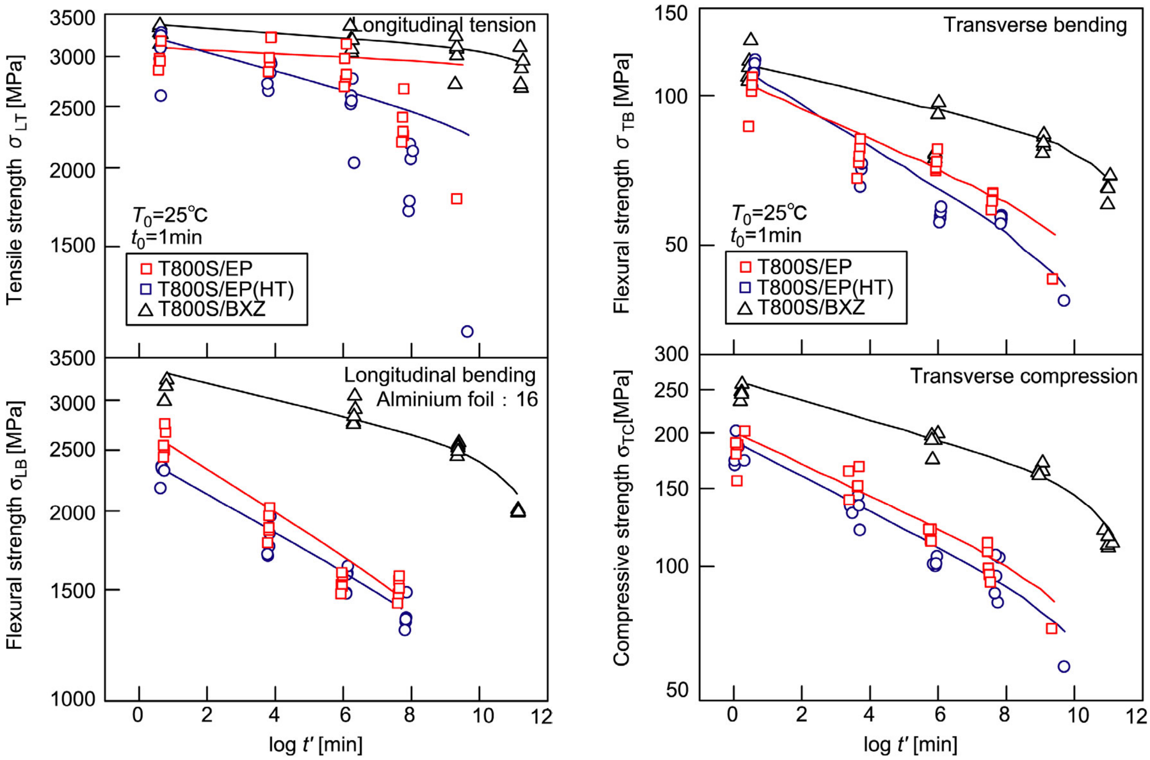
The relation between tensile static strength in the longitudinal direction of unidirectional CFRP and viscoelastic compliance of matrix resin can be shown by the straight line with the slope of $1/(2m)$ where m is Weibull shape parameter of tensile strength of carbon fiber [5]. In the upper side of Fig.5(a), the straight line with slope of 1/16 (m=8.0 for T800S carbon fiber) captures the test data approximately except the data at high temperatures. The flexural fracture in the longitudinal direction of unidirectional CFRP is the microbuckling of carbon fibers in the compression side of specimen. In this case, the relation between flexural static strength in the longitudinal direction of unidirectional CFRP and viscoelastic compliance of matrix resin can be shown by the straight line with the slope of 1/2 [5]. In the lower side of Fig.5(a), the straight line with slope of 1/2 captures the test data adequately. The flexural fracture and compressive fracture in the transverse direction of unidirectional CFRP are triggered by the fracture of matrix resin. Figure 5(b) shows the flexural static strength and compressive static strength in the transverse direction of unidirectional CFRP versus viscoelastic compliance of matrix resin. The straight line with slope of 1/1 captures the test data adequately for unidirectional CFRP with epoxy resin and benzoxazine resin, respectively. It can be considered from these facts that the time and temperature dependence of these static strengths of unidirectional CFRP is controlled by the viscoelastic behavior of matrix resin.

Figure 6 show the master curves of unidirectional CFRP obtained from Eq.(4) using time-temperature shift factors a_{T0} shown in Fig.3(a) and master curve of creep compliance of matrix resin in Fig.4. The master curves of these static strengths captures the test data, therefore, the applicability of ATM can be confirmed. The parameters obtained by formulation are shown in Table 1. For longitudinal tension, the test data for T=25 °C, 80 °C and 120 °C are used for formulation.



(a) Longitudinal direction (b) Transverse direction

Figure 5. Static strength of unidirectional CFRP versus viscoelastic compliance D^* of matrix resin



(a) Longitudinal direction (b) Transverse direction

Figure 6. Master curve of static strength for unidirectional CFRP

Table 1. Parameters for shift factors and creep compliance of matrix resin and static strength of unidirectional CFRP (LT: longitudinal tension, LB: longitudinal bending, TB: transverse bending, TC: transverse compression)

	EP	EP(HT)	BXZ
T_0[°C]	25	25	25
T_g[°C]	221	223	206
$D_{c,0}$[1/GPa]	0.299	0.310	0.185
t'_g[min]	9.83×10^{11}	2.93×10^{12}	4.71×10^{12}
m_g	0.0241	0.0227	0.0119
m_r	0.372	0.356	0.434
ΔH_1	147	156	205
ΔH_2	619	640	414
b_0	-9.45×10^{-3}	2.09×10^{-2}	-4.53×10^{-4}
b_1	4.01×10^{-4}	-1.51×10^{-3}	1.69×10^{-5}
b_2	-2.89×10^{-6}	3.49×10^{-5}	6.95×10^{-8}
b_3	2.38×10^{-8}	-2.39×10^{-7}	-6.09×10^{-10}
b_4	-7.28×10^{-11}	5.40×10^{-10}	1.83×10^{-12}

		LT	LB	TB	TC
T800S/EP	n_r	0.11	1.43	1.26	1.52
	$\sigma_{0,s}$ [MPa]	3047	2647	107	192
	$\sigma_{0,r}$ [MPa]	3102	2669	106	197
	$\alpha_{0,s}$	20.8	17.3	8.9	8.9
	$\alpha_{0,r}$	18.7	16.4	12.5	12.2
T800S/EP(HT)	n_r	0.65	1.35	1.84	1.76
	$\sigma_{0,s}$ [MPa]	3178	2350	115	188
	$\sigma_{0,r}$ [MPa]	3229	3400	113	187
	$\alpha_{0,s}$	9.20	23.8	18.5	10.7
	$\alpha_{0,r}$	11.9	22.0	11.7	11.9
T800S/BXZ	n_r	0.33	1.11	1.37	1.91
	$\sigma_{0,s}$ [MPa]	3314	3163	120	250
	$\sigma_{0,r}$ [MPa]	3379	3364	116	259
	$\alpha_{0,s}$	32.5	23.4	11.2	27.2
	$\alpha_{0,r}$	22.9	20.7	12.0	19.4

5. Conclusion

The tensile and compressive strengths in the longitudinal and transverse directions of three types of unidirectional CFRP which consist of same carbon fiber and different types of matrix resin are evaluated under various temperatures using accelerated testing methodology (ATM). The applicability of ATM 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.

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