TIME AND TEMPERATURE DEPENDENCE OF TENSILE STRENGTH OF UNIDIRECTIONAL CFRP

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Abstract
The tensile static strength of various unidirectional CFRP are evaluated under various loading rates and temperatures. Unidirectional CFRPs are four types of resin impregnated carbon fiber strand, which consist of four types of carbon fibers and same epoxy resin. Four types of carbon fibers are high strength PAN based carbon fiber, low modulus pitch based carbon fibers, high modulus PAN based and pitch based carbon fibers. As results, it was cleared that the tensile static strength of unidirectional CFRP using high strength PAN based and low modulus pitch based carbon fibers remarkably depends on time and temperature, while that using high modulus PAN based and pitch based carbon fibers scarcely depends on time and temperature.

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 (ATM) for the long-term life prediction of composite structures exposed under the actual environments of temperature and others is established.
In our previous papers [1-3], the time and temperature dependence of 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.
In this paper, the tensile static strength of various unidirectional CFRP are evaluated under various loading rates and temperatures. Unidirectional CFRPs are four types of resin impregnated carbon fiber strand (CFRP strand), which consist of four types of carbon fibers and same epoxy resin. Four types of carbon fibers are high strength PAN based carbon fibers, low modulus pitch based carbon fibers, high modulus PAN based and pitch based carbon

fibers. The time and temperature dependence of tensile strengths of these unidirectional CFRP are discussed based on the viscoelastic behavior of matrix resin.

2 Experiments

2.1 Test materials

Four types of CFRP strand were employed as the tensile test specimen along the longitudinal direction of unidirectional CFRP. These four CFRP strands were produced by filament winding method using four types carbon fibers; PAN based high strength carbon fiber T300 (TORAY) and PAN based high modulus carbon fiber HR40 (MITSUBISHI RAYON), pitch based low modulus carbon fibers XN05, pitch based high modulus carbon fibers XN50 (NIPPON GRAPHITE FIBER) with same epoxy resin EPIKOTE®828 (YUKA SHELL EPOXY). The composition of epoxy (EP) resin and cure condition for the CFRP strand are shown in Table 1.

	Composition	Weight ratio
Epoxy	Epikote828	100
Hardener	Methyl himic anhidride	103.6
Cure accelerator	2-Ethyl-4-methylimidazol	1
Cure Condition		
70℃×12h+150℃×4h+190℃×2h		

Table 1. Composition of epoxy resin and cure condition for CFRP strand

2.2 Test method

The bending creep tests for EP resin were carried out under various temperatures for getting the creep compliance as one of viscoelastic coefficients and the tensile static tests for CFRP strand were carried out under various loading rates (0.01, 0.1, 1, 10 mm/min) and temperatures for getting tensile static strength. These testing methods are shown in Figure 1.

The creep compliance D_c of EP resin was calculated from the deflection δ at the center of specimen using Equation (1),

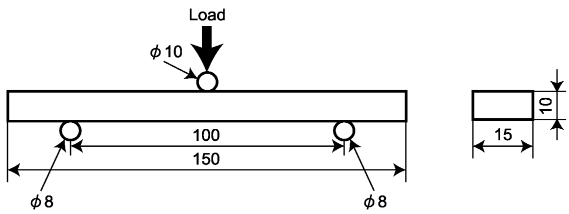
$$D_c = \frac{4bh^3\delta}{P_0 L^3} \tag{1}$$

where P_0 is dead load, L is the span, b and h are the width and thickness of specimen, respectively.

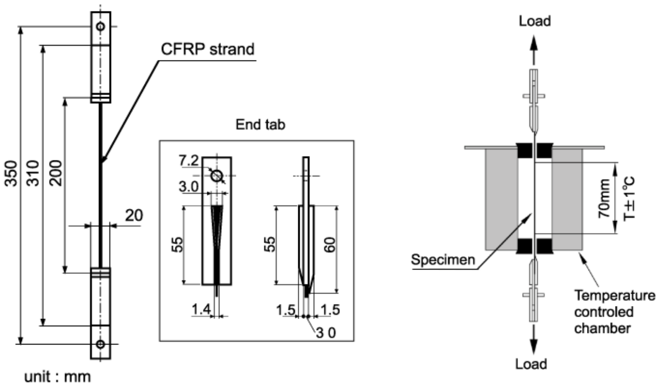
The longitudinal tensile static strength σ_s of CFRP strand is defined by Equation (2),

$$\sigma_s = P_s \frac{\rho}{t_e} \tag{2}$$

where P_s, ρ, t_e are the maximum load of the strand, the fiber density and the tex of fiber strand, respectively. Therefore, the tensile strength of CFRP strand is calculated using the cross sectional area of carbon fiber bundle in the strand.



(a) Bending creep test for EP resin



(b) Longitudinal tensile static test for CFRP strand

Figure 1. Configurations of specimen and test methods

3 Results and Discussion

3.1 Creep compliance of matrix resin

The left side of Figure 2 shows the creep compliance D_c versus loading time t at various temperatures T for EP resin. The master curve of D_c versus reduced loading time t' was constructed by shifting D_c at various constant temperatures along the log scale of time and log scale of D_c. Since the smooth master curve of D_c can be obtained as shown in the right side graph, the TTSP is applicable for D_c. The time-temperature (horizontal) shift factor a_{T0} and the temperature (vertical) shift factor b_{T0} are shown in Figure 3.

The master curve of D_c for EP resin formulated by Equation (3) are shown by solid line in Figure 2. The shift factors a_{T0} and b_{T0} are formulated by Equations (4) and (5) and the formulated results are shown by solid lines in Figure 3. The parameters in these equations are shown on Table 2.

$$\log D_c = \log D_{c,0}(t'_0, T_0) + \log\left[\left(\frac{t'}{t'_0}\right)^{m_g} + \left(\frac{t'}{t'_g}\right)^{m_r}\right] \tag{3}$$

where, $D_{c,0}$ is the creep compliance at 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.

$$\begin{aligned}\log a_{T0}(T) &= \frac{\Delta H_1}{2.303G}\left(\frac{1}{T}-\frac{1}{T_0}\right)\mathrm{H}(T_g - T)\\ &+\left[\frac{\Delta H_1}{2.303G}\left(\frac{1}{T_g}-\frac{1}{T_0}\right)+\frac{\Delta H_2}{2.303G}\left(\frac{1}{T}-\frac{1}{T_g}\right)\right](1-H(T_g-T))\end{aligned} \tag{4}$$

$$\log b_{T0}(T) = b_1(T - T_0)\mathrm{H}(T_g - T) + [b_1(T_g - T_0) + b_2(T - T_g)](1 - \mathrm{H}(T_g - T)) \tag{5}$$

where G is gas constant, 8.314×10^{-3} [kJ/(K•mol)], ΔH_1 and ΔH_2 are the activation energies below and above glass transition temperature T_g respectively. T and T_0 are test temperature and reference temperatures, respectively. H is the Heaviside step function. b_1 and b_2 are the fitting parameters, respectively.

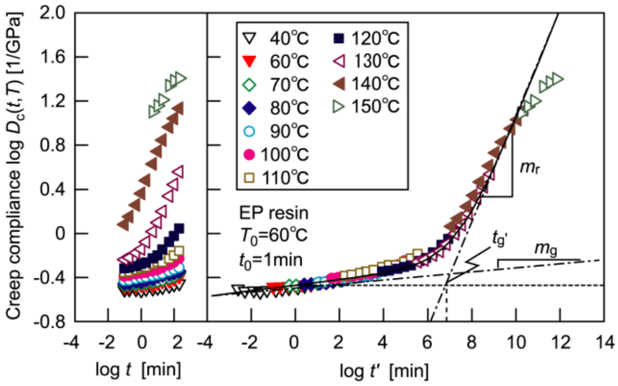


Figure 2. Master curve of creep compliance for EP

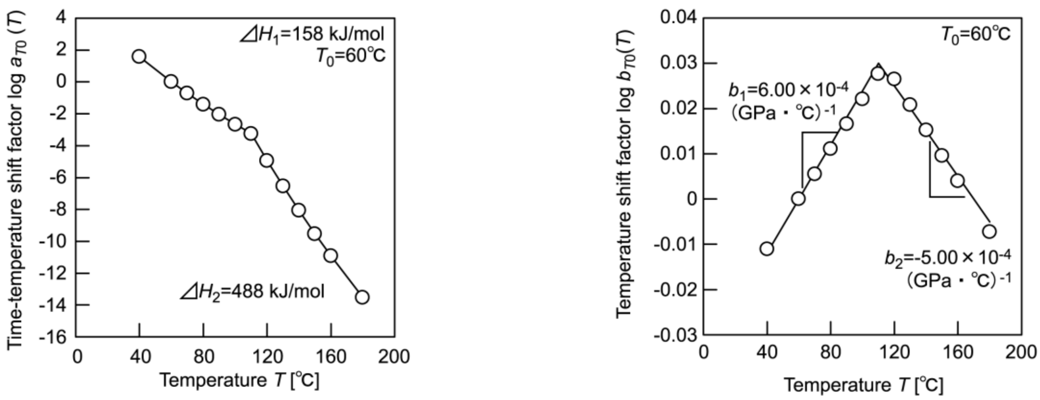


Figure 3. Horizontal and vertical shift factors for EP resin

T_0 [°C]	: 60	t'_0 [min]	: 1
$D_{c,0}(t'_0, T_0)$	: 0.339	t'_g at T_0 [min]	: 1.00×10^7
m_g	: 0.025	m_r	: 0.5
⊿H$_1$ [kJ/mol]	: 158	⊿H$_2$ [kJ/mol]	: 488
b_1 [(GPa・°C)$^{-1}$]	: 6.00×10^{-4}	b_2 [(GPa・°C)$^{-1}$]	: -5.00×10^{-4}
T_g [°C]	: 110		

Table 2. Formulation parameters of EP

3.2 Tensile strength of CFRP strand

The left side of Figures 4 and 5 show the tensile static strength σ_s versus time to failure t_s at various temperatures T for CFRP strands, where t_s is the time to failure from initial loading to maximum load during test. The master curves of σ_s versus reduced time to failure t'_s were constructed by shifting σ_s at various constant temperatures along the log scale of t_s using the same a_{T0} for D_c shown in Figure 3.

The master curve of σ_s is formulated by the following equation,

$$\log\sigma_s(t',T_0) = \log\sigma_{s,0}(t'_0,T_0) + \frac{1}{\alpha_s}\log[-\ln(1-P_f)] - \log\left[\frac{D^*(t',T_0)}{D_c(t'_0,T_0)}\right]^{n_r} \quad (6)$$

where $\sigma_{s,0}$ is the static strength at reference failure time t'_0 and reference temperature T_0, α_s is the shape parameter of static strength and P_f is the failure probability. $D_c(t'_0,T_0)$ is the creep compliance of matrix resin at t'_0 under T_0. n_r is the viscoelastic parameter determined by failure mode which is independent of time and temperature. D^* is viscoelastic compliance at constant deformation rate is obtained by the following relation for the creep compliance D_c,

$$D^*(t',T_0) = D_c(t'/2,T_0). \quad (7)$$

The formulated master curves of σ_s are shown in Figures 4 and 5. The parameters in this equation are shown on Table 3. From there graphs, the tensile strength of T300/EP and XN05/EP depend clearly on time and temperature. However, the tensile strength of HR40/EP and XN50/EP depend scarcely on time and temperature.

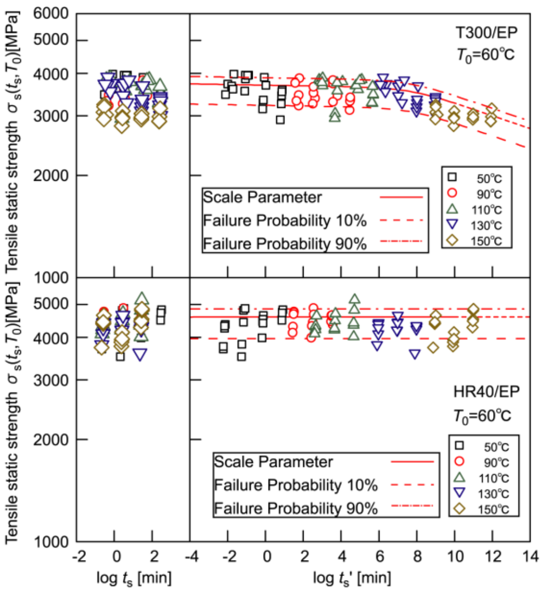


Figure 4. Master curves of tensile static strength for PAN-based CFRP strand

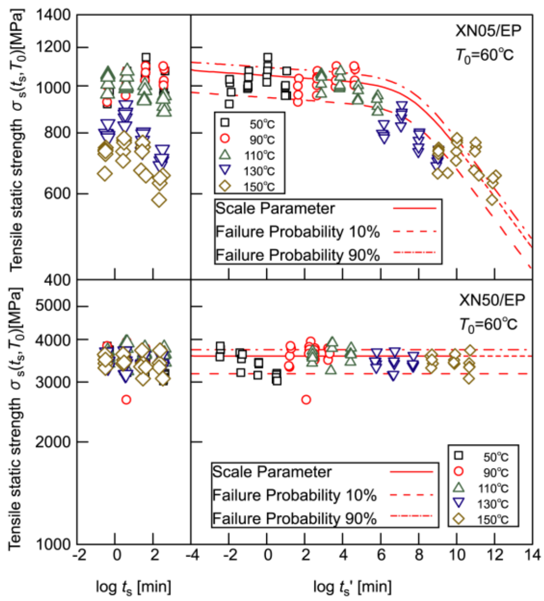


Figure 5. Master curves of tensile static strength for pitch-based CFRP strand

	T300/EP	HR40/EP	XN05/EP	XN50/EP
$\sigma_{s,0}(t'_0,T_0)$	3690	4594	1049	3576
α_s	16.5	15.4	21.5	19.6
n_r	0.038	0	0.106	0

Table 3. Formulation parameters of CFRP

3.3 Theoretical Consideration for Role of Matrix Resin to Static Strength of CFRP strand

The tensile static strength in the longitudinal direction of unidirectional CFRP can be shown by the following equation based on Rosen's shear lag model [4],

$$\frac{\sigma_{LT}(t_s,T)}{\sigma_{L,T,g}}=\left[\frac{G_m(t,T)}{G_{m,g}}\right]^{1/(2m)} \quad (8)$$

where σ_{LT} and $\sigma_{LT,g}$ is the tensile static strength at time to failure t_s and temperature and its glassy value, $G_m(t,T)$ and G_{mg} are the shear relaxation modulus of matrix resin at relaxation time and temperature and its glassy value, and m is Weibull shape parameter of tensile strength of carbon fiber. G_m/G_{mg} is nearly equal to E_m/E_{mg}, where E_m and E_{mg} are the relaxation modulus of matrix resin at relaxation time and temperature and its glassy value. Weibull plots of tensile strength measured for four type of mono filament are shown in Figure 6 which indicates m= 5.5 for XN05, m=5.6 for XN50, m=8.2 for T300, m=7.8 for HR40.

Figures 7 and 8 show the relationship between static strength of CFRP strands and inverse viscoelastic compliance of matrix resin at the same conditions of time and temperature. Solid lines in there figures are the predicted value of the tensile strength determined by Equation (8) using m values in Figure 6. From these figures, the predicted value of tensile strength agrees well with experimental results for T300/EP and XN05/EP, while that does not agree with experimental results for HR40/EP and XN50/EP.

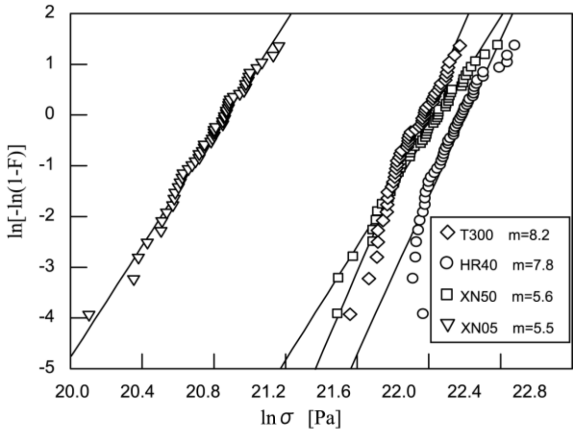


Figure 6. Weibull plot for failure probability F of mono filament

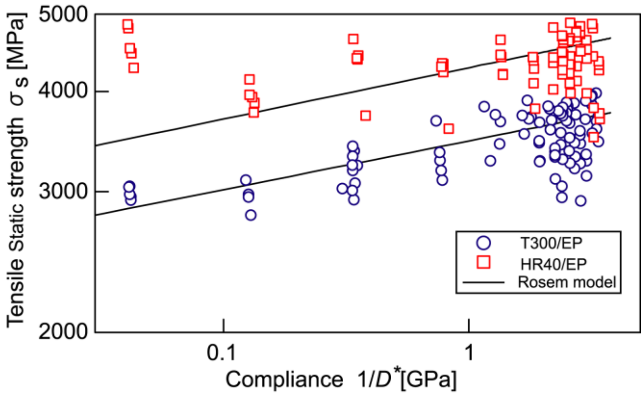


Figure 7. Static strength and compliance of matrix resin

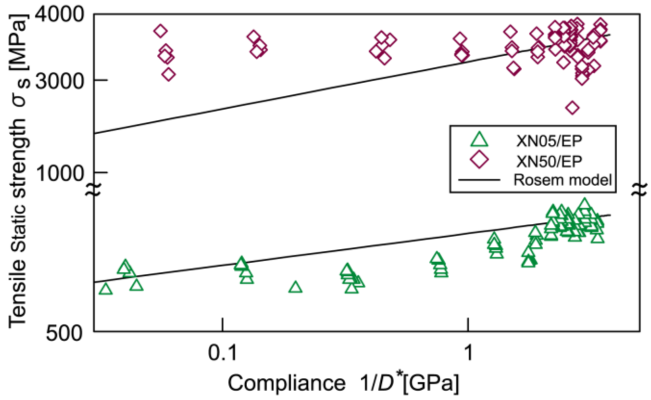
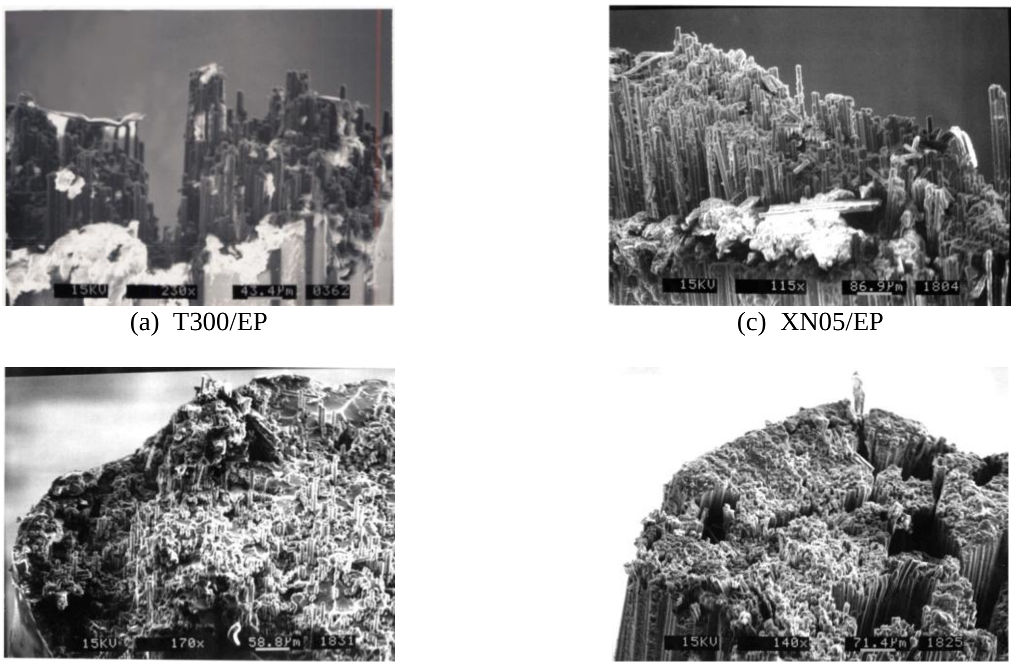


Figure 8. Static strength and compliance of matrix resin

Figure 9 shows SEM photographs of tensile fracture surface of four types of CFRP strand. Many pull-out fibers are observed on the fracture surface of T300/EP and XN05/EP shown in Figures 9 (a) and (c). For HR40/EP and XN50/EP, the fracture surface is flat as shown in Figures 9 (b) and (d). It can be considered from these results that the accumulation of fiber failure occurs in CFRP strand for T300/EP and XN05/EP, therefore the predicted strength agrees well with experimental results. The tensile fracture of CFRP strand for HR40/EP and XN50/EP occurs without the accumulation of fiber failure, therefore the predicted strength does not agree with experimental results.



(a) T300/EP (c) XN05/EP

(b) HR40/EP (d) XN50/EP

Figure 9. Fracture surfaces of CFRP strand

4 Conclusion

The tensile static strength of various unidirectional CFRP are evaluated under various loading rates and temperatures. Unidirectional CFRPs are four types of resin impregnated carbon fiber strand, which consist of four types of carbon fibers and same epoxy resin. Four types of carbon fibers are high strength PAN based carbon fiber, low modulus pitch based carbon fibers, high modulus PAN based and pitch based carbon fibers. As results, it was cleared that the tensile static strength of unidirectional CFRP using high strength PAN based and low modulus pitch based carbon fibers remarkably depends on time and temperature, while that using high modulus PAN based and pitch based carbon fibers scarcely depends on time and temperature.

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References

[1] Miyano Y., Nakada, M., M. K. McMurray and R. Muki, “Prediction of Flexural Fatigue Strength of CFRP Composites under Arbitrary Frequency, Stress Ratio and Temperature”, Journal of Composite Materials, **31**, 619-638 (1997)

[2] Miyano, Y., Nakada, M., Kudoh, H. and Muki, R., “Prediction of tensile fatigue life under temperature environment for unidirectional CFRP”, Advanced Composite Materials, **8**, 235-246 (1999).

[3] Miyano, Y., Nakada, M. and Muki, R., “Applicability of Fatigue Life Prediction Method to Polymer Composites”, Mechanics of Time-Dependent Materials, **3**, 141-157 (1999).

[4] Nakada, M., Miyano, Y., Kinoshita, M., Koga, R., Okuya, T. and Muki, R., “Time-Temperature Dependence of Tensile Strength of Unidirectional CFRP”, Journal of Composite Materials, **36**, 2567-2581 (2002).