EFFECT OF WATER ABSORPTION ON TIME-TEMPERATURE DEPENDENT STRENGTH OF UNIDIRECTIONAL CFRP

S. Hara[1*], M. Nakada[2], Y. Miyano[2]

[1] *Graduate School, Kanazawa Institute of Technology, 7-1, Ohgigaoka, Nonoichi, Ishikawa, 921-8501, Japan*
[2] *Materials System Research Laboratory, Kanazawa Institute of Technology, 3-1, Yatsukaho, Hakusan, Ishikawa, 924-0838, Japan*
** s-hara@venus.kanazawa-it.ac.jp*

Keywords: Unidirectional CFRP, Static strength, Water absorption, Time-temperature dependence

Abstract
The static strengths for typical four directions of unidirectional CFRP were measured under various temperatures at a single loading rate for Dry and Wet specimens. The four directions were the longitudinal tension and bending, transverse bending and compression, respectively. The effect of water absorption on the time-temperature dependence of these static strengths of unidirectional CFRP were discussed. As results, the static strengths in these four directions of unidirectional CFRP decrease with an increase in time-temperature and water absorption. The effect of water absorption on the time and temperature dependence of these static strengths can be characterized by the viscoelastic behavior of matrix resin.

1 Introduction
Carbon fiber reinforced plastics (CFRP) are now being used for the primary structures of airplanes, ships and others, in which the high reliability should be kept during the long-term operation. Therefore, it would be expected that the accelerated testing methodology for the long-term life prediction of CFRP structures exposed under the actual environments of temperature, water and others must be established.

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 viscoelastic compliance 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 static strengths in the longitudinal and transverse directions of unidirectional CFRP under wet condition are evaluated using ATM-2. The applicability of ATM-2 and the effect of water absorption on time and temperature dependence of these static strengths are discussed.

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).

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

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 depend on temperature and load histories. n_{r} is the material parameter. The viscoelastic compliance D^* in (1) can be shown by the following equation:

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

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. The 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. The 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

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

where the viscoelastic compliance D^* in (4) can be shown by the following equation assumed the stress history under constant deformation rate loading (static loading) as the step loading shown in Fig.2.

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

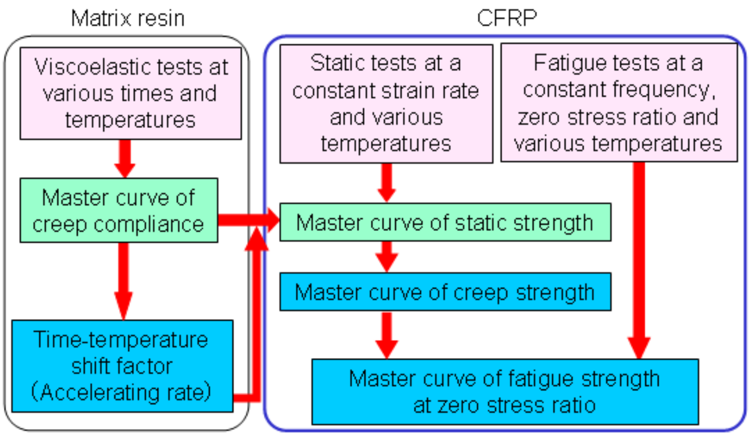


Figure 1. Procedure of ATM-2

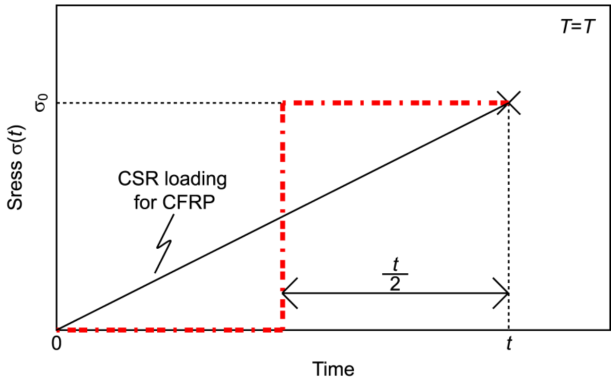


Figure 2. Stress history under constant deformation rate loading (static loading) for determination of the viscoelastic compliance D^*

3 Experimental procedures

Unidirectional CFRP laminates which consist of carbon fiber T300 and epoxy resin 2500 were molded by autoclave technique. The CFRP laminates were cured at 135 °C for 2 hours and then post-cured at 160 °C for 2 hours. The aging treatment for post-cured specimen was conducted at 110 °C for 50 hours. The Wet specimens by soaking the aged specimen (Dry specimen) in hot water of 95 °C for 121 hours for 1mm thick specimen in longitudinal direction, 95 °C for 144 hours for 2mm thick specimen in longitudinal direction and 95 °C for 121 hours for 2 mm thick specimen in transverse direction were respectively prepared. The water weight content of all of wet specimen was 1.9%.

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.

4 Results and discussion

4.1 Viscoeolastic behaviour of matrix resin

The left side of Fig.3(a) shows the loss tangent tan δ for the transverse direction of unidirectional CFRP (Dry specimen) 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 the reference temperature 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 master curve of tan δ for Wet specimens can be also constructed as shown in Fig.3(b). The TTSP is also applicable for tan δ under wet condition. The master curve of tan δ is shifted to the left side by water absorption 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 (Dry specimen) 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 applicable for E' for the transverse direction of unidirectional CFRP. The master curve of E' for Wet specimens can be also constructed as shown in Fig.4(b). The TTSP is also applicable for E' under wet condition.

The time-temperature shift factor $a_{T0}(T)$ which is the horizontal shift amount shown in Fig.5(a) can be formulated by the following equation:

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

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.5(b) can be fit with the following equation:

$$\log b_{T_0}(T) = \left[\sum_{i=1}^{5} b_{i-1}(T-T_0)^{i-1}\right]\mathrm{H}(T_g - T) + \left[\sum_{i=1}^{5} b_{i-1}(T_\mathrm{g}-T_0)^{i-1} + \log\frac{T_\mathrm{g}}{T}\right]\left(1-\mathrm{H}(T_\mathrm{g}-T)\right) \tag{7}$$

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]

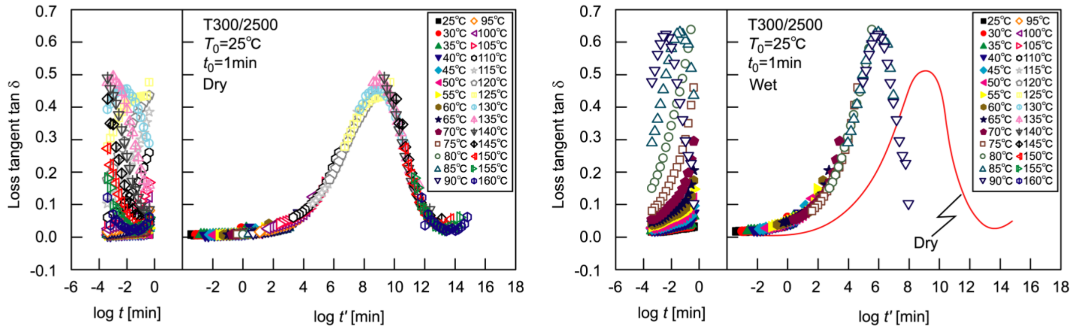
$$D_\mathrm{c}(t) \sim 1/E(t), \qquad E(t) \cong E'(\omega)\,|_{\omega\to 2/\pi t} \tag{8}$$

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:

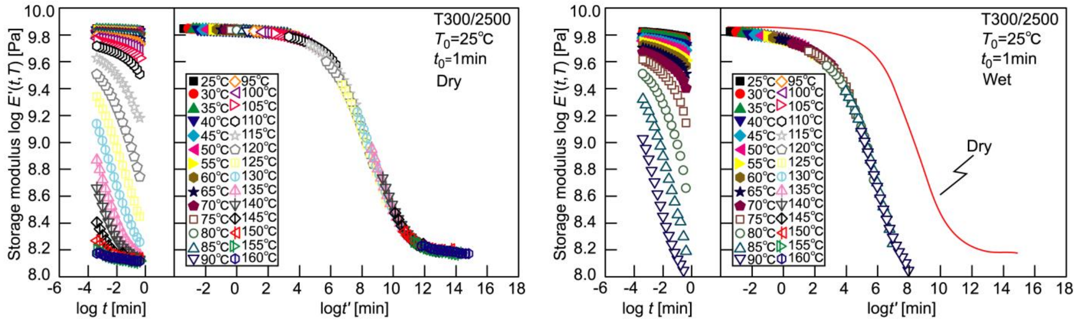
$$\log D_c = \log D_{c,0}(t'_0, T_0) + \log\left[\left(\frac{t'}{t'_0}\right)^{m_g} + \left(\frac{t'}{t'_g}\right)^{m_r}\right] \tag{9}$$

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.



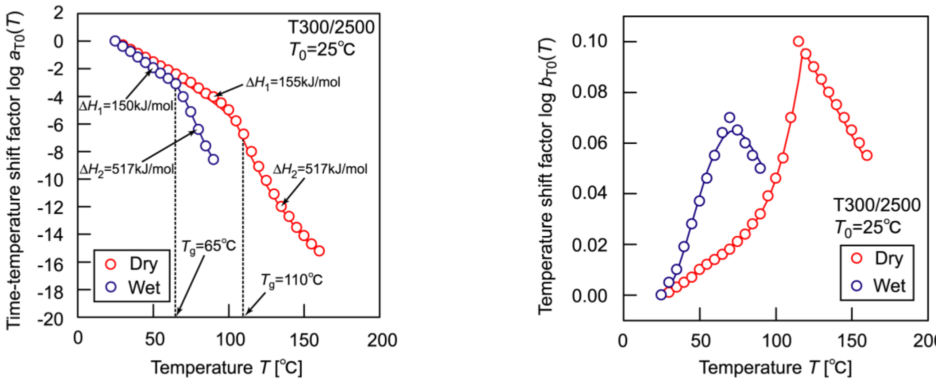
(a)Dry (b)Wet

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



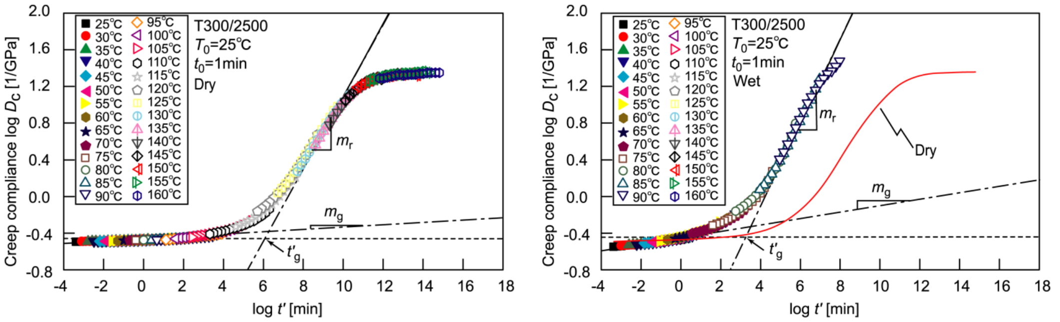
(a)Dry (b)Wet

Figure 4. Master curves of storage modulus for transverse direction of unidirectional CFRP



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

Figure 5. Shift factors of storage modulus for transverse direction of unidirectional CFRP



(a)Dry (b)Wet

Figure 6. Master curves of creep compliance for matrix resin calculated from the storage modulus for the transverse direction of unidirectional CFRP

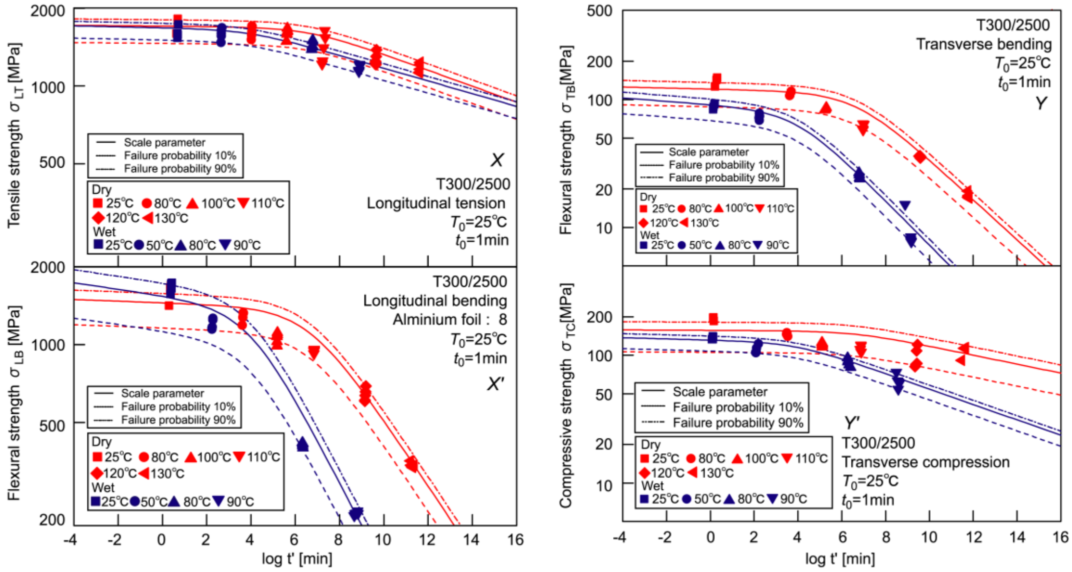
Table 1. Parameters for master curve and shift factors of creep compliance for matrix resin

	Dry	Wet		Dry	Wet
T_0 [°C]	25	25	ΔH_1 [kJ/mol]	155	150
T_g [°C]	110	65	ΔH_2 [kJ/mol]	517	547
D_{c0} [1/GPa]	0.337	0.351	b_0	1.65E-02	0.150
t'_0 [min]	1	1	b_1	3.81E-09	1.73E-08
t'_g [min]	1.54E06	2.34E03	b_2	-8.29E-07	-4.71E-06
m_g	0.0101	0.0348	b_3	6.64E-05	4.26E-04
m_r	0.405	0.466	b_4	-1.86E-03	-1.39E-02

4.2 Master curves of static strengths for unidirectional CFRP

Figure 7 show the master curves of static strengths for longitudinal tension X, longitudinal compression X', transverse tension Y and transverse compression Y' for Dry and Wet specimens of unidirectional CFRP obtained from the strength data at various temperatures by using the time-temperature shift factors a_{T_0} 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 2.

From Fig.7, the static strengths of unidirectional CFRP decrease with increasing time, temperature and water absorption. The time, temperature and water absorption dependencies of static strength of unidirectional CFRP are different with the loading direction. 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 2. The slope depends on the loading direction while that changes scarcely with water absorption. It is cleared from these facts that the time, temperature and water absorption dependencies of static strength of unidirectional CFRP can be determined by the viscoelastic behavior of matrix resin.



(a) Longitudinal direction (b) Transverse direction

Figure 7. Master curve of static strength for unidirectional CFRP

Table 2. Parameters for master curve of static strength of unidirectional CFRP

	X		*X'*		*Y*		*Y'*	
	Dry	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
σ_{s0} **[MPa]**	1700	1675	1446	1535	121	90.6	156	131
n_r	0.0762	0.0528	0.316	0.356	0.387	0.371	0.0868	0.130
α	14.7	20.7	10.0	7.18	7.04	7.97	5.68	11.4

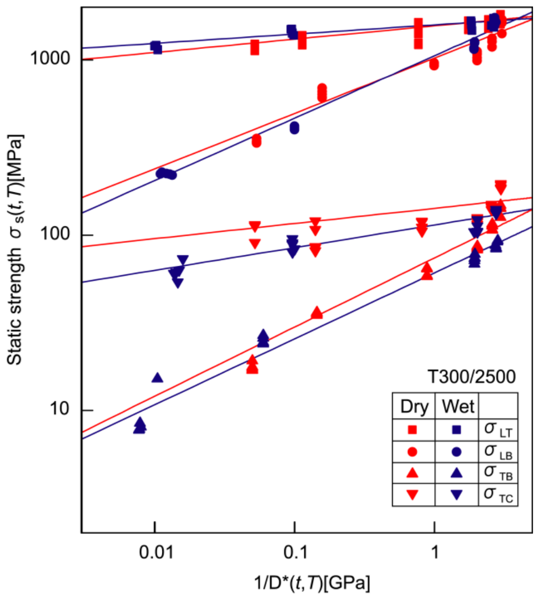


Figure 8. Static strength of unidirectional CFRP versus viscoelastic compliance D^* of matrix resin

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 under wet condition are evaluated using ATM-2. The applicability of ATM-2 can be confirmed for these static strengths. The time, temperature and water absorption dependencies of static strength of unidirectional CFRP can be determined by the viscoelastic behavior of matrix resin.

Acknowledgements

The authors thank the Office of Naval Research for supporting this work through an ONR award with Dr. Yapa Rajapakse as the ONR Program Officer. Our award is numbered to N000140611139 and titled "Verification of Accelerated Testing Methodology for Long-Term Durability of CFRP laminates for Marine Use". The authors thank Professor Richard Christensen, Stanford University as the consultant of this project.

References

[1] Y. Miyano, M. Nakada and H. Cai, J. Composite Materials, pp.42, pp.1897 (2008)
[2] R. M. Christensen and Y. Miyano, Int. J. Fracture, pp.137, pp.77 (2006)
[3] R. M. Christensen, Theory of Viscoelasticity, 2nd edition, Dover Publications, Inc., pp.142(1982).
[4] M. Uemura and N. Yamada, J. Soc. Material Sci., Japan, pp.24, pp.156 (1975).