Mech Time-Depend Mater (2013) 17:137–146
DOI 10.1007/s11043-012-9174-0

Simplified determination of long-term viscoelastic behavior of amorphous resin

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Received: 6 December 2011 / Accepted: 7 March 2012 / Published online: 26 May 2012

Abstract The time-temperature superposition principle has been applied to predict accurately the long-term viscoelastic behavior of amorphous resin at a temperature below the glass transition temperature from measuring the short-term viscoelastic behavior at elevated temperatures. A simplified method for the determination of the long-term viscoelastic behavior of amorphous resin using dynamic mechanical analysis is proposed. The automatic horizontal and vertical shifting method is used to construct the smooth storage modulus master curve, and then the accurate time-temperature shift factors can be obtained. The validity of our simplified determination method is confirmed experimentally.

Keywords Amorphous resin · Viscoelastic behavior · Time-temperature superposition principle

1 Introduction

Recently fiber reinforced plastics (FRPs) have been widely used in advanced light-weight structures for their high specific strength and high specific modulus. For design the FRP structures in which high reliability is required during long-term run, the long-term durability of FRP should be evaluated under actual environments. The evaluation of the long-term durability of FRP based on the short-term test data is strongly required by the industrial field.

The mechanical behavior of polymer resin shows time and temperature dependence, called viscoelastic behavior not only above the glass transition temperature T_g but also below T_g. Therefore, the mechanical behavior of FRP also shows time and temperature dependence even below T_g which is within the normal operating temperature ranges. These

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examples were shown by Aboudi et al. (1989), Gates (1992), Miyano et al. (1986) and Sullivan (1990).

We proposed the accelerated testing methodology to predict the long-term creep and fatigue strengths of FRP based on the time-temperature superposition principle (TTSP) for the viscoelastic behavior of matrix resin and confirmed the applicability of this methodology for various kinds of FRP (Miyano et al. 1997, 2008). Furthermore, we predicted the long-term creep and fatigue strengths of FRP structures based on the TTSP and the micromechanics of failure (Cai et al. 2008). It is concluded from these results that the long-term viscoelastic behavior of matrix resin in the range of temperature below T_g should be accurately evaluated from the short-term measured data at elevated temperatures for the reliable prediction of the long-term strength of FRP.

Based on the TTSP, the master curve of the viscoelastic behavior versus reduced time at a reference temperature is constructed by shifting the measured data at elevated temperatures along the log time axis (the horizontal axis). However, the measured data at elevated temperatures below T_g cannot be superimposed smoothly by only horizontal shifting as shown in Fig. 1(a). As shown in Fig. 1(b), the smooth master curve may be obtained by shifting measured data vertically as well as horizontally. This vertical shifting is well known as the thermal correction based on the entropy elasticity at the temperature above T_g.

In our previous paper (Nakada et al. 2011), TTSP was applied to predict accurately the long-term creep compliance of amorphous resin at a temperature below T_g from measuring the short-term creep compliance at elevated temperatures. The master curve of creep compliance can be constructed from the measured data by shifting vertically as well as horizontally. The master curve of creep compliance agrees well with those measured by long-term creep tests. Therefore, the long-term viscoelastic behavior at a temperature below T_g can be predicted accurately from measuring the short-term viscoelastic behavior at elevated temperatures based on the TTSP with vertical shift as well as horizontal shift.

The long-term creep test is suitable to predict accurately the long-term viscoelastic behavior, however it is a time-consuming method. Even the short-term creep test will take several hours to obtain the data in each temperature level. Figure 2 compares schematically the durations of creep test and dynamic mechanical analysis (DMA). Comparing to the creep test, the frequency multiplexing DMA can be performed during a single DMA by scanning the effect of temperature as well as time (frequency) on the viscoelastic properties of the tested material.

In this paper, the rapid and simplified determination method using frequency multiplexing DMA is proposed to determine the long-term viscoelastic behavior of amorphous resin at a temperature below T_g. The short-term viscoelastic behavior is measured by DMA under various frequencies and temperatures. The automatic shifting method is proposed to get the smooth master curve and the accurate time-temperature shift factors. The validity of the simplified determination method is discussed by comparing the creep compliance master curves obtained from DMA and creep tests.

2 Theories

2.1 Formulation of master curves of creep compliance

The viscoelastic behaviors of polymer resin can be represented by the storage modulus E', which can easily be measured by DMA conducted at various frequencies and temperatures.

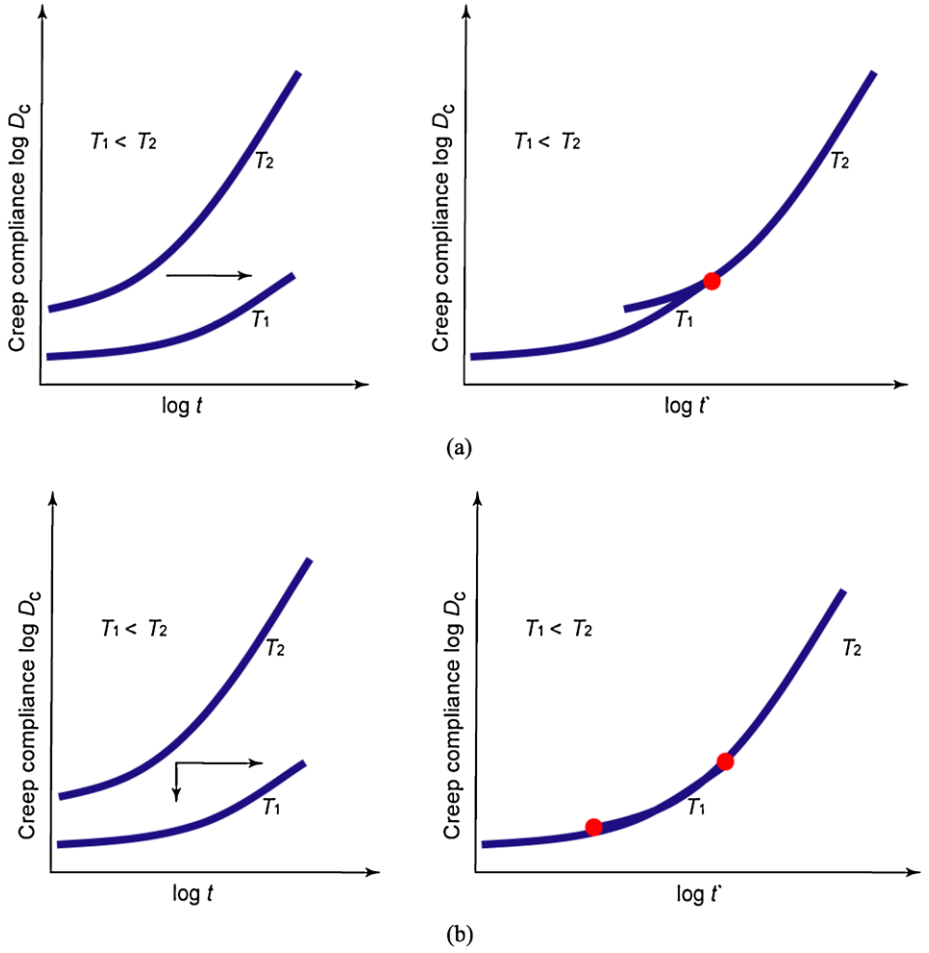

Fig. 1 Construction for master curve of creep compliance by horizontal shift (**a**) and horizontal and vertical shifts (**b**)

The creep compliance D_c can approximately be obtained from E' by using the approximate formula (Christensen 1982)

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

where E is Young's modulus and ω is angular velocity.

The master curve of D_c can be represented by two tangential lines, whose slopes are m_g and m_r, respectively, as shown in Fig. 3(a). The reduced time at an intersection of the tangential lines are called the reduced glass transition time t'_g at a reference temperature T_0. With these parameters, the master curve of D_c can be fitted with the following formula:

$$\log D_c = \log D_{c,0}(t'_0, T_0) + \log\left[\left(\frac{t'}{t'_0}\right)^{m_g} + \left(\frac{t'}{t'_0}\right)^{m_r}\right] \tag{2}$$

where $D_{c,0}$ is an initial creep compliance at the initial reduced time t'_0 at a reference temperature T_0.

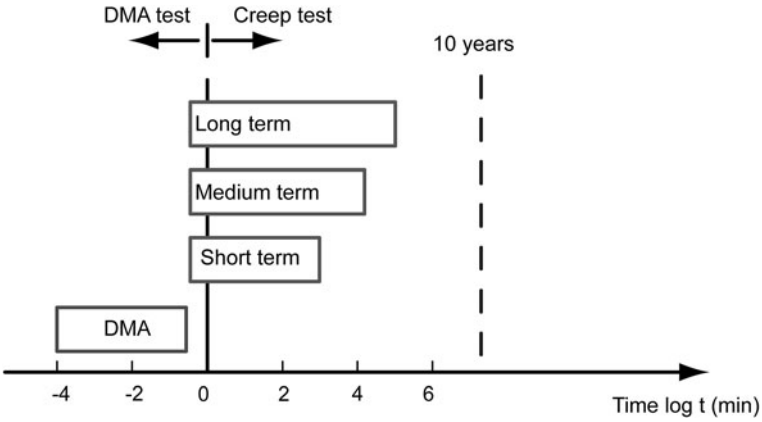

Fig. 2 Comparison of test periods between the DMA test and the conventional creep test

The time-temperature shift factor $a_{T0}(T)$ that is the amount of the horizontal shift shown in Fig. 3(b), can be fitted with the following equation:

$$\log a_{T0}(T) = \frac{\Delta H_1}{2.303G}\left(\frac{1}{T} - \frac{1}{T_0}\right)H(T_g - T) + \left[\frac{\Delta H_1}{2.303G}\left(\frac{1}{T_g} - \frac{1}{T_0}\right) + \frac{\Delta H_2}{2.303G}\left(\frac{1}{T} - \frac{1}{T_g}\right)\right]\left(1 - H(T_g - T)\right) \quad (3)$$

where G is gas constant, ΔH is activation energy, T_g is glass transition temperature. H is the Heaviside step function.

The temperature shift factor, $b_{T0}(T)$, which is the amount of the vertical shift shown in Fig. 3(c), can be fitted with the following equation:

$$\log b_{T0}(T) = b_1(T - T_0)H(T_g - T) + \left[b_1(T_g - T_0) + b_2(T - T_g)\right]\left(1 - H(T_g - T)\right) \quad (4)$$

where b_i is a coefficient.

2.2 TTSP automatic shifting procedure

Smooth master curves can be obtained by both horizontal and vertical translation of individual creep compliance curves. In order to minimize the error by manual shift, an automatic shifting procedure with high order degree polynomial is used to fit the master curve.

The shifting procedure for construction of master curve is shown in Fig. 4. This shifting procedure is performed in two stages. Figure 4(a) is the original data points of creep compliance obtained at two temperature levels. As first stage, take T_1 as the reference temperature, move the data point plots of temperature T_2 horizontally and vertically by adjusting the shift values a and b until a primary smooth curve is obtained, as shown in Fig. 4(b). Use the high order degree polynomial to approximate the master curve and record the sum of square of error for all data points. Finally, refine the master curve using the optimization method by adjusting a and b until the smoothest master curve with minimal sum of square of error is reached, as shown in Fig. 4(c). In this way, the smoothest master curve can be obtained without manual influence. The largest degree of the polynomial will influence the degree of the smooth of the master curve. The highest fourth degree polynomial is used to construct the master curve. The higher order degree of polynomial has been tried and gave almost

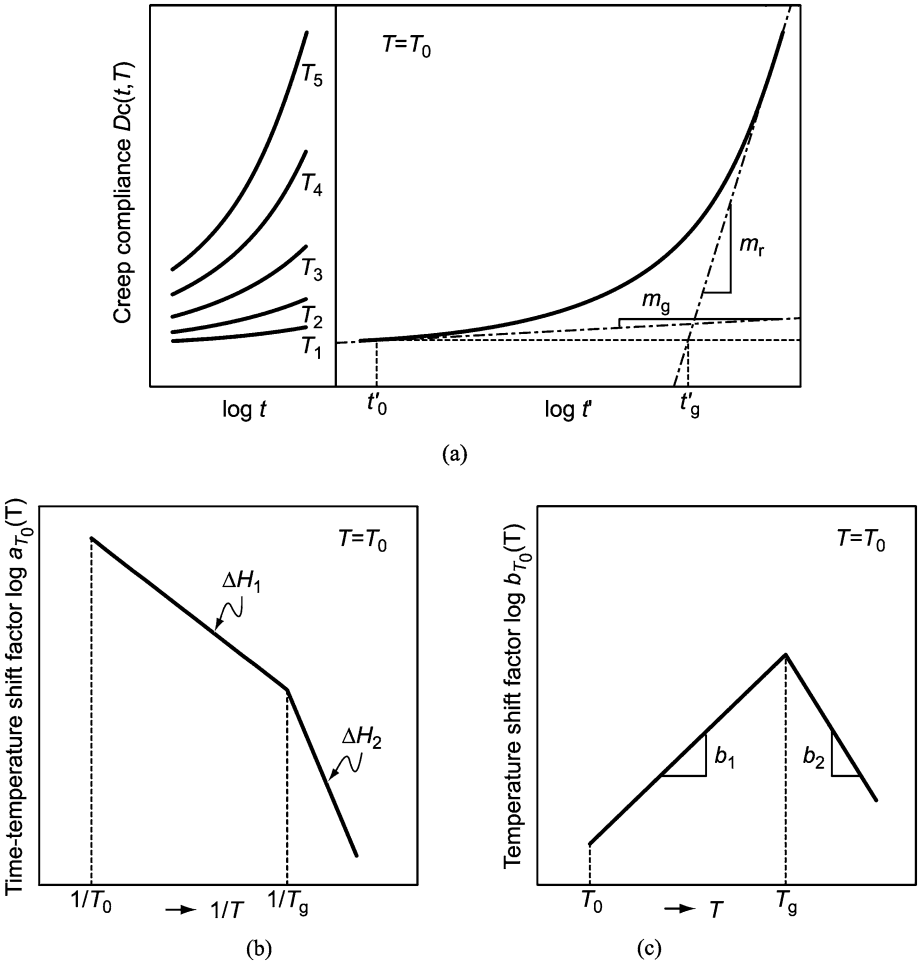

Fig. 3 Concept of formulation of master curve of creep compliance (**a**), time-temperature shift factor (**b**) and temperature shift factor (**c**)

the same result as the fourth degree polynomial. Therefore, the fourth degree polynomial is enough to construct the master curve.

This procedure is repeated for subsequent data points of higher temperature levels, and the complete master curve can be constructed, and also the time-temperature shift factors by constructing the master curve can be obtained. The same procedure can be applied to the data measured by DMA.

3 Experimental procedures

The material used in this study is a general purpose epoxy resin jER 828. The hardener and cure accelerator used are MHAC-P and 2-ethyl-4-methylimidazole, respectively. The epoxy resin plates were molded by casting and cured at 70 °C for 12 hours. The test specimens for DMA were cut from epoxy resin plates and were post-cured at 150 °C for 4 hours and at

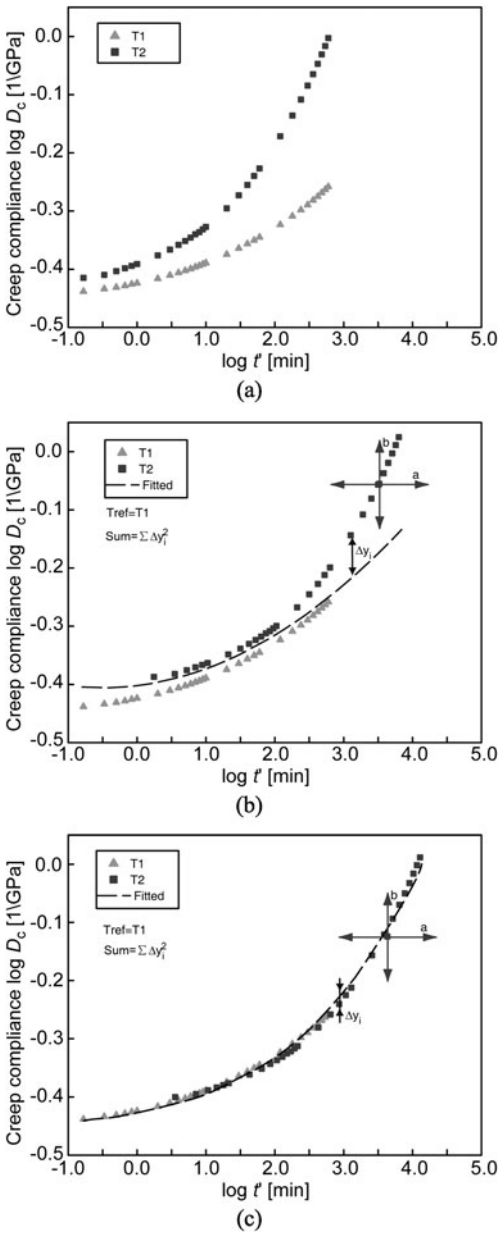

Fig. 4 Automatic shifting procedure for construction of master curve of creep compliance (**a**) original experiment data points, (**b**) primary shift horizontally and vertically, and (**c**) refinement of shift by optimization

190 °C for 2 hours. Then the cured specimens were cooled at a rate of 0.5 °C per minute. In order to minimize the physical aging effect during the tests, the heat treatment for the cured specimens was conducted at 100 °C for 167 hours in a constant temperature chamber before the test.

The width, thickness and length of DMA specimen are 6.4, 1.6 and 50 mm, respectively. The span is 38.6 mm. The temperatures ranged from 25 to 140 °C. The strain amplitude of

0.06 % by the sinusoidal wave with frequency range of 0.005–10 Hz was applied to the test specimen by dual cantilever bending method.

For comparison, long-term creep tests for same epoxy resin were performed. The details of creep tests were described in Nakada et al. (2011).

4 Results and discussion

4.1 Master curve of storage modulus by DMA

The left side of Fig. 5 shows the storage modulus E' versus testing time t $(= 1/f)$ at various temperatures T of epoxy resin. The master curve of E' versus reduced time t' was constructed by shifting E' at various constant temperatures along the log scale of t and log scale of E' as shown in the right side of Fig. 5. Since E' at various temperatures can be superimposed smoothly, the TTSP is applicable for E'.

In the DMA experiment, both the storage modulus E' and loss modulus E'' were measured. From E' and E'', we can calculate tan delta (the ratio of E'' to E'), the relative degree of damping of the material. Since the tan delta is the ratio of E'' to E', therefore, the vertical shift does not need to be made for constructing the master curve of tan delta. The smooth master curve of tan delta can be easily constructed by only horizontal shifting as shown in Fig. 6.

Figure 7 shows time-temperature shift factor a_{T0} and temperature shift factor b_{T0} obtained by constructing the master curve of E' shown in the right side of Fig. 5. The a_{T0} obtained by constructing the master curve of tan delta is also shown by the solid symbols in Fig. 7(a). Since the good agreement of a_{T0} obtained from E' and tan delta can be seen, the accurate a_{T0} can be evaluated from E' with automatic shifting.

4.2 Comparison of master curves of creep compliance

The left side of Fig. 8 shows the creep compliance D_c versus time t at various temperatures T of epoxy resin measured by creep tests. The smooth master curve of D_c can be constructed

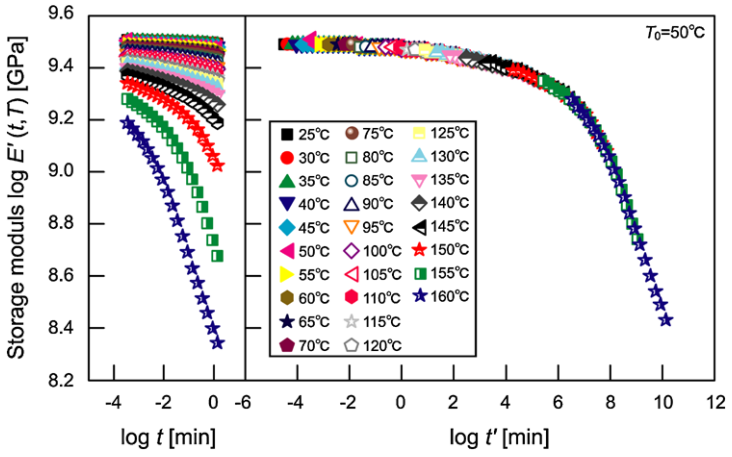

Fig. 5 Master curve of storage modulus by DMA tests

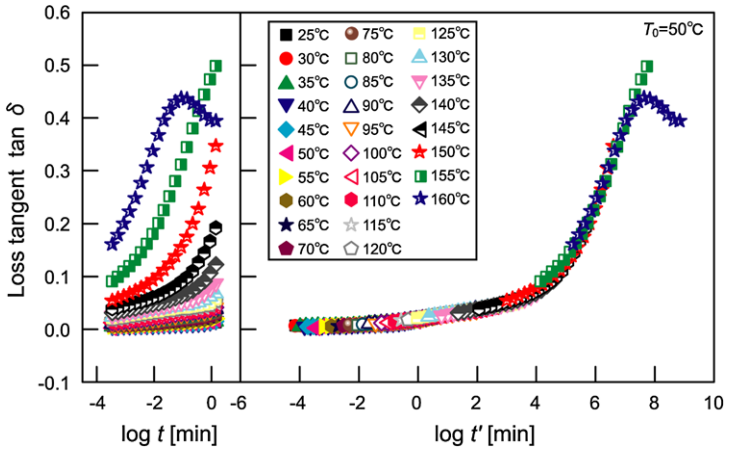

Fig. 6 Master curve of tan delta by DMA tests

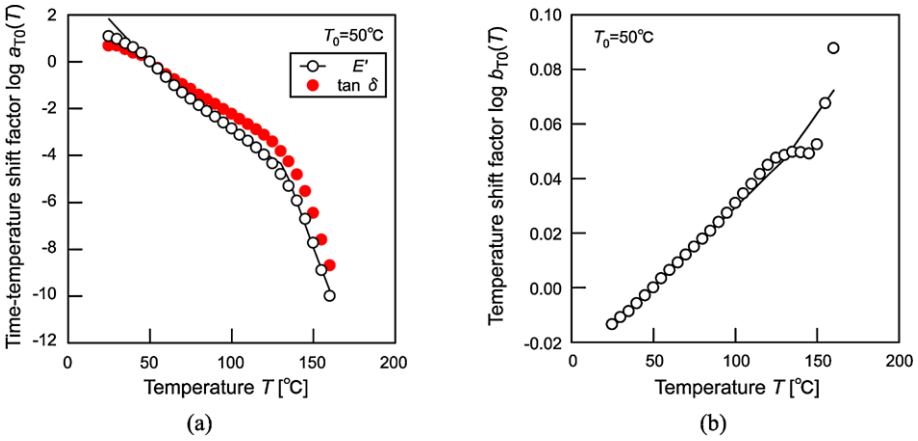

Fig. 7 Time-temperature shift factor (**a**) and temperature shift factor (**b**) for the storage modulus and loss tangent

by shifting D_c at various constant temperatures vertically as well as horizontally using automatic shift method, as shown in the right side of Fig. 8. The master curve of D_c obtained by DMA is shown by solid curve, where the D_c obtained by DMA is calculated from E' using Eq. (1). The master curves of D_c from DMA and creep tests agree well with each other. Therefore, the same master curve can be obtained from DMA and creep tests based on our simplified determination method.

Figure 9 shows the time-temperature shift factor a_{T0} and temperature shift factor b_{T0} obtained from constructing the master curves of D_c by DMA and creep tests. The shift factors obtained by DMA and creep tests agree well with each other. Since the good agreement of shift factors by DMA and creep tests can be seen, the accurate shift factors a_{T0} and b_{T0} can be evaluated by DMA with automatic shifting.

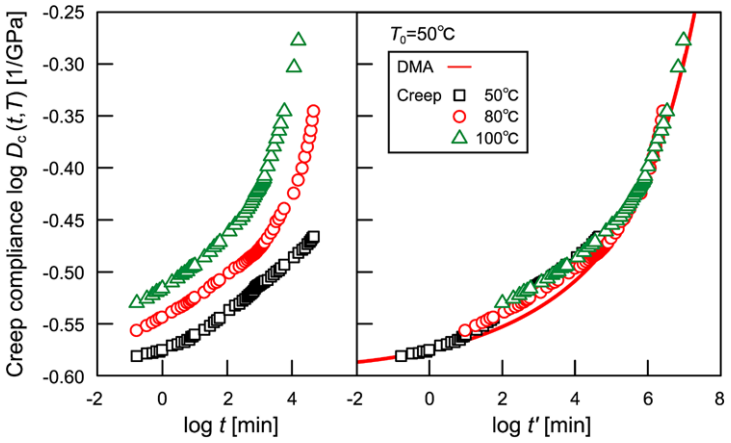

Fig. 8 Master curves of creep compliance by DMA and creep tests

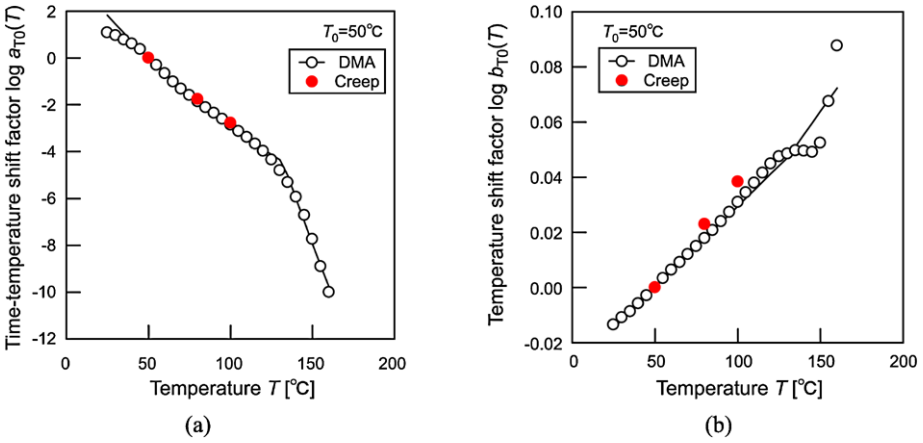

Fig. 9 Time-temperature shift factor (**a**) and temperature shift factor (**b**) for creep compliance by DMA and creep tests

5 Conclusions

The time-temperature superposition principle (TTSP) has been applied to predict accurately the long-term viscoelastic behavior of amorphous resin at a temperature below the glass transition temperature from measuring the short-term viscoelastic behavior at elevated temperatures. The simplified determination method for measuring the long-term viscoelastic behavior of amorphous resin using dynamic mechanical analysis (DMA) is proposed. The DMA was conducted under various frequencies and temperatures for epoxy resin. The creep tests were also conducted for various temperatures. As results, the time-temperature shift factors can be obtained accurately and easily by using DMA by measuring the storage modulus and the tan delta with automatic shifting method. Furthermore, the same master curve of creep compliance and time-temperature shift factor can be obtained from DMA and creep tests with automatic shifting method. Therefore, the simplified determination method of

long-term viscoelastic behavior for amorphous resin using DMA based on the TTSP was verified.

Acknowledgements This work is supported by National Science Foundation of China and Civil Aviation Administration of China (No. 61079011), and supported by the Fundamental Research Funds for the Central Universities.

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