EFFECT OF PHYSICAL AGING ON TIME-TEMPERATURE SUPERPOSITION PRINCIPLE FOR VISCOELASTIC BEHAVIOR OF THERMOSETTING RESINS

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Abstract

This paper is concerned with an experimental study of the influence of physical aging and temperature on viscoelastic behavior of epoxy resin. Master curves of storage modulus for various aging conditions were found to collapse into a single smooth curve corresponding to a reference aging condition after suitable horizontal and vertical translations. It is proposed that the resulting curve be designated the grand master curve. In addition, the amount of horizontal and vertical translations, the aging progressive rate, can be used to estimate the aging process. We have also shown that there is one-to-one correspondence between the aging progressive rate and polymer density.

1 Introduction

Mechanical behavior of thermosetting resins exhibit time and temperature dependence not only above the glass-transition temperature T_g but also below T_g. These resins generally do not exist in thermodynamic equilibrium state below T_g. The current state gradually moves towards the equilibrium state. The non-equilibrium state, however, is characterized by the transport mobility, which depends primarily on the degree of packing, or on the free volume. This state is approached asymptotically. Such a process is called physical aging and significantly affects mechanical behavior, especially the viscoelastic behavior of thermosetting resins. These examples have been shown by Struik [1], Kong [2], Sullivan [3], Sullivan et al [4], Hastie and Morris [5], Kasamori et al [6], Miyano and Kasamori [7], Feldman and Gates [8].

In this paper, the experimental study has been carried out to shed light on the role of physical aging and temperature on viscoelastic behavior of epoxy resins. We first construct the master curves of storage modulus at the reference temperature for various aging conditions. We then select a reference aging condition corresponding to specific aging temperature T_{a0} and aging time t_{a0}. Master curves for various aging conditions were found, after suitable horizontal and vertically shifts, to collapse into a single smooth curve corresponding to the master curve for the reference. The single smooth curve thus obtained is designated as the grand master curve. In this process, we introduce the aging progressive rate similar to the time-temperature shift factor used in the construction of the master curves.

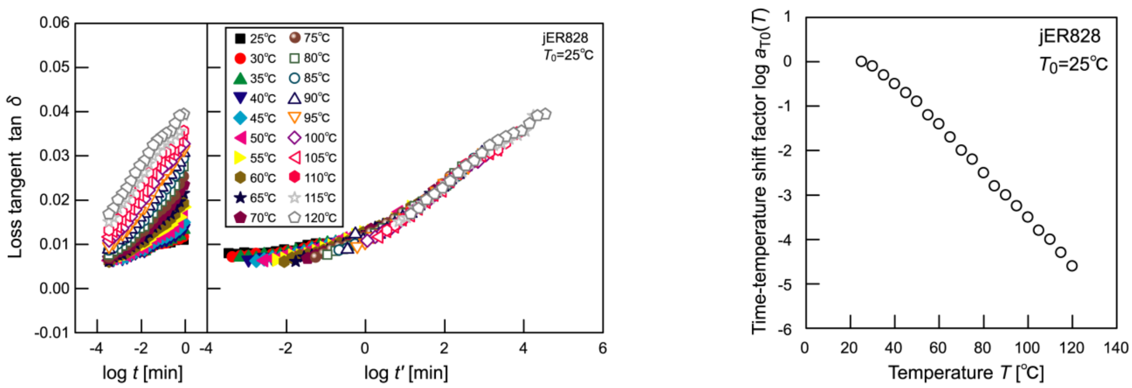
2 Experimental procedure

The composition of resin used in this study is deglycidyl ether of bis-phenol A (jER 828) for epoxy resin, metylnadic anhydride for hardener, and 2-ethyl-4-methyl-imidazole. Epoxy resin was cured by casting with a cure schedule of 70°C for 12 hours, 150°C for 4 hours, 190°C for 2 hours followed by a slow cooling at 0.5°C per minute. Epoxy resin cured as mentioned above is heat-treated at nine different conditions which are combined three levels of aging temperature T_a =80°C, 100°C, 120°C and three levels of aging time t_a=10^3min, 3x10^3min, 10^4min. The viscoelastic behavior for aged epoxy resin was measured using dynamic mechanical analysis (DMA) under various frequencies and temperatures. In addition, the density of epoxy resin was measured by the density gradient column using calcium nitrate solution.

3 Results and discussion

3.1 Master curve of loss tangent and storage modulus

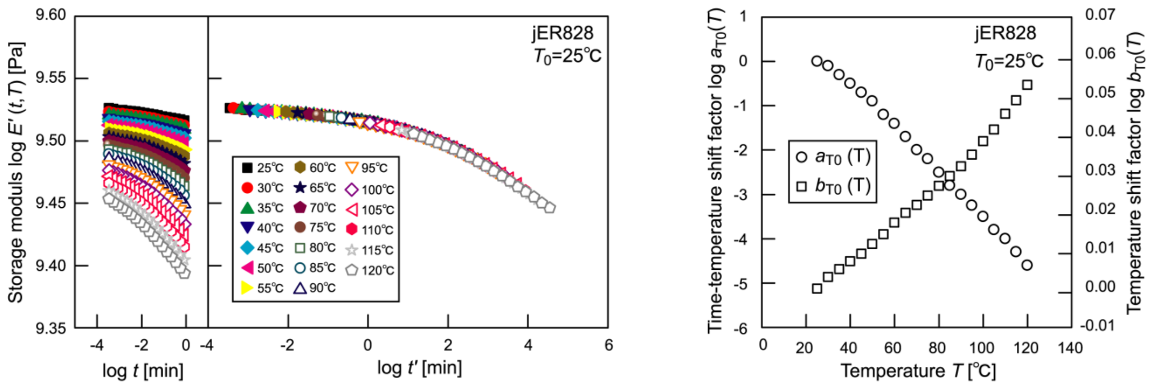
The left side of Figure 1(a) shows the loss tangent tanδ versus time t (=1/f) at various temperatures T of epoxy resin. The master curve of tanδ versus reduced time t' was constructed by shifting tanδ at various constant temperatures along the log scale of t as shown in the right side of Figure 1(a). Figure 1(b) shows time-temperature shift factor a_{T0} obtained by constructing the master curve of tanδ shown in the right side of Figure 1(a).



(a) Master curve of loss tangent (b) Time-temperature shift factors

Figure 1. Master curve and time-temperature shift factors of loss tangent

The left side of Figure 2(a) shows the storage modulus E' versus 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 Figure 2(a). Figure 2(b) 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 Figure 2(a). The time-temperature shift factor a_{T0} for E' is the same to that for tanδ.



(a) Master curve of storage modulus (b) Shift factors

Figure 2. Master curve and shift factors of storage modulus

3.2 Grand master curve of loss tangent and storage modulus

The master curves of tanδ for epoxy resins aged under nine conditions were constructed as shown on the left side of Figure 3. The right side of Figure 3 shows the grand master curve of tanδ at the reference aging conditions t_{a0}=10^3 min and T_{a0}=80°C obtained by shifting master curves of tanδ horizontally for various aging times at a constant aging temperature.

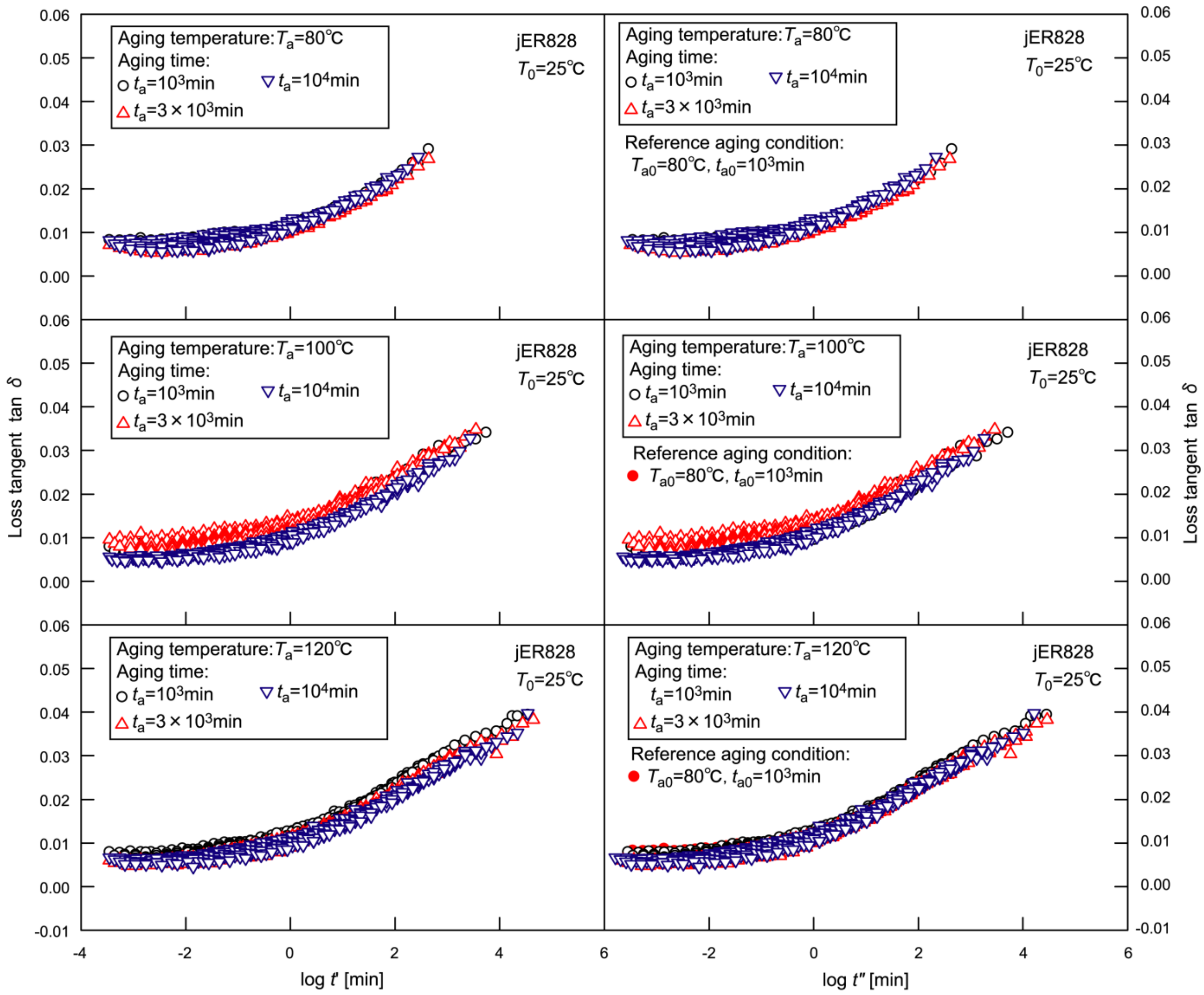


Figure 3. Grand master curve of loss tangent

The master curves of *E'* for epoxy resins aged under nine conditions were constructed as shown on the left side of Figure 4. In addition, each of the shift factors for constructing the master curves of *E'* are shown in Figure 5. The right side of Figure 4 shows the grand master curve of *E'* at the reference aging conditions $t_{a0}=10^3$ min and T_{a0}=80°C obtained by shifting master curves of *E'* horizontally and vertically for various aging times at a constant aging temperature. The horizontal shift factor of grand master curve for *E'* is the same to that for tanδ.

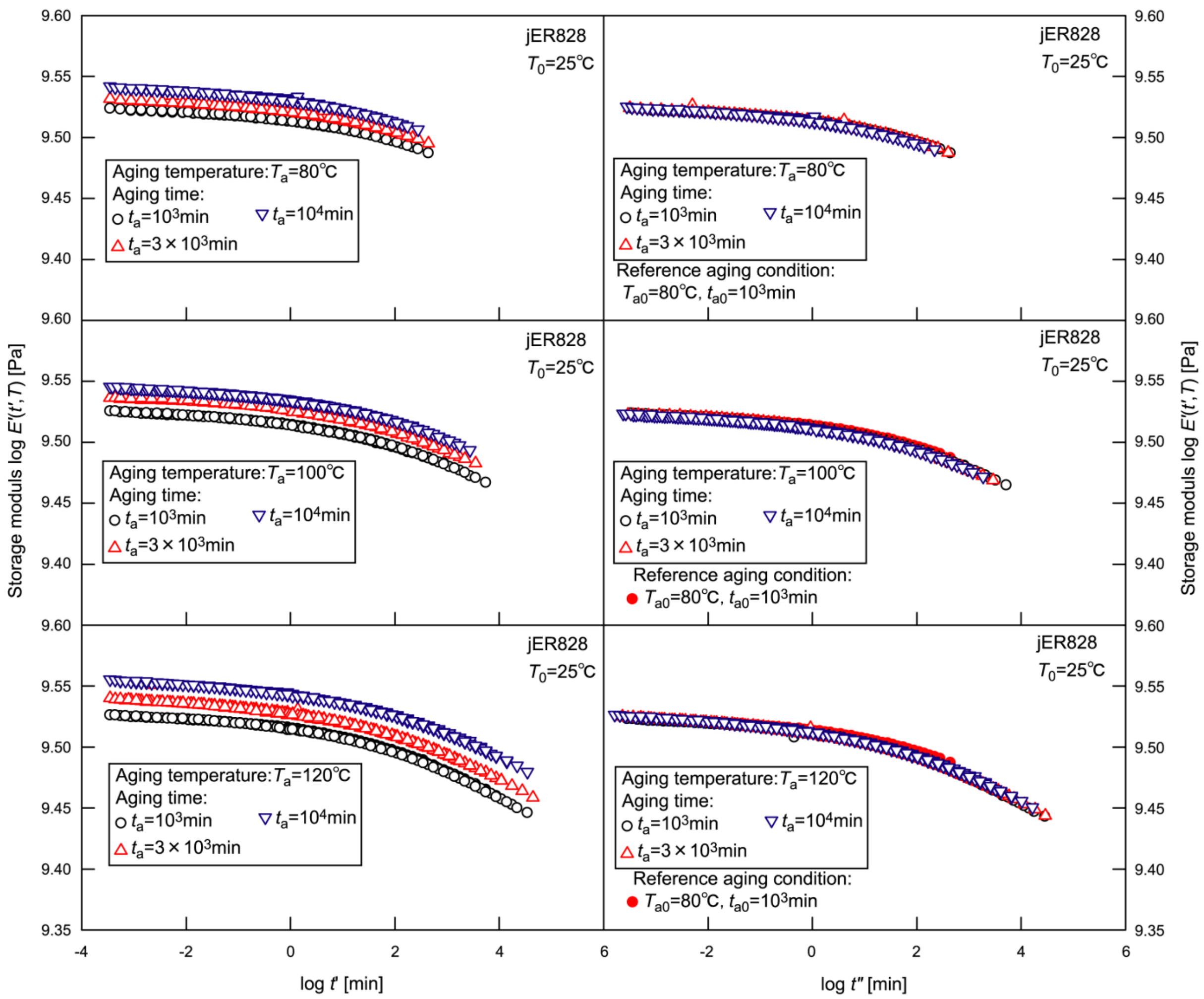


Figure 4. Grand master curve of storage modulus

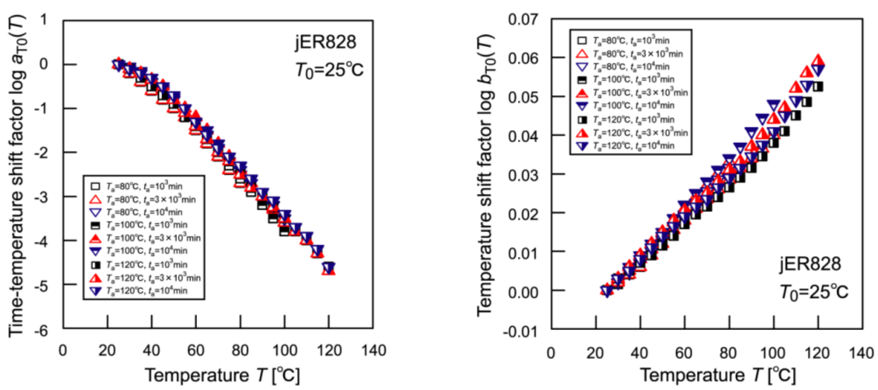


Figure 5. Time-temperature shift factors and temperature shift factors of storage modulus

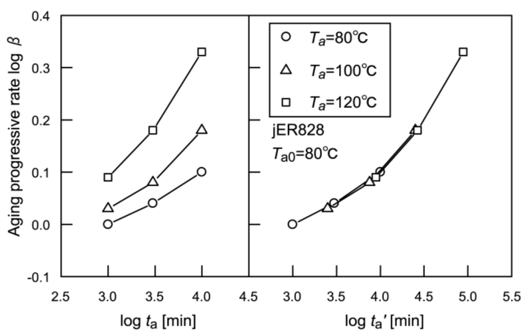
The aging progressive rates β and γ which are horizontal and vertical shift factors for constructing the grand master curve defined by

$$\beta = \frac{t'}{t''} \quad , \quad \gamma = \frac{E'(t',T)}{E'(t'',T)} \quad . \tag{1}$$

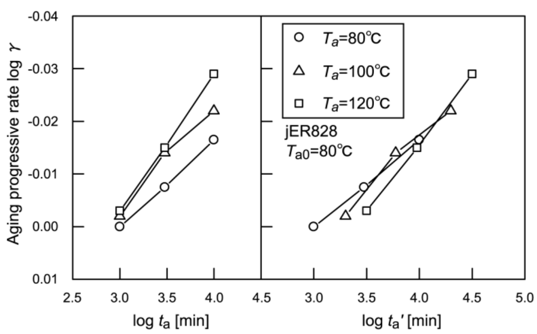
The β and γ versus aging time t_a at various aging temperatures T_a are shown on the left side of Figure 6. Master curves of β and γ are constructed by shifting β and γ at various aging temperatures along the log scale of aging time until they overlap each other as shown in the right side of Figure 6. The density ρ versus aging time t_a at various aging temperatures T_a are shown on the left side of Figure 7. Master curve of ρ is constructed by shifting at various aging temperature along the log scale of aging time until they overlap each other as shown in the right side of Figure 7.

Figure 8 shows the time-temperature shift factors for constructing the master curves of β, γ and ρ. The time-temperature shift factors for β and ρ agree with each other, however that for γ does not agree with that for ρ. It is considered that the difference in the shift factors between γ and ρ was caused by the scatter of *E'* for each test specimen.

Figure 9 shows the relationship between β, γ and ρ for nine aging conditions. These figures show the aging progressive rate and the density satisfy the one-to-one correspondence regardless the aging time and aging temperature. Figure 10 shows the relationship between a_{T0}, b_{T0} and ρ for nine aging conditions. These figures show the time-temperature shift factors, the temperature shift factors and the density satisfy the one-to-one correspondence regardless the aging time and aging temperature. The scatters in the aging progressive rate γ and temperature shift factor b_{T0} shown in Figures 9 and 10 were caused by the scatters of storage modulus *E'* for each test specimen.



(a) Aging progressive rate β



(b) Aging progressive rate γ

Figure 6. Master curve of aging progressive rate

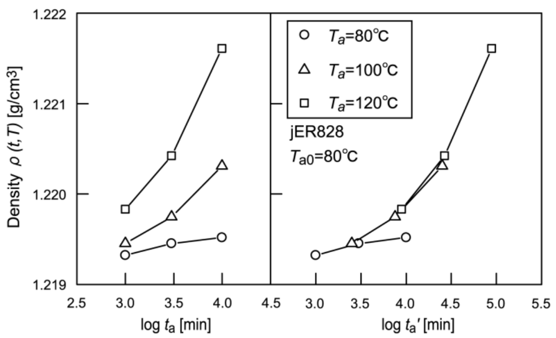


Figure 7. Master curve of density

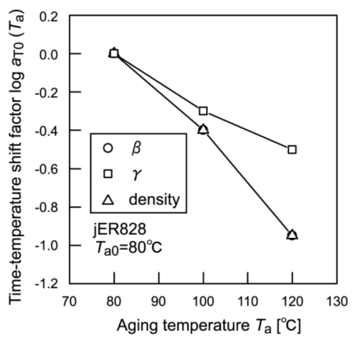
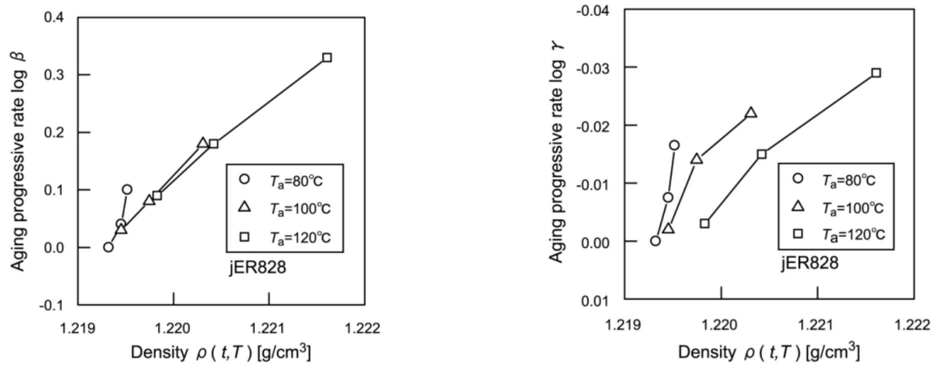
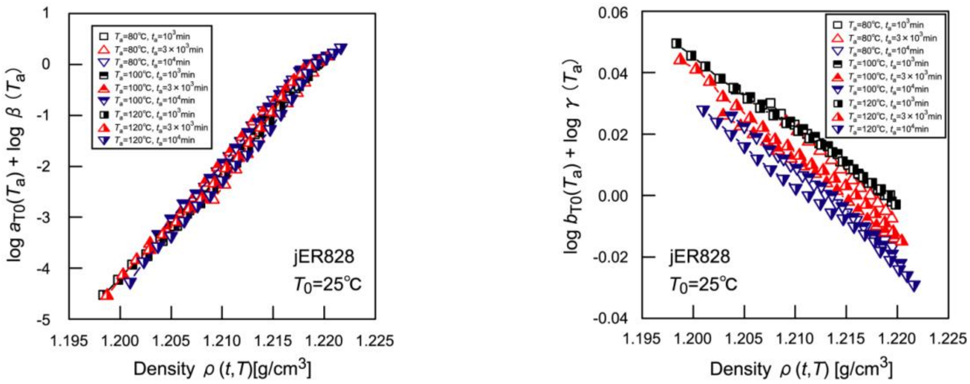


Figure 8. Shift factors for aging progressive rate and density



(a) Aging progressive rate β (b) Aging progressive rate γ

Figure 9. Relationship between aging progressive rate and density



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

Figure 10. Relationship between shift factor and density

4 Conclusion

The master curves of storage modulus of epoxy resin for various aging conditions were found to collapse into a single smooth curve corresponding to a reference aging condition after suitable horizontal and vertical translations. The aging progressive rate which are the amount of horizontal and vertical translations can be used to estimate the aging process. We have also shown that there is one-to-one correspondence between the time-temperature shift factor and polymer density.

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