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# Strain rate and temperature dependence of shear properties of epoxy resin with various molecular weight between cross-linkings

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Epoxy resins with various molecular weights between cross-linkings were prepared. In order to examine the strain rate and temperature dependence of the shear yield strength and the shear strength, test specimens were subjected to shear deformation at various strain rates and temperatures. The shear yield strength and the shear strength increased almost linearly as the logarithm of the strain rate increased. The strain rate-temperature superposition held for these shear properties. In particular, an experimental equation of the strain rate-temperature superposition for the shear yield strength was found. The shift factor to obtain a master curve was given with the temperature dependence of an Arrhenius type. Furthermore, the strain rate-temperature-molecular weight between cross-linkings superposition held for the shear properties. © *1999 Kluwer Academic Publishers*

## 1. Introduction

Fracture toughness of thermosetting resins such as epoxy and unsaturated polyester resin used as a matrix is generally less than that found in thermoplastic resins. Efforts have been made to improve this disadvantage by mixing various fillers or by blending thermoplastic resins. It has been suggested that shear bands of resin matrix surrounding the fillers contribute to improving fracture toughness [1–5]. In discontinuous fiber-reinforced composites, the shear strength at the fiber-matrix interphase also plays an important role in determining the reinforcing effect. The strongest relation has been observed between the shear yield strength at the fiber-matrix interphase and the shear yield strength of a resin matrix [6–8].

We previously reported the strain rate and temperature dependence of shear properties of epoxy resins with various ratios from two kinds of curing agents [9]. In this work, resin matrixes with various molecular weight between cross-linkings were prepared by changing ratio of curing agent and epoxy resin. Strain rate and temperature dependence of the shear yield strength and the shear strength of these resin matrixes was investigated.

## 2. Experimental

Epoxy resin used in this study was a bisphenol “A” type (Epikote 828, Yuka Shell Epoxy). Curing agent was an amine type (S-Cure 661, Kayaku Akuzo). As described in a previous paper [10], we prepared epoxy resins with molecular weight between cross-linkings by changing ratio of curing agent. These resin and curing agent were mixed to prepare epoxy materials with four mixing ratios of curing agents as shown in Table I. Hereafter, specimens were designated with the symbols A, B, C, D (Table I) as the quantity of the curing agent increases.

First, epoxy resin, curing agent were weighed with a weight ratio as shown in Table I. Only epoxy resin was defoamed in vacuum at 80 °C for 1 h. Epoxy resin and curing agents were then mixed and agitated thoroughly. Next, this mixture was poured into a mould and subjected to curing at 80 °C for 17 h. The specimen was then allowed to cool to room temperature.

Second, test specimens were prepared for measuring storage modulus to obtain the molecular weight between cross-linkings. The dimension of a test specimen measured 1.5 mm thickness, 6 mm width, and 60 mm length. The test specimens were subjected to tensile test at increasing rate with temperature of 3 °C min$^{-1}$, a frequency of 10 Hz, and a distance of grip of 45 mm to storage moduli with the aid of a dynamic mechanical tester (DMT, DDV-25FP, Orientec).

Third, test specimens for measuring shear properties were cut from the material prepared as mentioned above in accordance with JIS K 7214. The dimensions of a test specimen measured 3 mm in thickness, 60 mm in width and 60 mm in length. A hole, 11 mm in diameter, was made in the center of the test specimens. A shear test (JIS K 7214) was carried out by a circular punch.

In order to investigate the strain rate and temperature dependence of shear properties of epoxy resin, each specimen was subjected to the shear test at various test rates and temperatures (Table II) with the aid of

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TABLE I Formulation and properties of epoxy resins. Epoxy resin is 100 p.h.r.

| Symbol | Curing agent (p.h.r.) | Specimen density (g/cm$^3$) | Molecular weight between cross-linkings |
|---|---|---|---|
| A | 2.0 | 1.175 | 479 |
| B | 5.0 | 1.170 | 374 |
| C | 10.0 | 1.157 | 366 |
| D | 13.5 | 1.158 | 398 |

TABLE II Conditions of shear test

| | | | | | | |
|---|---|---|---|---|---|---|
| Temperature (°C) | 40 | 60 | 70 | 80 | 90 | 100 |
| Strain rate (min$^{-1}$) | 10 | 100 | 1000 | 10000 | | |

a Tensilon UTM-I-2500 (Orientec). Five to eight specimens were tested for each epoxy resin.

## 3. Results and discussion

Storage modulus values of epoxy resins with various molecular weight between cross-linkings are shown in Fig. 1. The storage moduli of 2–3 GPa were obtained at room temperature and 0.01–2 GPa in the region of 80–100 °C.

Nielsen [11] has proposed the following empirical equation which agrees with the experimental results at various degrees of cross-linking

$$\log_{10} G = 7.0 + 293\rho/M_c \qquad (1)$$

where $G$ is the shear modulus of the specimen, $\rho$ is the density of the specimen, and $M_c$ is the molecular weight between cross-linkings.

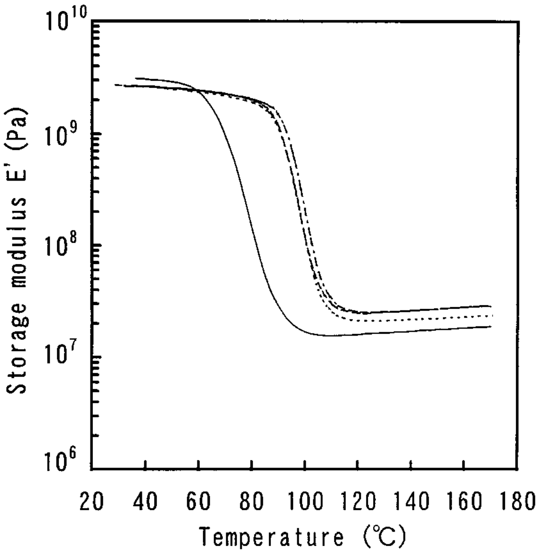

*Figure 1* Storage modulus of epoxy resins. (——) Sample A, (– – –) sample B, (- - - - - -) sample C, (—·—) sample D.

For isotropic materials the equation, $E = 2G(1+v)$, is confirmed, where $E$ is Young's modulus, $G$ is shear modulus, and $v$ is Poisson's ratio. We assumed $v = 0.49$ in the region of the rubber state and calculated $M_c$. The results are shown in Table I. $M_c$ increases with decreasing content of curing agent. This means that the degrees of cross-linking decrease with decreasing content of curing agent. When the content of curing agent is 10.0 p.h.r. for 100 p.h.r. epoxy resin, the molecular weight is the lowest, i.e., the degree of cross-linkings is the highest. When the content of curing agent is 10.0 p.h.r. for 100 p.h.r. epoxy resin, an absorption (914 cm$^{-1}$) in the infrared spectrum by epoxy rings has never been observed. Consequently, it is conceivable that the degree of reaction is about 100%.

The relationship between shear yield strength, $\tau_y$, at various temperatures and the logarithm of the strain rate for the epoxy resins with various molecular weight between cross-linkings is shown in Fig. 2a–d, while the relationship between shear strength, $\tau_s$, and the logarithm of the strain rate is shown in Fig. 3a–d. At all molecular weight between cross-linkings and temperatures, $\tau_y$ and $\tau_s$ increase almost linearly with the increase in the logarithm of the strain rate. This tendency is the same as that found for the tensile yield properties [12].

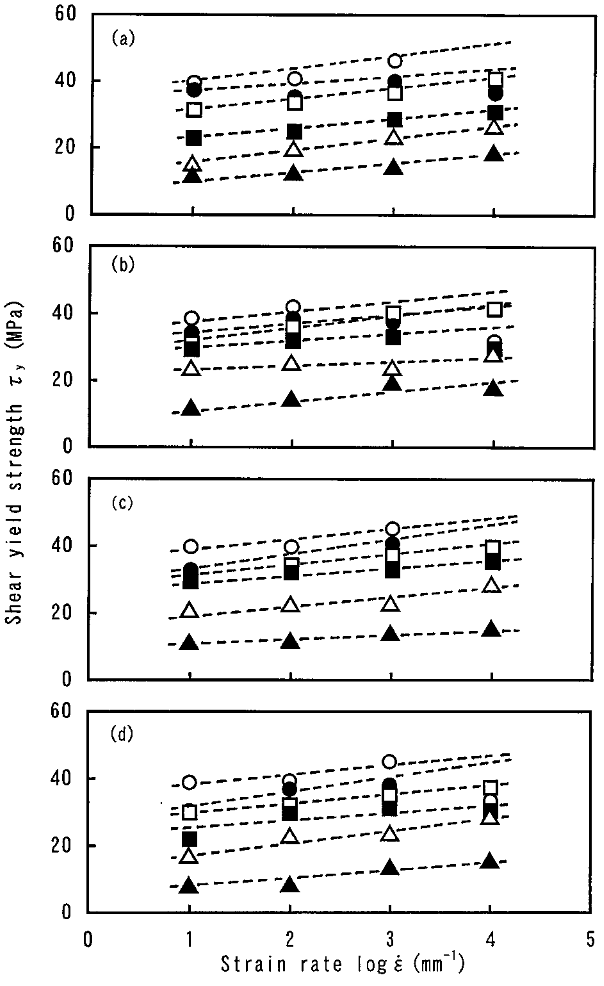

*Figure 2* Relation between strain rate and shear yield strength at various temperatures. (a) Sample A, (b) sample B, (c) sample C, (d) sample D. ○, 40 °C; ●, 60 °C; □, 70 °C; ■, 80 °C; △, 90 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

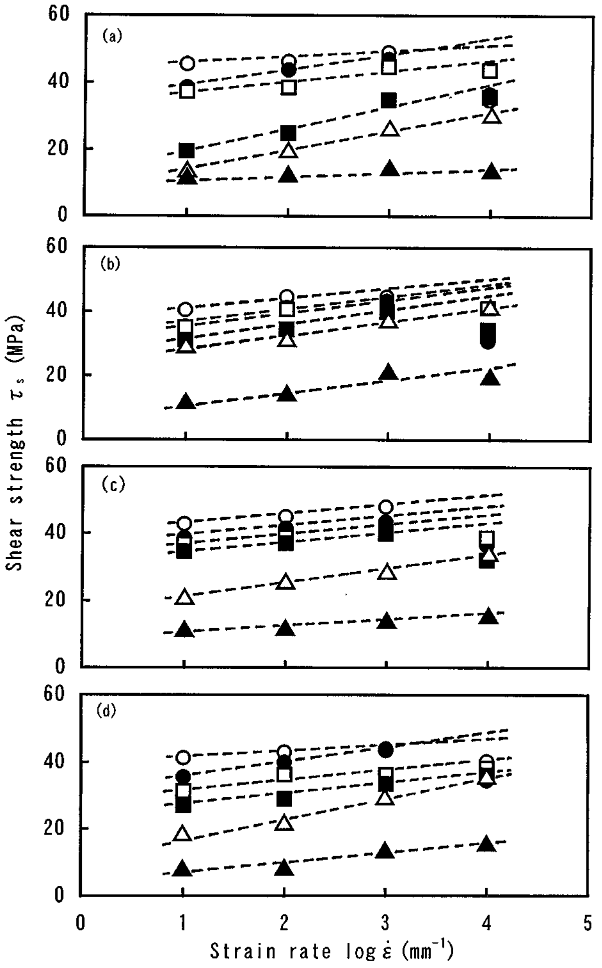

*Figure 3* Relation between strain rate and shear strength at various temperatures. (a) Sample A, (b) sample B, (c) sample C, (d) sample D. ○, 40 °C; ●, 60 °C; □, 70 °C; ■, 80 °C; △, 90 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

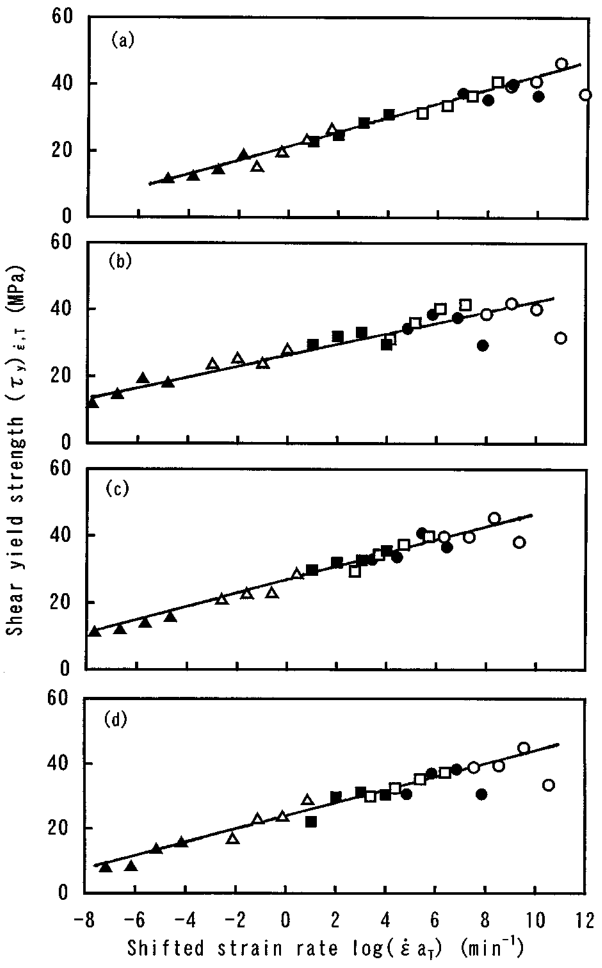

*Figure 4* Shear yield strength master curve: reference temperature is 80 °C. (a) Sample A, (b) sample B, (c) sample C, (d) sample D. ○, 40 °C; ●, 60 °C; □, 70 °C; ■, 80 °C; △, 90 °C; ▲, 100 °C. –, values calculated from Equation 2. Refer to Table I for the sample symbols.

However, both the shear yield strength and shear strength at a higher strain rate and lower temperature range was considerably smaller. A possible cause for this was brittle fracture effected strongly by local defects. It is conceivable that the effect of local defects on the shear properties is remarkable at a lower temperature and higher strain rate.

Data in Figs 2 and 3 have been shifted along the logarithm of the strain rate axis to obtain master curves of the shear properties, as shown in Figs 4 and 5. In these figures, the reference temperature is 80 °C (curing temperature). Although there exists a slight deviation in all cases of molecular weight between cross-linkings, it is possible to reduce the data to a single master curve. This implies that the strain rate-temperature superposition holds for the shear yield strength and the shear strength.

The shear yield strength, $(\tau_y)_{\dot{\varepsilon},T}$, shown in Fig. 4a–d increases almost linearly, which is the same tendency as the results of the tensile yield stress of some macromolecule materials [13, 14] and glass bead-filled composites [15]. We have also found the same tendency for the shear yield strength at the fiber-matrix interphase for glass fiber-thermosetting resin systems [8, 16], a carbon fiber-epoxy resin system [7, 8], and epoxy resins with various mixing ratios of curing agent [9], i.e., the shear yield strength, $(\tau_y)_{\dot{\varepsilon},T}$, of epoxy resin increases in proportion to the logarithm of the shifted strain rate, log $(\dot{\varepsilon}a_T)$. The strain rate and temperature dependence of the shear yield strength, $(\tau_y)_{\dot{\varepsilon},T}$, can be related by the following equation

$$(\tau_y)_{\dot{\varepsilon},T} = K_1 + K_2 \log(\dot{\varepsilon}a_T) \qquad (2)$$

where $\dot{\varepsilon}$ is the strain rate, $a_T$ is the shift factor and subscript $T$ represents the environmental temperature. $K_1$ and $K_2$ are constants depending on the material and the reference temperature. $K_1$ and $K_2$ obtained from Fig. 4 are shown in Fig. 6, with $K_2$ being the gradient in Equation 2 and remaining almost unchanged regardless of the molecular weight between cross-linkings, while $K_1$ is the point of the intersection in Equation 2 which begins decreasing with the increase in the molecular weight between cross-linkings.

The relationship between the logarithm of the shift factor to obtain these master curves and the reciprocal of absolute temperature is shown in Fig. 7. The shift factors, $\log(a_T)$, give essentially straight lines, but they have an inflection point in the range of 70–80 °C, i.e., the shift factors to obtain the master curves of the shear

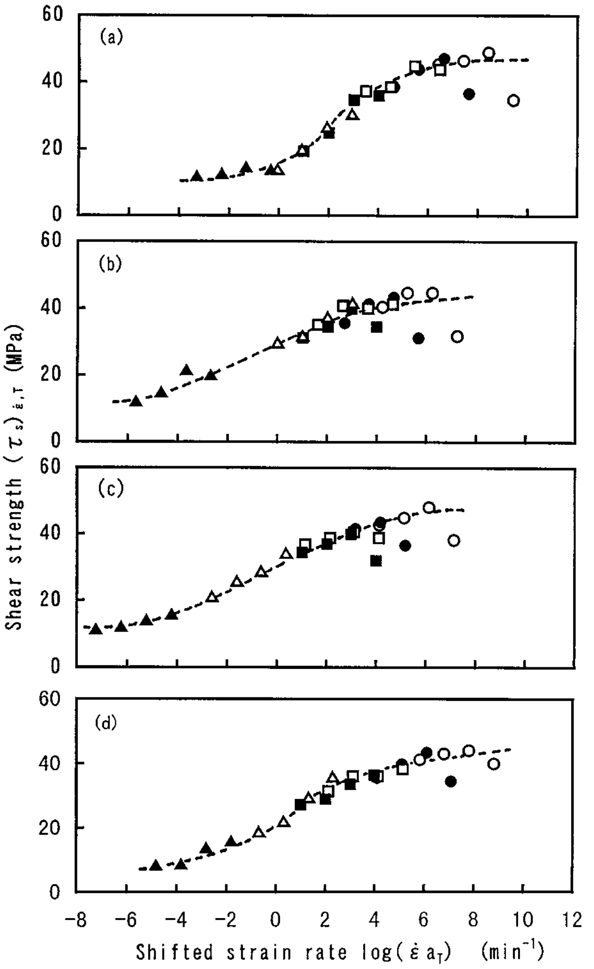

*Figure 5* Shear strength master curve: reference temperature is 80 °C. (a) Sample A, (b) sample B, (c) sample C, (d) sample D. ○, 40 °C; ●, 60 °C; □, 70 °C; ■, 80 °C; △, 90 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

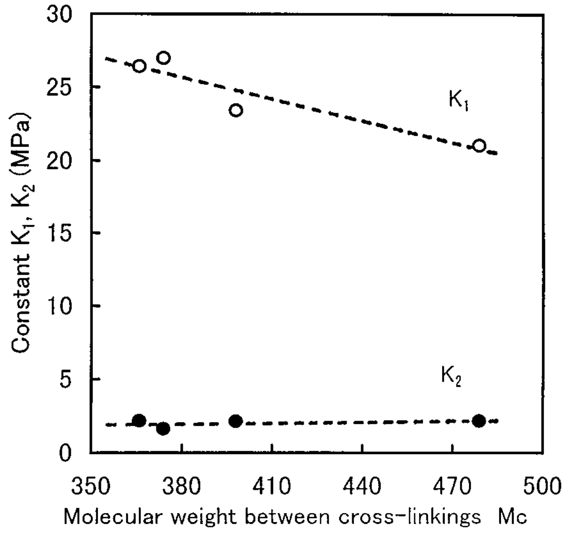

*Figure 6* Relation between constants $K_1$ and $K_2$ in Equation 2 and molecular weight between cross-linkings. ○, $K_1$; ●, $K_2$.

yield strength and the shear strength are all given a temperature dependence of an Arrhenius type.

Apparent activation energy, $\Delta H$, obtained from the gradient of the straight lines (Fig. 7), is shown in Fig. 8. The $\Delta H$ at a lower temperature range is lower than that at a higher temperature range. For both the shear yield strength and the shear strength, the $\Delta H$ increases with increasing molecular weight between cross-linkings at a lower temperature range, while it decreases at a higher temperature range. At a lower temperature range where epoxy resin is the glass state, the higher $\Delta H$ is necessary to move a molecule with higher molecular weight between cross-linkings, i.e., a larger molecule, while at a higher temperature range where it is the rubber state, the mobility of a molecule increases, but the higher $\Delta H$ is necessary to move many cross-linkings which means lower molecular weight between cross-linkings.

The temperature, $T_i$, at the inflection point of the shift factors (Fig. 8) is shown in Fig. 9. With these shear properties, the $T_i$ decreases with increasing the molecular weight between cross-linkings. The transition temperature of sample A estimated from modulus (Fig. 1) measured by dynamic mechanical tester (DMT) was 75–80 °C and those of samples (B-D) were 95–100 °C. The inflection temperatures, $T_i$, are lower than those by DMT, however, the difference between samples shows a similar tendency.

As mentioned above, in all cases of molecular weight between linkings, the shear yield strength, $(\tau_y)_{\dot{\varepsilon},T}$, increases almost linearly with the logarithm of the shifted strain rate, and the gradient of straight line is almost the same as shown in Fig. 6. Master curves in Fig. 4 have again been shifted along the logarithm of the shifted strain rate axis to obtain a single master curve as shown in Fig. 10. In this figure, the master curves of epoxy resins (samples A, B, D) with various molecular weights between cross-linkings are reduced to the master curve of epoxy resin (sample C) with about 100% reaction degree. Although there exists a slight deviation, it is possible to reduce the data to a single master curve. This implies that the strain rate-temperature-molecular weight between cross-linkings superposition holds for the shear yield strength, i.e., the shear yield strength of epoxy resin with a higher molecular weight between cross-linkings corresponds to one at a lower strain rate for the epoxy resin with about 100% degree of reaction. The broken line is the value calculated from Equation 2 by using the constants $K_1$, and $K_2$ for sample C as shown in Fig. 6.

Fig. 11 shows a single master curve obtained by again shifting each master curve for the shear strength as shown in Fig. 5 along the logarithm of the shifted strain rate axis. In this figure, the reference curve is the master curve for epoxy resin with about 100% degree of reaction (sample C). Although there exists a considerable deviation at the higher strain rate region, it is possible to reduce the data roughly to a single master curve. The strain rate-temperature-molecular weight between cross-linkings superposition holds also for the shear strength.

Fig. 12 shows the relationship between the logarithm of the shift factor, log ($a_M$), used to obtain a single master curve (Figs 10 and 11) and the molecular weight between cross-linkings. With both the shear yield strength and the shear strength, the increase in the shift factor, $a_M$, is similar to the increase in molecular weight between cross-linkings.

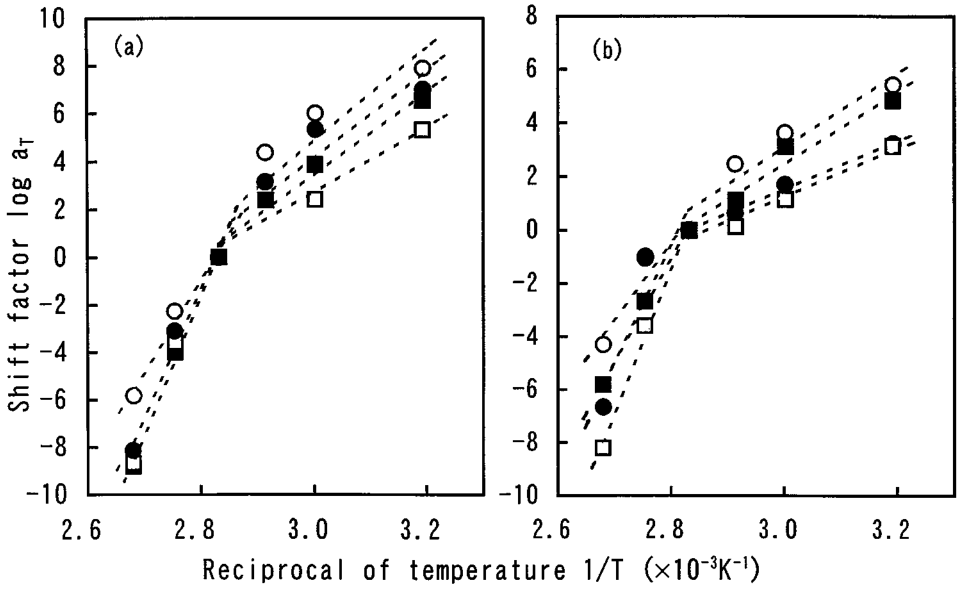

*Figure 7* Shift factors as a function of the reciprocal of temperature. (a) Shear yield strength, (b) shear strength. ○, Sample A; ●, sample B; □, sample C; ■, sample D. Refer to Table I for the sample symbols.

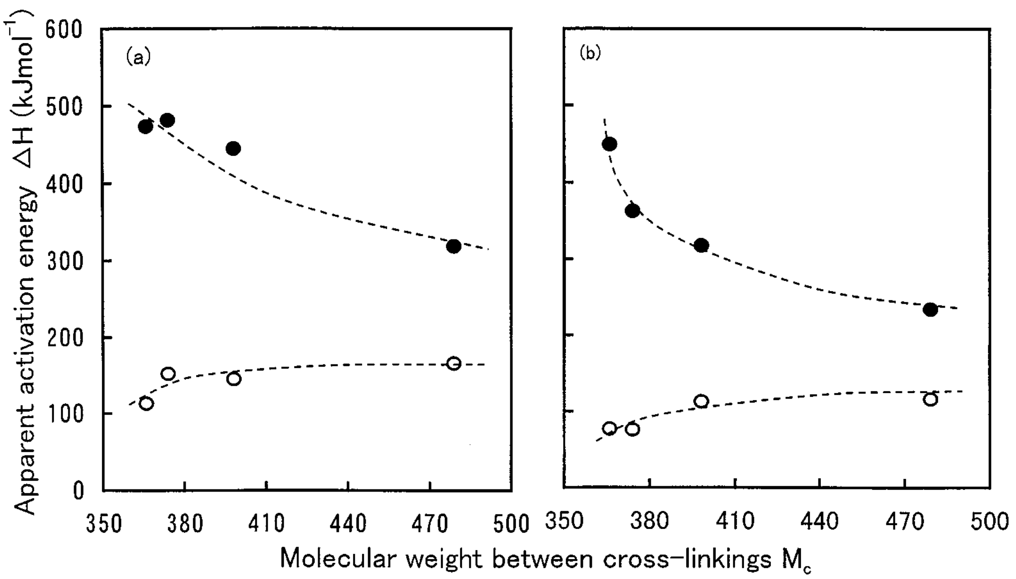

*Figure 8* Relation between apparent activation energy and molecular weight between cross-linkings. (a) Shear yield strength, (b) shear strength. ○, At higher temperature range; ●, at lower temperature range.

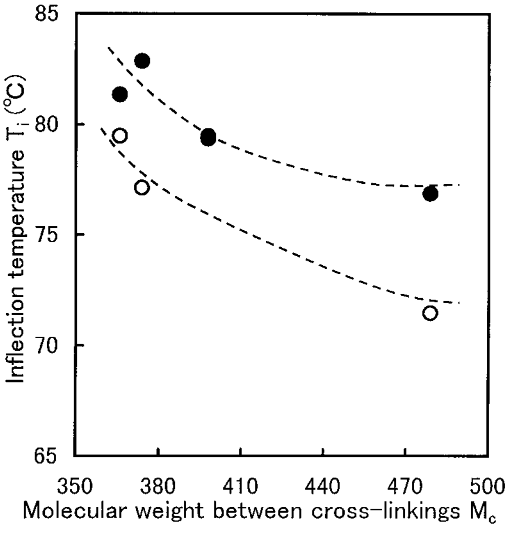

*Figure 9* Relation between inflection temperature and molecular weight between cross-linkings. ○, Shear yield strength, ●, shear strength.

## 4. Conclusions

Epoxy resins with various molecular weights between cross-linkings were prepared by changing ratio of curing agent and epoxy resin. In order to examine the strain rate and temperature dependence of the shear yield strength and the shear strength, test specimens were subjected to shear deformation at various strain rates and temperatures. Both the shear yield strength and the shear strength increased almost linearly as the logarithm of the strain rate increased. Furthermore, the strain rate-temperature superposition held for both shear properties. In particular, an experimental equation of the strain rate-temperature superposition for the shear yield strength was found. The shift factor to obtain a master curve was given with the temperature dependence of an Arrhenius type. Apparent activation energy at lower temperature range was lower than that at a higher temperature range. As the molecular weight between cross-linkings increased, apparent activation

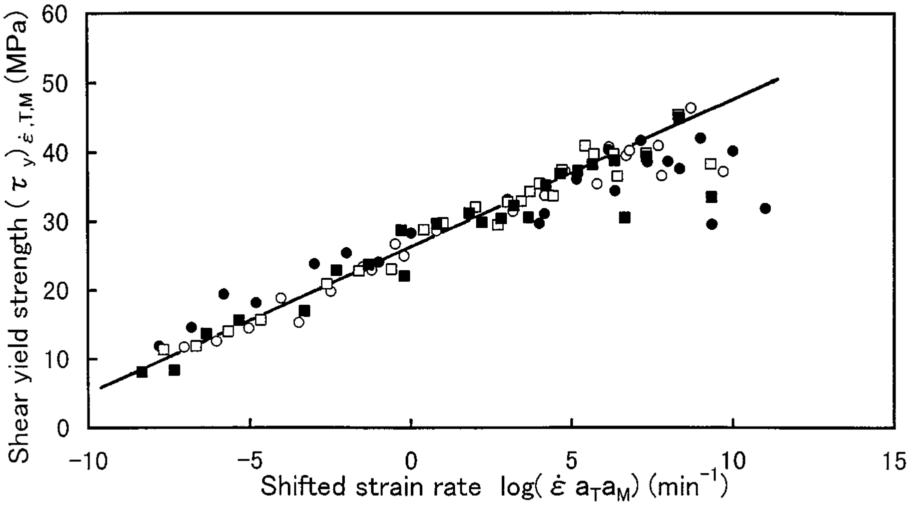

*Figure 10* Shear yield strength master curve: reference sample is C. ○, Sample A; ●, sample B; □, sample C; ■, sample D; —, value calculated from Equation 2. Refer to Table I for the sample symbols.

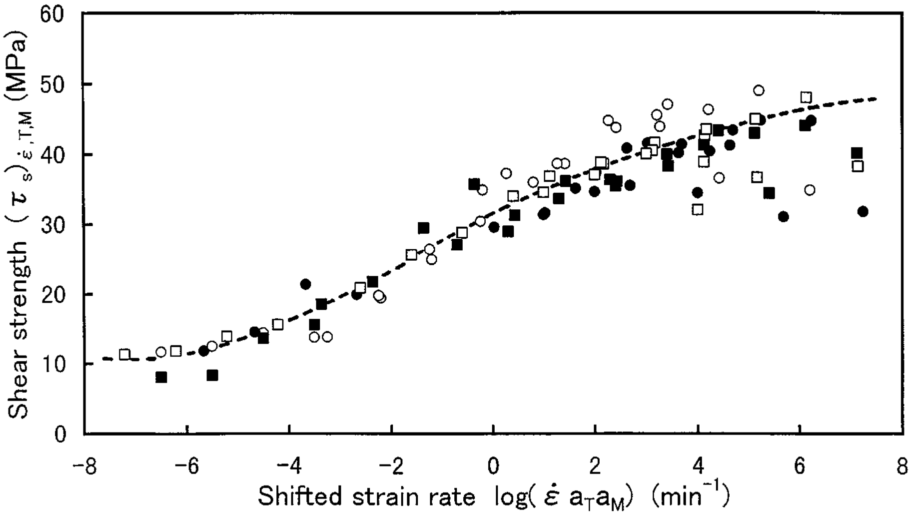

*Figure 11* Shear strength master curve: reference sample is C. ○, Sample A; ●, sample B; □, sample C; ■, sample D. Refer to Table I for the sample symbols.

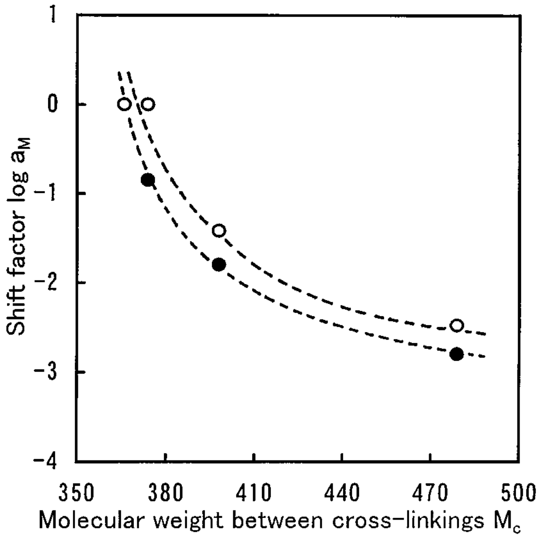

*Figure 12* Shift factors as a function of the molecular weight between cross-linkings. ○, Shear yield strength, ●, shear strength.

energy increased at a lower temperature range and decreased at a higher temperature range. Furthermore, the strain rate-temperature-molecular weight between cross-linkings superposition held for the shear properties, and the shift factor for these superposition increased with the increase in the molecular weight between cross-linkings.

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