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Strain rate and temperature dependence of shear properties of epoxy resin

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Epoxy resins with various ratios from two kinds of curing agents, ethylenediamine (EDA) and N,N′-dimethylethylenediamine (MeEDA), 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 temperature. 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–mixing ratio of curing agent superposition held for the shear properties, and the shift factor for these superpositions increased with the increase in MeEDA.

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 fibre-reinforced composites, the shear strength at the fibre–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 fibre–matrix interphase and the shear yield strength of a resin matrix [6–8].

In this work, resin matrixes with various ratios of curing agents were prepared from two kinds 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 procedure

Epoxy resin used in this study was a bisphenol type (Epikote 828, Yuka Shell Epoxy) (Fig. 1). Curing agents were a ethylenediamine (EDA, Nakalaytesk) and a N,N′-dimethylethylenediamine (MeEDA, Tokyo-kaseikogyo) (Fig. 2). These resin and curing agents were mixed to prepare epoxy materials with five mixing ratios of curing agents as shown in Table I; i.e., quantities of EDA and MeEDA were weighed at 4:3:2:1:1:0 and 0:1:2:3:4 (by weight ratio), respectively. Hereafter, specimens were designated with the symbols A, B, C, D, E (Table I) as the quantity of the curing agent EDA decreases (or MeEDA increases). The quantity of curing agents was decided stoichiometrically.

First, epoxy resin, EDA and MeEDA were weighed with a weight ratio as shown in Table I. Only epoxy resin was defoamed in vacuum at 60 °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 60 °C for 4 h and postcuring at 100 °C for 2 h. The specimen was then allowed to cool to room temperature.

Test specimens were cut from the material prepared in this manner 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 centre 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 a Tensilon UTM-I-2500 (Orientec). Five to eight specimens were tested for each epoxy resin.

3. Results and discussion

Tensile properties of epoxy resins cured with only EDA or MeEDA are shown in Table III. Young's modulus of epoxy resin cured with only EDA (sample A) is larger than that of sample E, while the breaking strain is smaller, i.e., sample A behaved in a brittle and sample E in a ductile manner.

The relationship between shear yield strength, τ_y, at various temperatures and the logarithm of the strain

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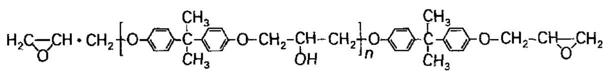

Figure 1 Structure of epoxy resin.

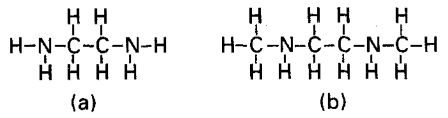

Figure 2 Structure of curing agents. (a) Ethylenediamine (EDA), (b) N,N′-dimethylethylenediamine (MeEDA).

TABLE I Formulation of epoxy resin and curing agents. Epoxy resin is 100 phr

Designation	EDA		MeEDA	
	(Phr)	(Ratio)	(Phr)	(Ratio)
A	7.89	4	0	0
B	5.92	3	5.79	1
C	3.95	2	11.58	2
D	1.97	1	17.37	3
E	0	0	23.16	4

TABLE II Conditions of shear test

Temperature (°C)	20	40	60	80	100
Strain rate (min^{-1})	3.33	33.3	333	3333	

TABLE III Tensile properties of epoxy resin at 20 °C. Strain rate 20 min^{-1}

Properties	Samples	
	A	E
Strength (MPa)	105	69
Young's modulus (MPa)	1502	930
Breaking strain (%)	6.6	13

rate for the epoxy resins with various mixing ratios is shown in Fig. 3 (a–c), while the relationship between shear strength, τ_s, and the logarithm of the strain rate is shown in Fig. 4 (a–c). At all mixing ratios and temperatures, τ_y and τ_s increase almost linearly with the increase in the logarithm of the strain rate. In particular, the slope of the straight line for shear yield strength is almost the same at various temperatures in all cases of mixing ratios. This tendency is the same as that found for the tensile yield properties [9].

Data in Figs 3 and 4 have been shifted along the logarithm of the strain rate axis to obtain master curves of the shear properties, as shown in Figs 5 and 6. In these figures, the reference temperature is 60 °C. Although there exists a slight deviation in all cases of mixing ratios of curing agents, 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. 5 (a–e) increases almost linearly, which is the same tendency as the results of the tensile yield stress of some

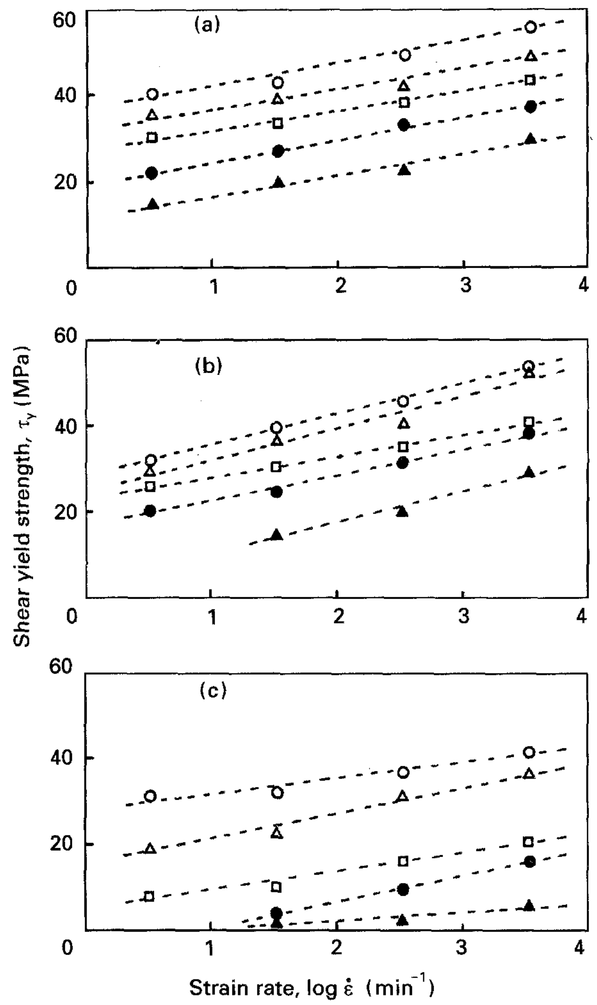

Figure 3 Relation between strain rate and shear yield strength at various temperatures. (a) Sample A, (b) sample C, (c) sample E. ○, 20 °C; △, 40 °C; □, 60 °C; ●, 80 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

macromolecule materials [10, 11] and glass bead-filled composites [12]. We have also found the same tendency for the shear yield strength at the fibre–matrix interphase for glass fibre–thermosetting resin systems [13] and a carbon fibre–epoxy resin system [7], 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

$$(\tau_y)_{\dot{\varepsilon},T} = K_1 + K_2 \log(\dot{\varepsilon}a_T) \qquad (1)$$

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. 5 are shown in Fig. 7, with K_2 being the gradient in Equation 1 and remaining almost unchanged regardless of the mixing ratio of curing agent, while K_1 is the point of the intersection in Equation 1 which begins decreasing with the increase in MeEDA.

The relationship between the logarithm of the shift factor to obtain these master curves and the reciprocal of absolute temperature is shown in Fig. 8. The shift factors, $\log(a_T)$, give essentially straight lines, but they

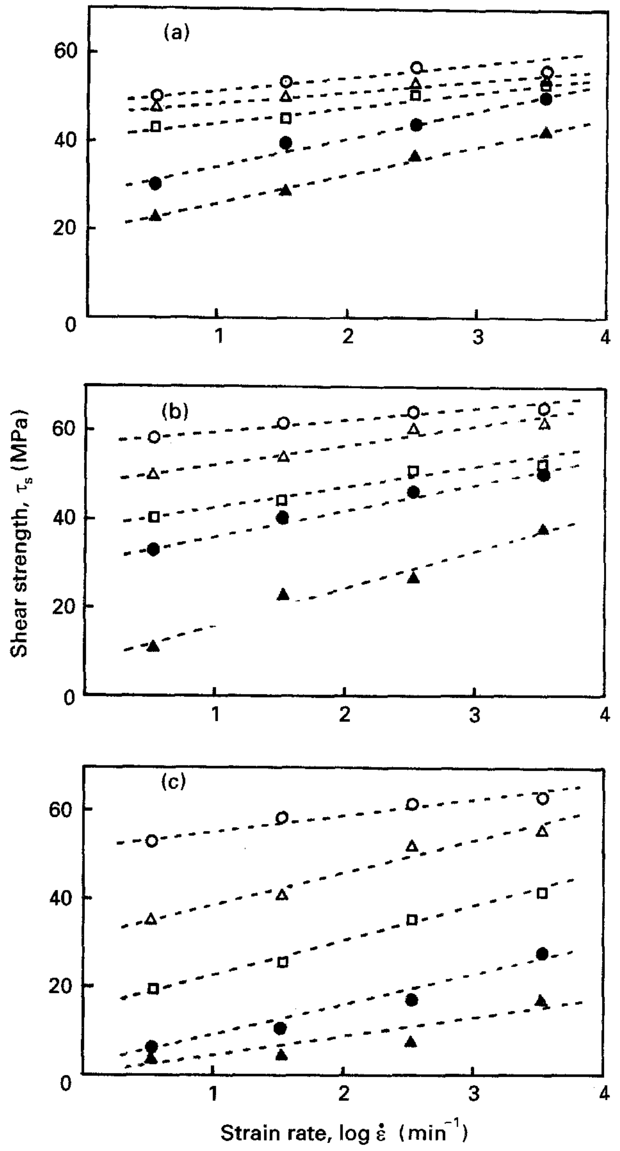

Figure 4 Relation between strain rate and shear strength at various temperatures. (a) Sample A, (b) sample C, (c) sample E. ○, 20 °C; △, 40 °C; □, 60 °C; ●, 80 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

have an inflection point in the range of 50–70 °C, i.e., the shift factors to obtain the master curves of the shear yield strength and the shear strength are all given a temperature dependence of an Arrhenius type.

Apparent activation energy, ΔH, obtained from the gradient of the straight lines (Fig. 8), is shown in Fig. 9. The ΔH at a lower temperature range is lower than that at a higher temperature range. In both temperature ranges, the ΔH of epoxy resin increases as the mixing ratio of MeEDA increases. It is conceivable that these results may be caused by two methyl groups at both ends of the MeEDA.

The temperature, T_i, at the inflection point of the shift factors (Fig. 8) is shown in Fig. 10. With these shear properties, the T_i decrease with increasing the MeEDA. For the shear yield strength, the T_i for samples A–D was almost the same as the transition temperature (about 61 °C) of sample A cured with only EDA measured by differential scanning calorimetry (DSC). The T_i for sample E cured with only the MeEDA was almost the same as the transition temperature (about 42 °C) of the sample. Regarding the shear strength, the T_i was almost the same as the transition temperature of sample A cured with only the EDA. Therefore, it is recognized that the thermal property of epoxy resin is reflected in the shear yield strength rather than in the shear strength.

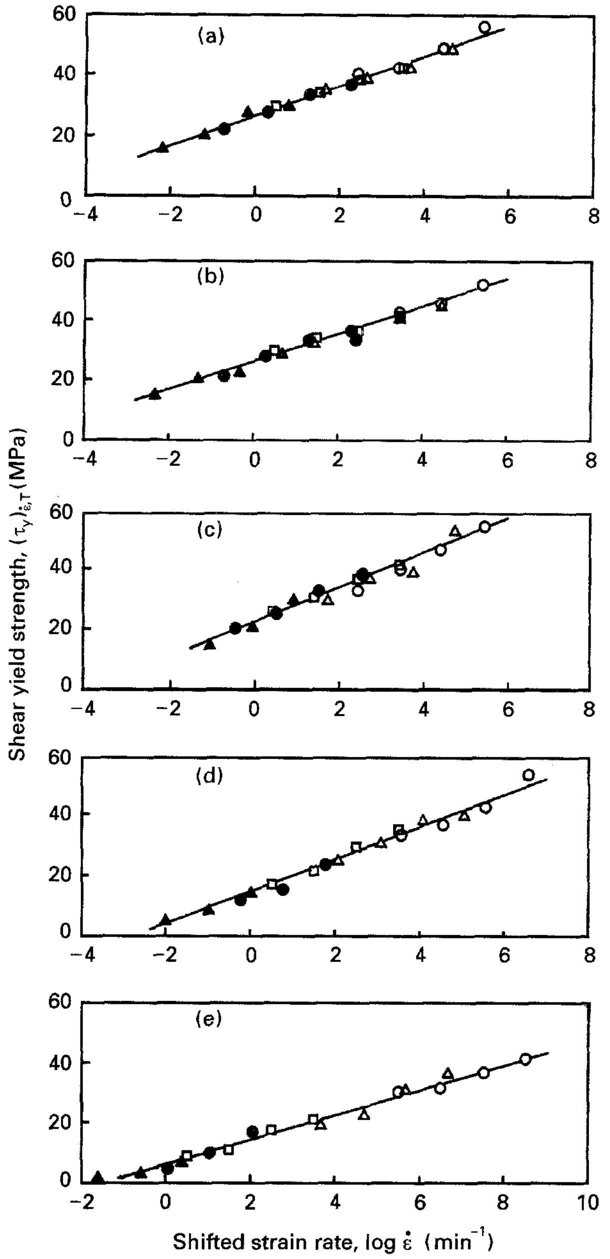

Figure 5 Shear yield strength master curve: reference temperature is 60 °C. (a) Sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E. ○, 20 °C; △, 40 °C; □, 60 °C; ●, 80 °C; ▲, 100 °C; –, values calculated from Equation 1. Refer to Table I for the sample symbols.

As mentioned above, in all cases of mixing ratio of the curing agent, 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. 7. Master curves in Fig. 5 have again been shifted along the logarithm of the shifted strain rate axis to obtain a single master curve as shown in Fig. 11. In this figure, the master curves of epoxy resins (samples B–E) with various mixing ratios are reduced to the master curve of epoxy resin (sample A) with only the EDA. Although there exists a slight deviation, it is possible to reduce the

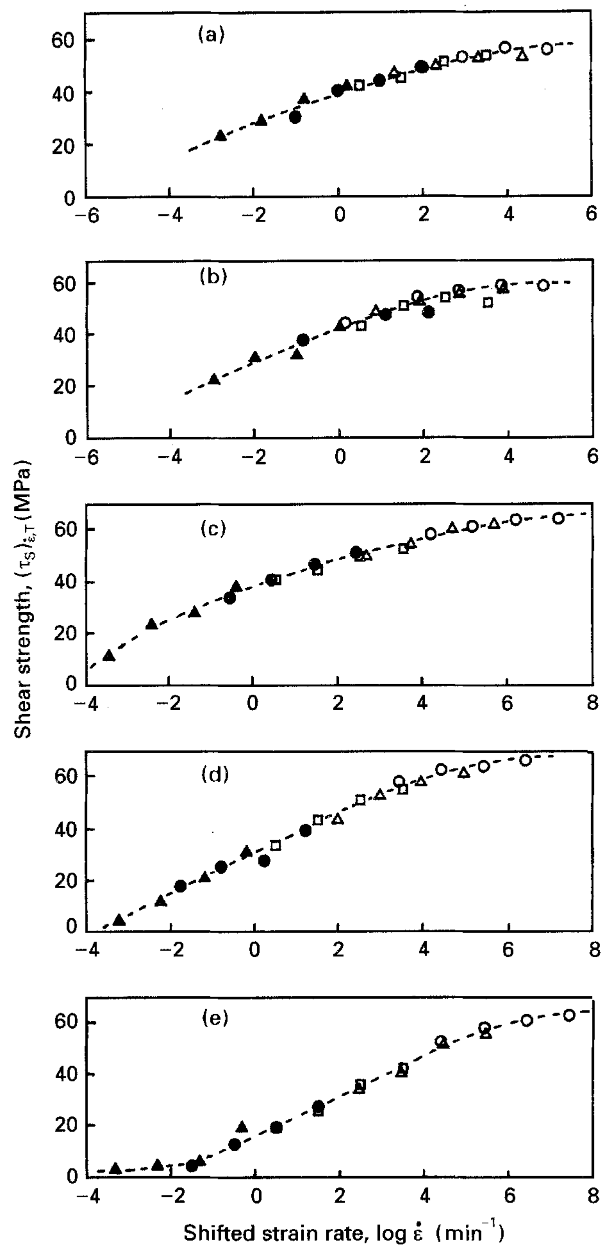

Figure 6 Shear strength master curve: reference temperature is 60 °C. (a) Sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E. ○, 20 °C; △, 40 °C; □, 60 °C; ●, 80 °C; ▲, 100 °C. Refer to Table I for the sample symbols.

data to a single master curve. This implies that the strain rate–temperature-mixing ratio of curing agent superposition holds for the shear yield strength, i.e., the shear yield strength of epoxy resin cured with a higher ratio of the MeEDA corresponds to one at a lower strain rate for the epoxy resin cured with only the EDA. The solid line is the value calculated from Equation 1 by using the constants K_1, and K_2 for sample A as shown in Fig. 7.

Fig. 12 shows a single master curve obtained by again shifting each master curve for the shear strength as shown in Fig. 6 along the logarithm of the shifted strain rate axis. In this figure, the reference curve is the master curve for epoxy resin cured with only the EDA (sample A). 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-mixing ratio of curing agent superposition holds also for the shear strength.

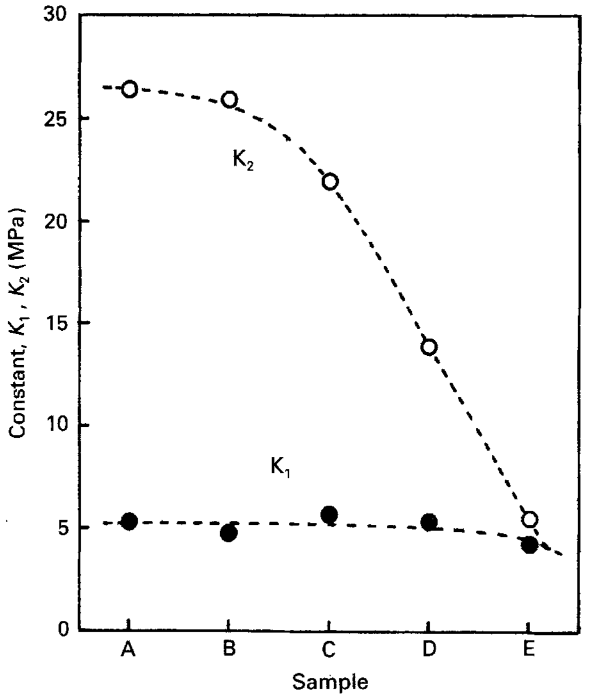

Figure 7 Relation between constants K_1 and K_2 in Equation 1 and curing agent ratio. Refer to Table I for the sample symbols.

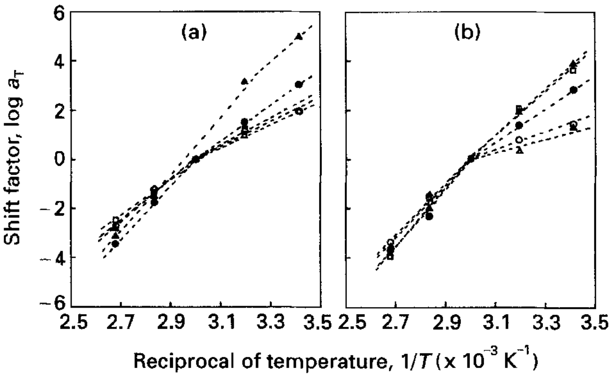

Figure 8 Shift factors as a function of the reciprocal of temperature. (a) Shear yield strength, (b) shear strength. ○, Sample A; △, sample B; □, sample C; ●, sample D; ▲, sample E. Refer to Table I for the sample symbols.

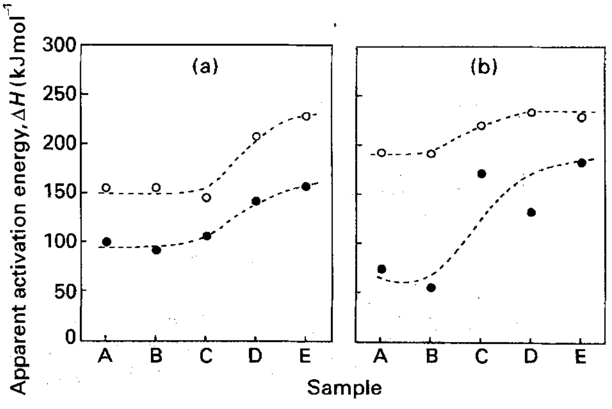

Figure 9 Relation between apparent activation energy and curing agent ratio. (a) Shear yield strength, (b) shear strength. ○, At higher temperature range; ●, at lower temperature range. Refer to Table I for the sample symbols.

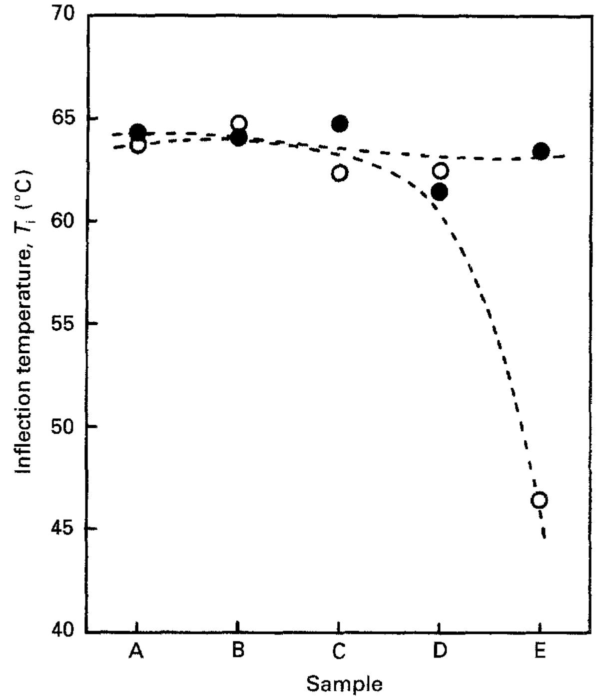

Figure 10 Relation between inflection temperature and curing agent ratio. ○, Shear yield strength, ●, shear strength. Refer to Table I for the sample symbols.

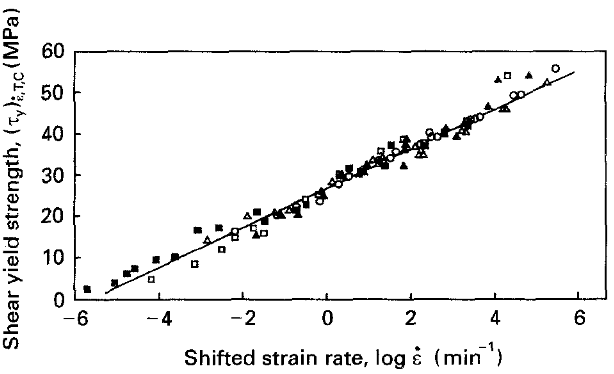

Figure 11 Shear yield strength master curve: reference sample is A. ○, Sample A; △, sample B; ▲, sample C; □, sample D; ■, sample E; values calculated from Equation 1. Refer to Table I for the sample symbols.

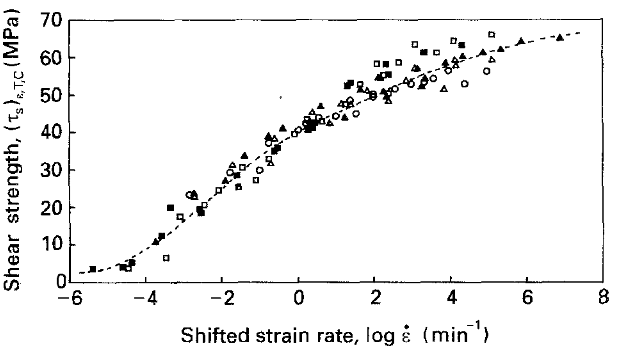

Figure 12 Shear strength master curve: reference sample is A. ○, Sample A; △, sample B; ▲, sample C; □, sample D; ■, sample E. Refer to Table I for the sample symbols.

Fig. 13 shows the relationship between the logarithm of the shift factor, log($a_{T,C}$), used to obtain a single master curve (Figs 11 and 12) and the mixing ratio of the curing agent. With both the shear yield

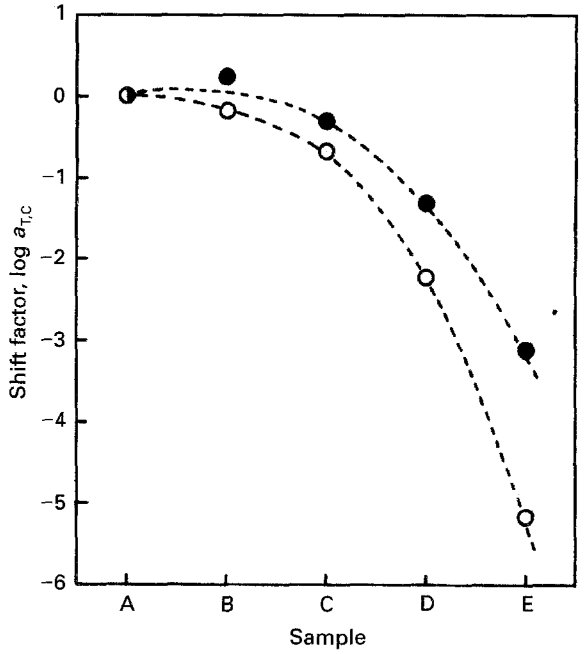

Figure 13 Shift factors as a function of the curing agent ratio. ○, shear yield strength; ●, shear strength. Refer to Table I for the sample symbols.

strength and the shear strength, the increase in the shift factor, $a_{T,C}$, is similar to the increase in MeEDA.

4. Conclusions

Epoxy resins with various ratios from two kinds of curing agents, ethylenediamine (EDA) and N,N′-dimethylethylenediamine (MeEDA), 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. Furthermore, 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. Apparent activation energy at the lower temperature range was lower than that at a higher temperature range. In both temperature ranges the apparent activation energy increased with an increase in the MeEDA. Furthermore, the strain rate–temperature-mixing ratio of curing agent superposition held for the shear properties, and the shift factor for these superpositions increased with the increase in the MeEDA.

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