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Flexural properties and dynamic mechanical properties of glass fibre–epoxy composites

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The viscoelastic behaviour of glass fibre (GF)–epoxy composites was studied by flexural tests and dynamic mechanical measurements. In relation, the influence of surface treatment of GF on viscoelastic behaviour was also examined. Using the results of flexural tests under a variety of constant temperature and strain rate, master curves of flexural strength (σ) and flexural strain (ε) were obtained for matrix epoxy and GF composites. The magnitudes of the master curves were different between matrix epoxy and GF composites. The fracture mode was influenced by temperature, strain rate, and GF surface treatment. The magnitude of storage modulus and effectiveness of adhesion at the GF–matrix interface were also influenced by GF surface treatment. Relationship between the results of flexural strain and loss modulus were considered for GF composites.

1. Introduction

It is well known that the mechanical properties of polymer materials show remarkable dependence upon time and temperature [1], i.e. polymer materials show viscoelastic behaviour. Polymer composites are also expected to exhibit similar behaviour; however, studies on viscoelastic behaviour of polymer composites are relatively rare. Time and temperature dependence of fracture strengths of glass fibre (GF)–unsaturated polyester [2] and carbon fibre (CF)–epoxy composites [3] have been studied. However, no consideration was given as to how the fibre surface treatments affect the viscoelastic behaviour of the composites. Several studies on dynamic mechanical analysis of polymer composites have been presented recently [4–9]; however, the relationship between dynamic mechanical properties and fracture behaviour has been little examined.

The purpose of this work was to obtain fundamental information concerning the viscoelastic properties of GF–epoxy composites. In relation, the influence of GF surface treatment was studied. Time and temperature dependence of flexural fracture properties and dynamic mechanical properties of GF composites were examined, and the relationship between these results was also investigated.

2. Experimental details

2.1. Materials

The epoxy resin used was a mixture of diglycidyl ether of bisphenol-A (Epikote 828, Yuka-shell Epoxy Co.) and curing reagent, 3,9, -*bis* (3-aminopropyl)-2,4,8,10-tetraoxaspiro (5,5) undercane (B-002W, Yuka-shell Epoxy). These were used in a stoichiometric ratio of 2 : 1.

Type E GF woven cloths YES-2101 were purchased from Nippon Glass Fibre Co. The cloths were treated with two kinds of silane coupling reagents, γ-glycidoxypropyltrimethoxysilane (ES) and vinyltris (β-methoxyethoxy)–silane (VS). GF woven cloths with only heat cleaning treatment (HC) were also used in the measurement of dynamic mechanical properties.

GF composite plates were prepared by a hand-lay-up method using seven sheets (for flexural test) or two sheets (for dynamic mechanical test) of GF woven cloths. The volume ratio of GF content was regarded as constant ($\sim$ 25 vol %). GF composite plates containing surface treated GF are denoted ES-P, VS-P, and HC-P.

Epoxy resin and composite plates were cured at room temperature for 24 h, and then at 80° C for 3 h. Samples for measurements were cut to dimensions 12.5 mm × 70 mm × 3.5 mm (for flexural tests) or 50 mm × 5 mm × 1 mm (for dynamic mechanical tests).

2.2. Measurements

An Instron testing instruments model 1114 was used for the measurements of flexural properties. The temperature was regulated by an Instron environment chamber. Flexural load was loaded by a three-point bending method. The span (50 mm) was fixed in all the measurements, and the diameter of the loading bar was 10 mm. Strain rates were calculated from the cross-head speed. σ and ε were calculated from maximum load and displacement at maximum load.

Dynamic mechanical properties were measured using a viscoelastic spectrometer VES II (Iwamoto Seisakusho Co.) above room temperature at a frequency of 10 Hz.

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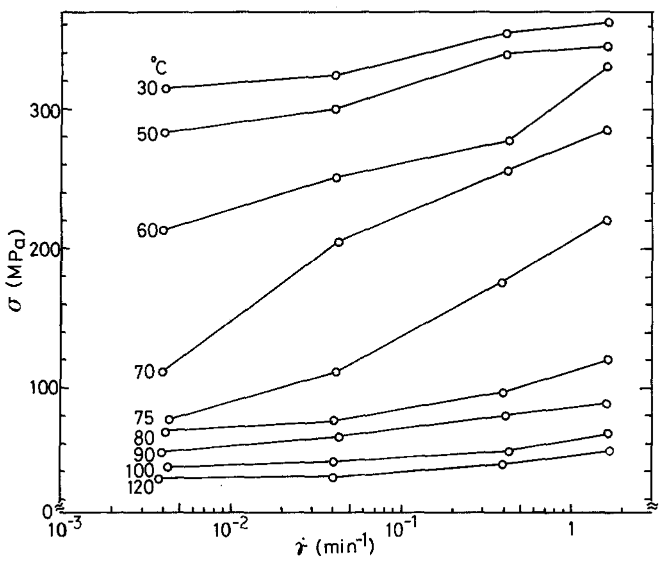


Figure 1 Obtained flexural strength for ES-P as a function of strain rate at various constant temperatures.

3. Results and discussion

3.1. Effect of temperature, strain rate and GF surface treatment on the flexural properties

Figs 1 and 2 show values of σ and ε obtained for ES-P as a function of strain rate ($\dot{\gamma}$) at various constant temperatures. Similar results were obtained for epoxy matrix and VS-P.

Fig. 3 shows the fracture surfaces of GF composites under several different temperatures. The fracture mode could be classified into three types [10].

(a) The fracture was caused at a tensional site. A gross failure of the GF composites was caused by a fracture of GF.

(b) The fracture was caused at the compressive site by shear or buckling, in addition to tensional site fracture.

(c) The fracture was caused at the compressive site and/or at interlaminar positions.

Fig. 4 shows the relationship between σ and ε (so called failure envelopes) of epoxy resin and GF composites. The direction of the arrow represents increasing temperature or decreasing $\dot{\gamma}$. Figure 4 also shows the fracture mode as mentioned above. It is obvious from this figure that failure envelopes could be related to fracture mode. Failure envelopes could be classified into three regions.

(i) ε remaining constant with increasing temperature.

(ii) σ decreasing but ε increasing with increasing temperature.

(iii) Both σ and ε decreasing with increasing temperature.

The boundary of (i) and (ii) is in agreement with T_g of the matrix epoxy. Regions (i) and (ii) correspond to the fracture mode A and B. Region (iii) corresponds to the fracture mode C. The boundary of A and B did not agree with that of (i) and (ii) in Fig. 4. However, there is a tendency in ES-P for fracture A to occur in region (i), and fracture B in region (ii). For VS-P, fracture mode B was manifested in low temperature region. This is due to the poor interfacial adhesion for VS-P. The difference in the magnitude of σ and ε in ES-P and VS-P should be due to the difference in the interfacial adhesion.

It is concluded that fracture mode varied with temperature, $\dot{\gamma}$ and GF surface treatment.

When the curves in Fig. 1 were joined as smoothly as possible to the curve at 60° C, by applying horizontal shift on a logarithmic scale of $\dot{\gamma}$, a master curve of σ for ES-P could be produced. In a similar manner, master curves of σ for epoxy and VS-P were produced. Fig. 5 shows the master curves of σ. Master curves of ε were also obtained as shown in Fig. 6. For the master curves of σ, σ decrease monotonically with decreasing $\dot{\gamma}$ (or increasing temperature), and the shapes of the master curves are similar to each other. On the other hand, master curves of ε have a minimum (for epoxy resin) or maximum value (for GF composites). It is clear from Fig. 2 that ε is dependent on temperature and $\dot{\gamma}$ in a complicated manner, and these results are responsible for the shapes of the master curves of ε.

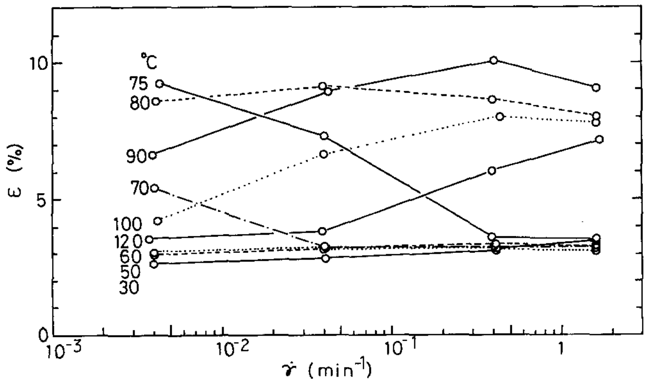


Figure 2 Obtained flexural strain for ES-P as a function of strain rate at various constant temperatures.

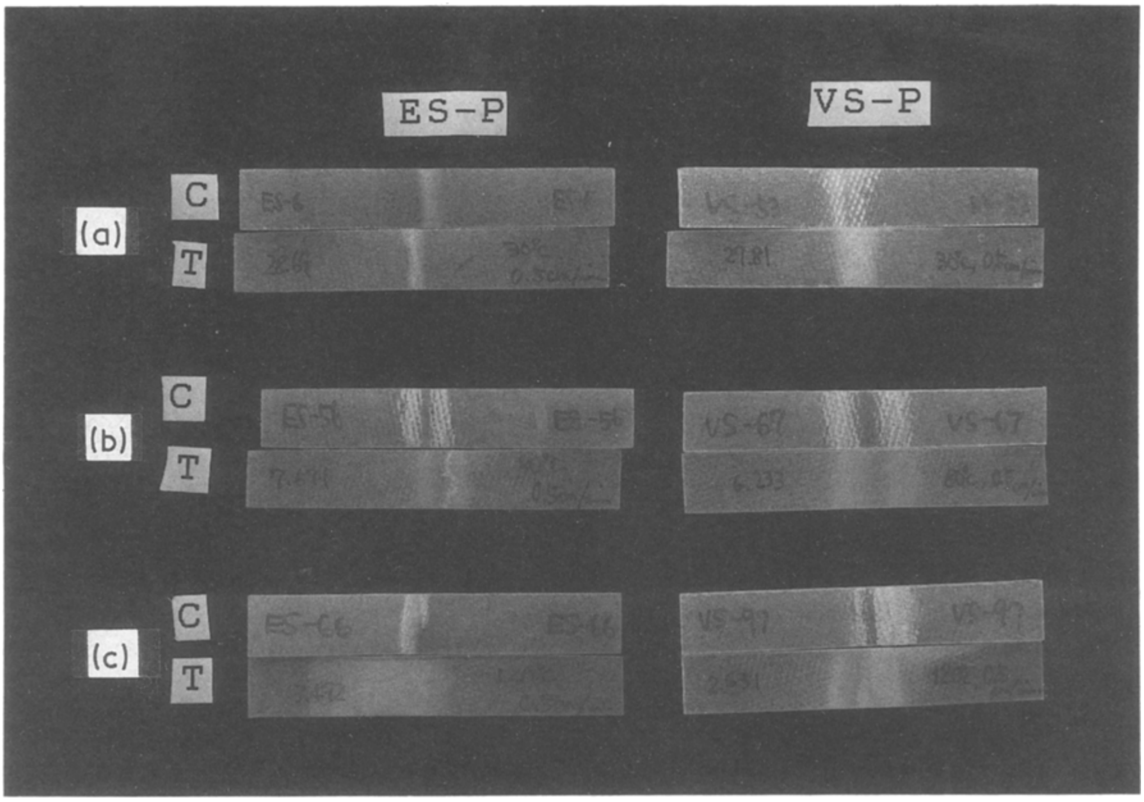


Figure 3 Flexural fracture surfaces of GF composites at several different temperatures. Cross-head speed 0.5 cm min^{-1}; C, compressive site; T, tensional site. Fracture mode: ES-P (a) 30° C, (b) 80° C, (c) 120° C; VS-P (a) 30° C, (b) 80° C, (c) 120° C.

Fig. 7 shows an Arrhenius plot of shift factor, a_T, obtained by production of master curves of σ and ε, for ES-P. Similar plots were also obtained for epoxy and VS-P. As shown in Fig. 5, each plot can be approximated by an Arrhenius equation using two different activation energies

$$\log a_T = \Delta H/2.303R\,(1/T - 1/T_0) \tag{1}$$

where ΔH is the activation energy, R is the gas constant (8.31 J K^{-1} mol^{-1}). ΔH and the temperature of the point of intersection (T_i) obtained from the plot are listed in Table I. All of the values of T_i obtained are closed to T_g of the matrix epoxy resin ($\sim$70° C) obtained by differential scanning calorimetry (DSC) and there are little differences between ΔH. For GF–unsaturated polyester composite, Suzuki and Miyano [2] studied the time and temperature dependence of flexural fracture strengths. They reported that ΔH obtained for GF-composite was in good agreement with that for matrix resin. Similar results were also reported for CF–epoxy [3]. Matrix and fibre are in good adhesion, and the temperature and $\dot{\gamma}$ dependence of fracture behaviour should be determined by the matrix resin. Similar results were also presented for adhesives [11]. In this study, adhesion at the matrix–GF interface for ES-P and VS-P should be not so clearly different as to manifest clearly a difference of ΔH.

TABLE I ΔH and the temperature of the point of intersection (T_i) obtained from Arrhenius plots

	ΔH (kJ K^{-1} mol^{-1})		T_i (K)
	low	high	
Resin	177	461	332.4
ES-P	149	430	335.0
VS-P	134	394	333.8

3.2. Relation between dynamic mechanical properties and flexural properties

Fig. 8 shows the temperature dependence of the storage moduli (E') obtained for epoxy, ES-P, and VS-P. Fig. 8 also shows the temperature dependence of E' for HC-P as a reference. As seen from this figure, E' values were larger for GF composites than epoxy

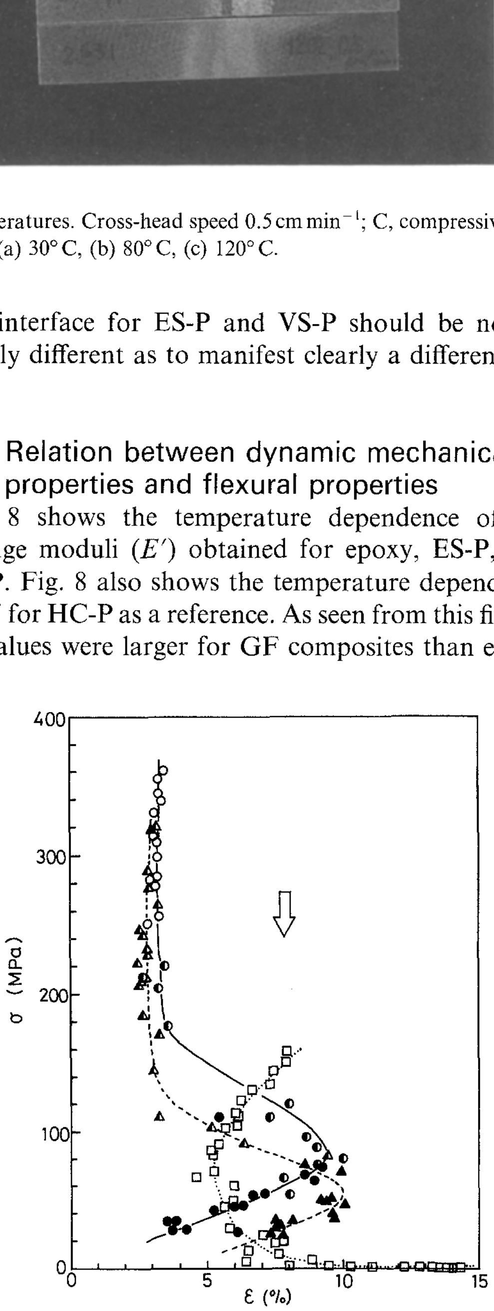


Figure 4 The relationship between σ and ε. (□) Matrix epoxy, (○) ES-P, (△) VS-P. Fracture mode of GF composites is represented as follows: (○) mode A; (◐, ▲) mode B; (●, ▲) mode C.

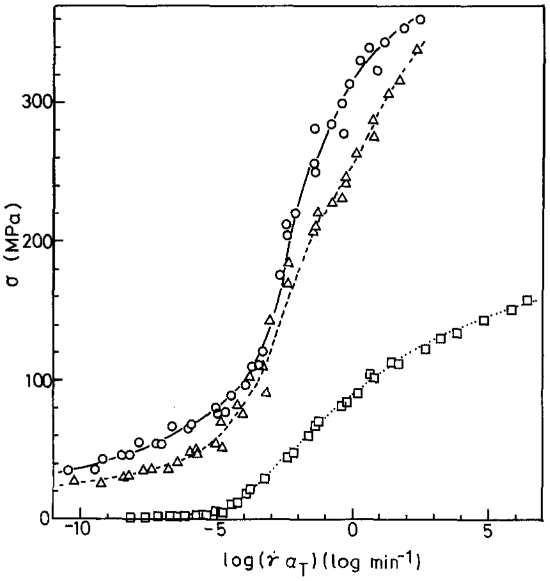


Figure 5 Master curves of flexural strength. (□) Matrix epoxy, (○) ES-P, (△) VS-P.

resin over all the temperature region, and the difference in the moduli was more remarkable in the rubbery region than in the glassy region. Such an increase in E' for composites in the rubbery region has been observed by Souma [8] and Lewis and Nielsen [12]. The magnitude of E' for GF composites was ES-P > VS-P over all the temperature region. On considering the results of flexural tests, this order is supposed to be the same as that of adhesion at the GF/epoxy interface. For convenient description of the effectiveness of fillers on the moduli of composites, a coefficient, C, has been introduced [9], such as

$$C = (E'_g/E'_r)_{\text{comp}}/(E'_g/E'_r)_{\text{resin}} \tag{2}$$

where E'_g and E'_r are E' values in the glassy and rubbery regions respectively, and the subscripts refer to the values for composites and matrix resin. The higher is this value, the lower is the effectiveness of the filler. Measured E' values at 50 and 120° C (for epoxy) or 150° C (for composites) were employed as E'_g and E'_r, respectively. Calculated values of C were 0.017 (ES-P), 0.020 (VS-P), and 0.027 (HC-P). This means that effectiveness of GF on E' is influenced by surface treatment of GF. Similar results were reported for the glass beads/epoxy system [8]. For ES-P and VS-P, this difference in C should cause a difference in the fracture mode; however, it should not cause a clear difference in ΔH.

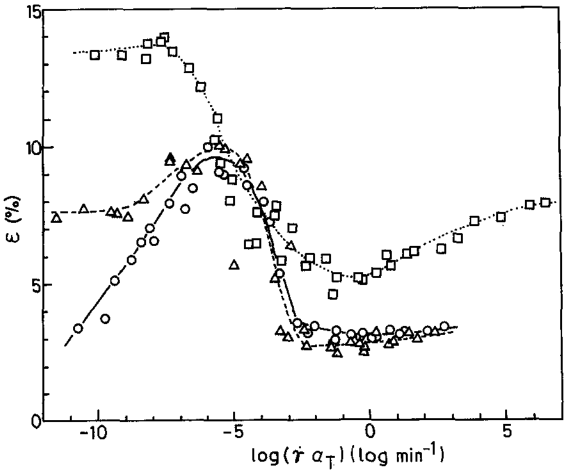


Figure 6 Master curves of flexural strain. (□) Matrix epoxy, (○) ES-P, (△) VS-P.

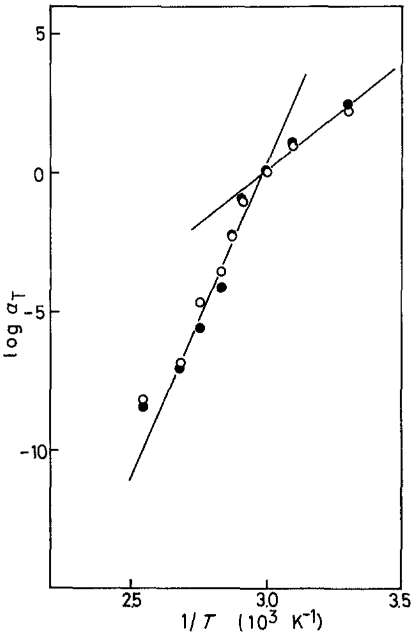


Figure 7 Arrhenius[1] plot of shift factor for ES-P, (○) obtained for σ, (●) obtained for ε.

Fig. 9 shows the temperature dependence of E''. As shown in Fig. 9, temperature dependence of E'' for epoxy has a peak maximum at ~ 75° C. This temperature is nearly equal to T_g obtained by DSC. The temperature dependence of E'' of GF composites also shows a shoulder ~75° C, and in addition, other peaks appear on the higher temperature side. Such peaks appearing on the higher temperature side of α dispersion have been reported by Kodama [4] and Reed [6]. Kodama proposed [4, 5] that the additional

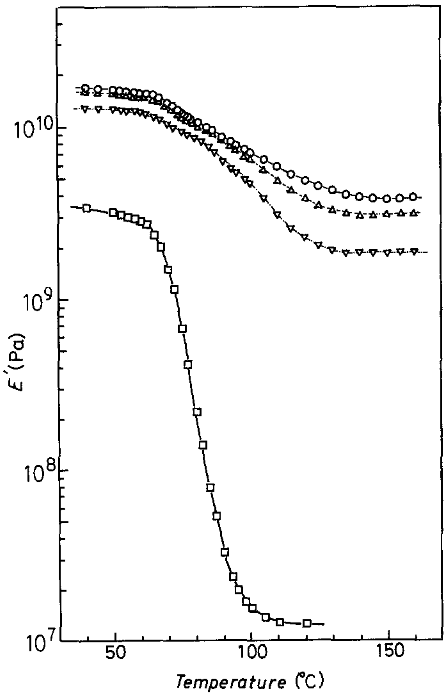


Figure 8 Temperature dependence of E'. (□) Matrix epoxy, (○) ES-P, (△) VS-P, (▽) HC-P.

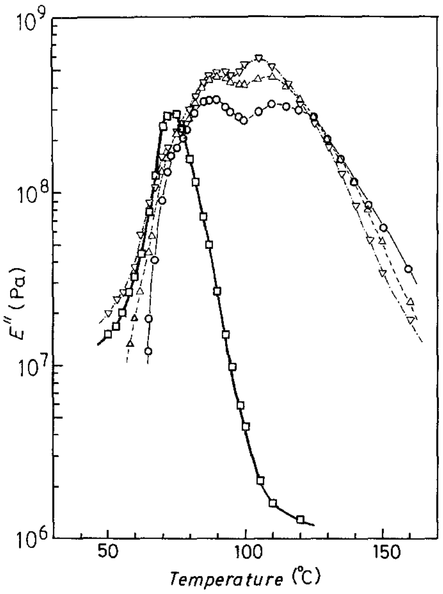


Figure 9 Temperature dependence of E''. (□) Matrix epoxy, (○) ES-P, (△) VS-P, (▽) HC-P.

dispersion was further divided according to two mechanisms (α', α''); α' dispersion was attributed to the matrix being strongly constrained by GF (because of lower mobility, constrained resin should exhibit a higher transition temperature compared with the matrix in a less constrained region), and α'' dispersion (at even higher temperature) was attributed to the friction or slippage between GF and the constrained resin. Although Kodama has shown that cyclic loading affected α' and α'' dispersion [5], little detailed consideration has been given to the relation between additional dispersion and fracture behaviour above T_g.

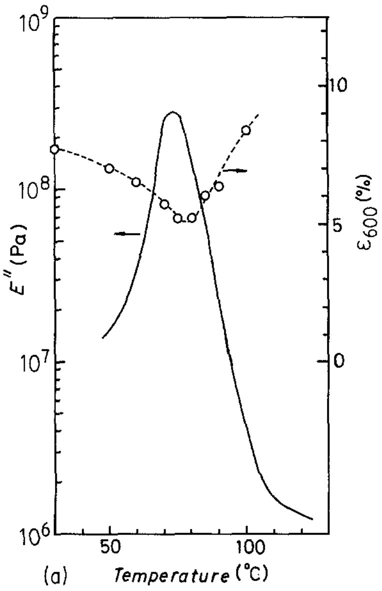
As shown in Figs 2 and 4, ε and the fracture mode depended appreciably upon temperature. Thermal mechanical analysis (TMA) showed that the thermal expansion coefficient (T_e) changed only at T_g for epoxy resin, while for GF composites, T_e changed at ~100 and ~130°C in addition to T_g. In order to clarify the relationship between ε and E'', the hypothetical flexural strains (ε_{600}) were estimated. By using master curves of ε in Fig. 6, ε_{600} were calculated for identical strain rates with dynamic mechanical analysis. Fig. 10 shows the temperature dependence of ε_{600} and E''. From this figure, ε_{600} shows a minimum value at the α dispersion peak temperature for epoxy.

Similar results were observed in Fig. 4. For ES-P and VS-P, ε_{600} increases from the α' (or α) peak temperature, and decreases from the α'' peak temperature. The decrease of ε in this temperature region is due to interlaminar fracture, as mentioned above, α'' dispersion could be ascribed to slippage or friction between GF and interfacial resin as described by Kodama. Although separation of the additional dispersion from log E–$1/T$ curves [4] is not carried out, it can be seen peak height and peak maximum temperature of α' and α'' dispersion are influenced by GF surface treatment. It has been reported for the glass flakes/epoxy system that peak height and peak maximum temperature of the α dispersion were affected by surface treatment of coupling agents [13]. This has been interpreted as interfacial adhesion between GF and matrix resin affecting the α dispersion. A similar situation may hold for α' and α'' dispersions.

4. Conclusions

Flexural fracture modes of GF composites were affected by temperature, strain rate and GF surface treatment. However, a clear difference in ΔH, obtained from the Arrhenius plot of a_T, could not be observed for the different surface treatments of GF.

Additional dispersions observed at higher temperatures for the α dispersion for GF composites were



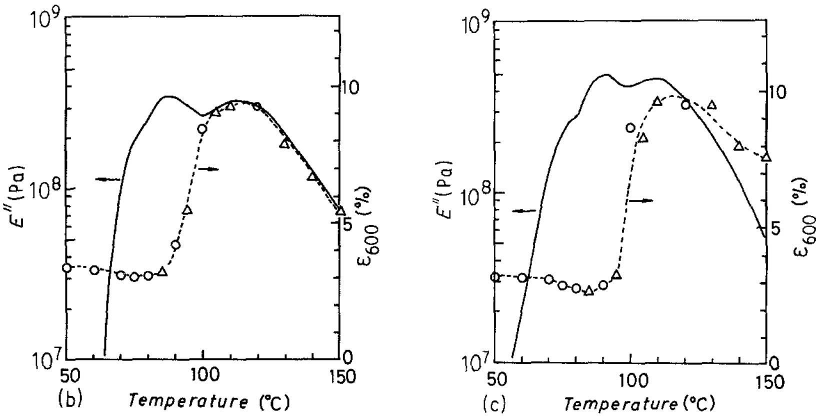


Figure 10 Temperature dependence of E'' and ε_{600}. (a) Matrix epoxy, (b) ES-P, (c) VS-P. (○) Calculated from master curves of ε, (△) calculated from the Arrhenius plot of a_T obtained for ε.

ascribed to the matrix being constrained by GF and interlaminar shear fracture by considering the results of flexural strain and loss modulus.

These results may contribute to the design of composites used in a high-temperature region.

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