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Effect of silicone on dynamic mechanical properties of epoxy resin filled with imide powder

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Abstract—The dynamic mechanical properties of epoxy resin and epoxy-silicone alloy filled with thermoplastic polyimide powder have been studied over a temperature range of −150 to 250°C at the frequencies of 35 and 110 Hz and related to the morphological structure of composites observed by scanning electron microscopy. The incorporation of polyimide raised the glass transition temperature (T_g) of both epoxy resin and epoxy-silicone alloy. The storage modulus (E') of composites increased with increasing volume fraction of imide powder. E' of epoxy-silicone alloy composites was higher than that of epoxy resin though the silicone had a low storage modulus. This fact was explained by assuming that below T_g, the presence of silicone in the matrix facilitated molecular rearrangement during cooling from the cure temperature and above T_g, increased the interaction between filler particles and the matrix.

Keywords: Epoxy resin; silicone; imide powder; dynamic mechanical properties.

1. INTRODUCTION

Many papers have been published on the use of rubber or silicone-modified epoxy resins to improve mechanical properties of materials, particularly toughness [1–6]. The presence of a polysiloxane component in the polymeric system imparts several unique advantages for high performance applications [7, 8]. For instance, polysiloxane reduces water absorption owing to its hydrophobic characteristics. It provides a high resistance to degradation in aggressive oxidizing environments [9] while maintaining the thermal and the mechanical properties and the process ability of the epoxy resin. We have been interested in the properties of epoxy-silicone alloys, especially in the effect of silicone on the mechanical properties.

In this study, the polymer alloy was prepared with epoxy resin and amino-terminated polysiloxane and, then, the thermoplastic polyimide powder was mixed with the epoxy resin or the polymer alloy. The polyimide filler exhibits excellent thermal and mechanical properties at high temperature [10, 11]. The composite was observed with a scanning electron microscope (SEM) and its mechanical properties were studied with dynamic mechanical analysis (DMA). The mechanical properties of the composite are discussed referring to the behavior of silicone and the morphology of the composites.

2. EXPERIMENTAL WORK

2.1. Materials

The epoxy resin is a diglycidyl ether of bisphenol A (DGEBA) supplied by Yuka-Shell Co. (Epicote 828, $M_n = 380$). The siloxane oligomer is an amino-propyl-terminated dimethyl siloxane supplied by Tisso Co. (Silaplane FM 3311, $M_n = 1000$). The curing agent for DGEBA is isophorone diamine (IPD) supplied by Chemische Werke HLS AG. The polyimide powder is thermoplastic polyimide NEW-TPI (T_g = 250°C, T_m = 388°C) supplied by Mitsuitoatsu Kagaku Co.

2.2. Composite preparation

Epoxy-silicone alloy composite was prepared as follows. Epoxy resin and polysiloxane (1% of the total weight of curing mixture) were reacted at 100°C for 1 h, cooled to room temperature and then polyimide powder (in varying volume fractions (ϕ_f) ranging from 0.01 to 0.36) was mixed with homogenizer, cooled again and then IPD (stoichiometric amount) was added. All the components were thoroughly mixed by homogenizer, degassed for 15 min and cured in a silicone rubber case at 80°C for 4 h, and then at 150°C for 1 h. The composites without silicone was prepared under slightly different conditions because of the fast curing during degassing. DGEBA and polyimide powder (volume fractions ranging from 0.01 to 0.18) were mixed with homogenizer, degassed at 60°C for 1 h under mechanical stirring, and cooled to room temperature. Then IPD was added and mixed with a glass rod, degassed for a short time (5–10 min) and cured in silicone case at the same conditions as that of epoxy-silicone alloy composites. As the control samples, epoxy-silicone alloy and epoxy resin without filler were prepared under the respective curing conditions.

The addition of imide powder prevents elimination of voids. This effect is more pronounced in composites without silicone and hence makes it impossible to prepare composites with a high volume fraction (0.36). All the samples were further cured at 150°C for 1 h before the characterization and testing.

2.3. Measurements

The test pieces for dynamic mechanical measurements ($0.2 \times 0.3 \times 5.0$ cm^3) were cut from the cured samples. The storage modulus, loss modulus and $\tan\delta$ were measured over the temperature range of −150 to 250°C, at the frequencies 35 and 110 Hz at a heating rate of 2°C/min, using a dynamic viscoelastometer (DMA), Rheovibron model DDV-EP (Orientec Co.). This apparatus applies a sinusoidal tensile strain to one end of the specimen and measures the stress response at the other end.

The grass transition temperature (T_g) was determined with DMA as the α-peak temperature of loss modulus (E'') at the frequency of 110 Hz. T_g was determined also with differential scanning calorimetry (DSC, using Thermoflex model DSC 10A, Rigaku Co.) at the heating rate of 20°C/min with a sensitivity of 2.5 mcal/s. Linear thermal expansion coefficient (α) was measured with the thermal mechanical analyzer (TMA) unit of the Thermoflex at a heating rate of 5°C/min and sensitivity range of ± 250 μm using $0.2 \times 0.3 \times 2.0$ cm^3 specimens.

The flexural properties were measured according to JIS (Japanese Industrial Standard) K 7203 with rectangular bar $0.3 \times 1.0 \times 8.0$ cm^3 specimens at a crosshead speed of 1 mm/min using an Instron universal testing machine.

The density was determined at 22°C using a pycnometer with water. Scanning electron microscope (JEOL JSM 5200) was used to observe the fractured surfaces of the samples. The fractured surfaces were previously coated with a thin layer of gold by an ion coater.

3. RESULTS

In Fig. 1, T_g is plotted against ϕ_f of filler. All the composites exhibit higher T_g than the respective control samples by 7 to 20°C. The T_g increases with increase in ϕ_f up to 0.04 and then decreases. The epoxy-silicone alloy and its composites have slightly lower T_g than that of epoxy resin.

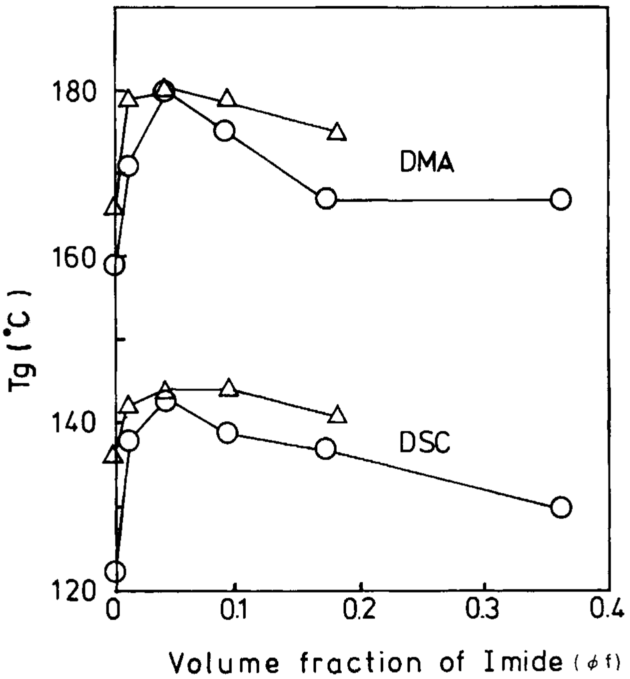

Figure 1. Relation between T_g and volume fraction of polyimide, filler: (○) epoxy-silicone alloy composites; (△) epoxy resin composites.

The storage modulus below T_g (E'_g) and above T_g (E'_r) are represented in Fig. 2. E'_g is almost independent of ϕ_f although E'_r increases with increasing ϕ_f. Both E'_g and E'_r of epoxy-silicone alloy composites are slightly larger than those of epoxy resin composites.

Figure 3 shows the dependence of relative modulus on ϕ_f. The relative modulus of all composites is larger than 1.0 and increases with increase in ϕ_f of polyimide. Below T_g, the relative modulus of epoxy-silicone alloy composites is smaller than that of epoxy resin composite while above T_g, the order is reversed.

Figure 4 shows the relationship between the ratio $\tan\delta_c/\tan\delta_m$ and ϕ_f. Here $\tan\delta_c$ and $\tan\delta_m$ correspond to α-peaks in $\tan\delta$–temperature curves of the composites and unfilled resin or alloy, respectively.

The ratio $\tan\delta_c/\tan\delta_m$ decreased with increasing ϕ_f. The solid line shows the following equation (1), proposed by Nielsen and co-workers [12].

$$\tan\delta_c/\tan\delta_m = (1 - \phi_f). \tag{1}$$

The dependence of the flexural strength on ϕ_f is shown in Fig. 5. The flexural strength decrease with increase in ϕ_f. The flexural strength of epoxy-silicone alloy composites is larger than that of epoxy resin composites at high ϕ_f (0.09).

Dependence of α on ϕ_f is represented in Fig. 6. Both above T_g and below T_g, α decreased with increasing ϕ_f. α of epoxy resin composites is smaller than that of epoxy-silicone alloy composites.

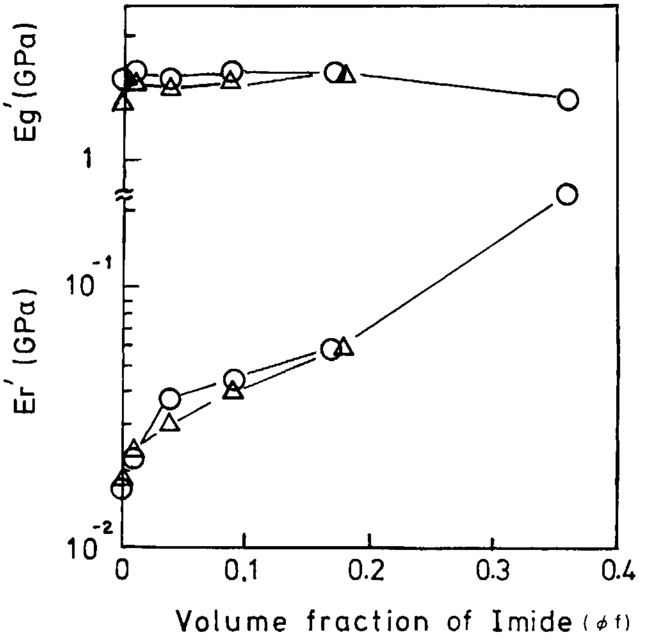

Figure 2. Dependence of storage modulus E'_g (measured at T_g −60°C) and E'_r (measured at T_g +60°C) of the composites on the volume fraction of imide: (○) epoxy-silicone alloy composites; (△) epoxy resin composites.

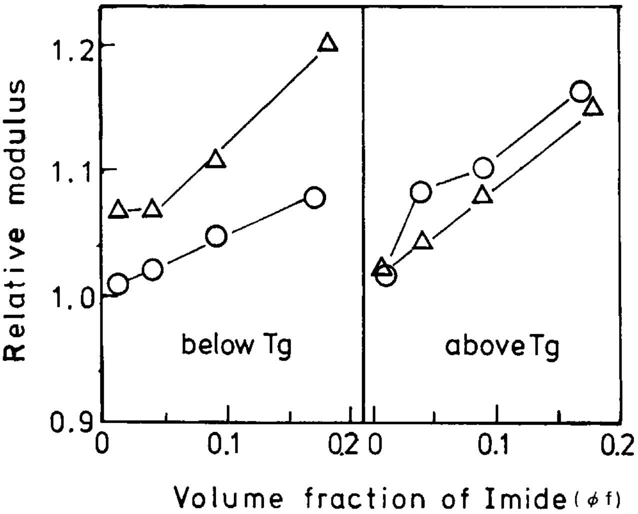

Figure 3. Dependence of relative modulus of the composites, on the volume fraction of polyimide filler: (○) epoxy-silicone alloy composites; (△) epoxy resin composites.

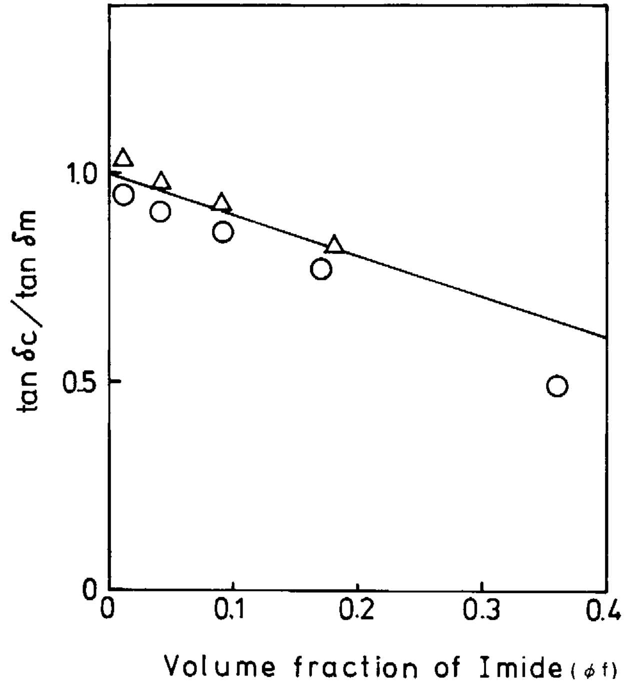

Figure 4. Relation between the ratio $\tan \delta_c / \tan \delta_m$ and volume fraction of polyimide filler. The solid line represents equation (1): (○) epoxy-silicone alloy composites; (△) epoxy resin composites.

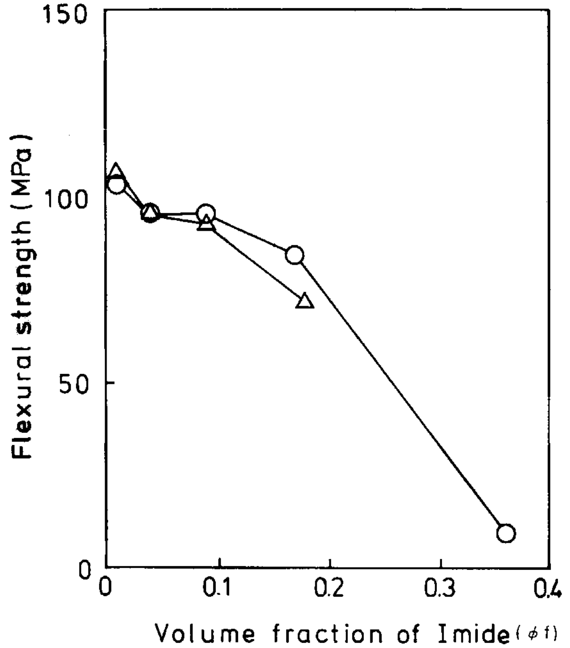

Figure 5. Relation between flexural strength and volume fraction of polyimide filler: (○) epoxy-silicone alloy composites; (△) epoxy resin composites.

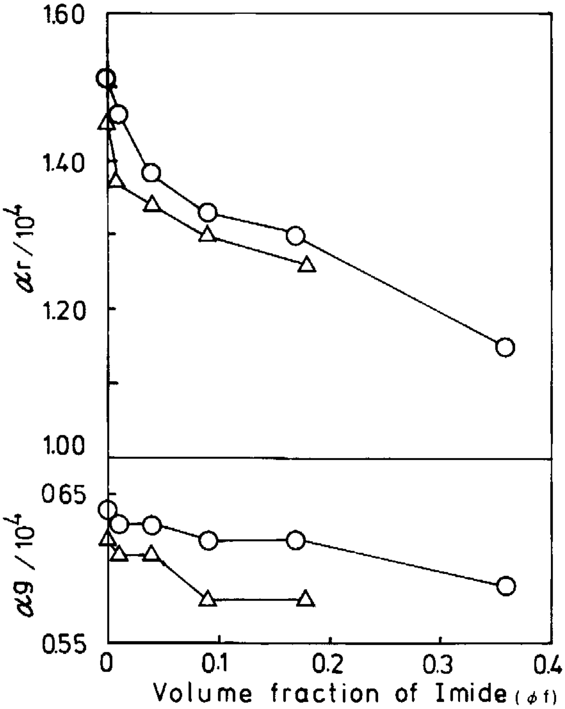

Figure 6. Relation between the coefficient of linear thermal expansion and volume fraction of polyimide filler. α_g, below T_g; α_r, above T_g: (○) epoxy-silicone composites; (△) epoxy composites.

Figure 7 represents the E' and $\tan\delta$ curves of composites with 0.01 volume fraction of filler. The temperature dependence of $\tan\delta$ reveals a small relaxation peak of epoxy-silicone alloy composites in the region of T_g of the silicone polymer with peak at about −124°C.

The morphological structures of the cured epoxy resin and epoxy-silicone alloy are shown in Fig. 8. While the epoxy resin is composed of one phase, the epoxy-silicone alloy has two phase morphology with the silicone rich spherical phase dispersed in the continuous epoxy rich phase. The size of dispersed phase ranges from 0.5 to 2 μm.

The SEM photographs shown in Fig. 9 reveal the fractured surface of composites. As seen in the figure, the filler polyimide particles are agglomerations of fine particles. The agglomerate particles are not covered completely with the matrices and there remain some voids between them. The composite of epoxy resin contains more residual voids than that of the epoxy-silicone alloy. The structure of matrix is not affected by the addition of the filler. The density of composites is listed in Table 1. The density was calculated from the measured density of the matrices and the density of the filler obtained from the manufacturer. The filler added to high volume fraction causes discrepancy between the calculated density and the measured density. The

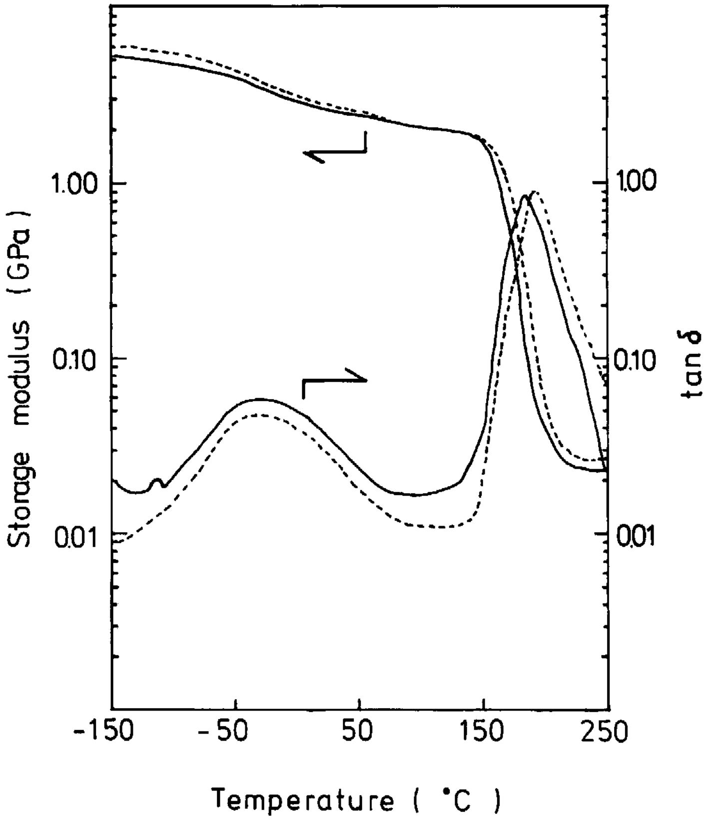

Figure 7. Temperature dependence of dynamic storage modulus and $\tan\delta$ (the volume fraction of polyimide filler is 0.01): (—) epoxy-silicone alloy composites; (- - -) epoxy resin composites.

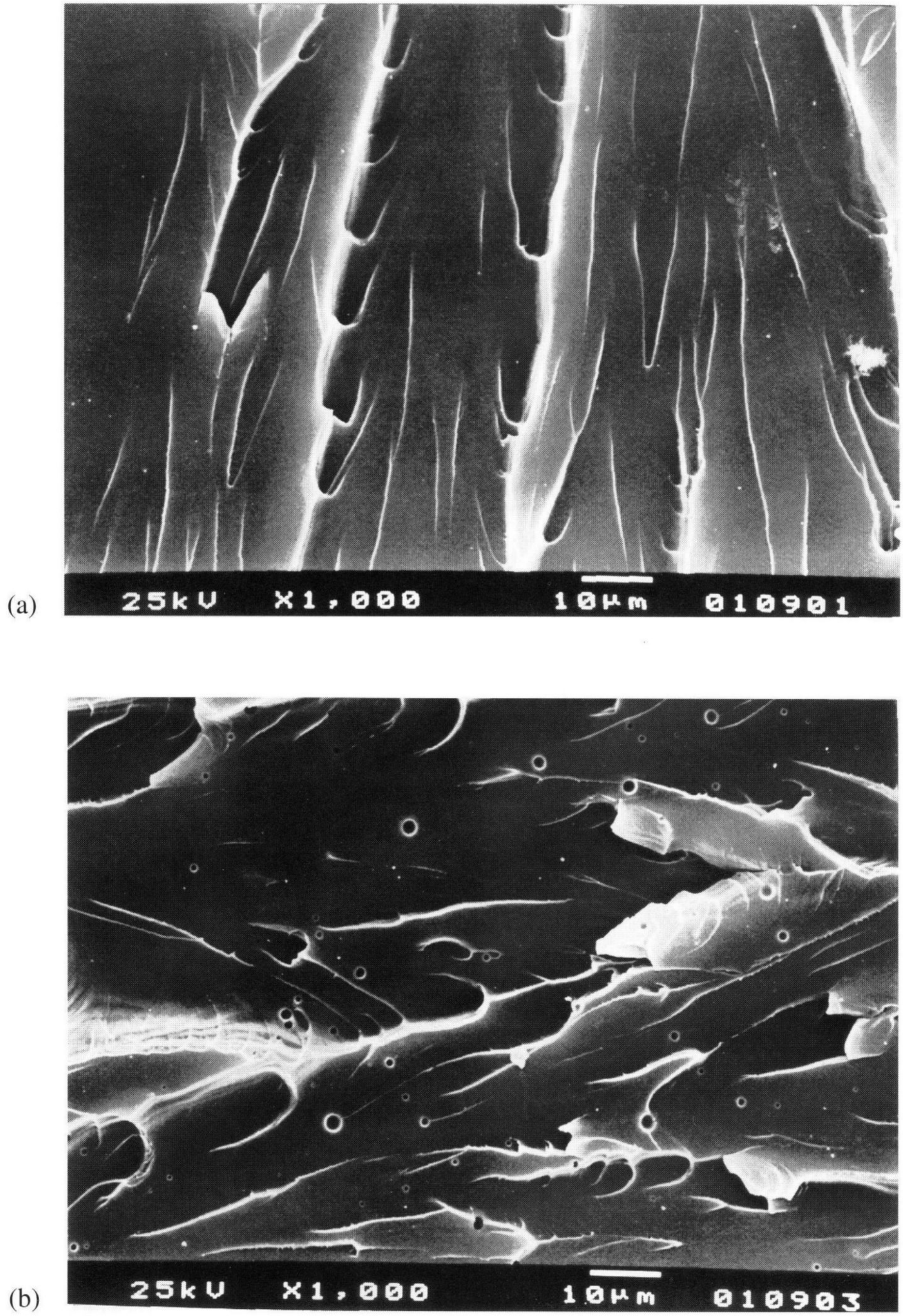

Figure 8. SEM photographs of the fractured surface of (a) epoxy resin and; (b) epoxy-silicone alloy.

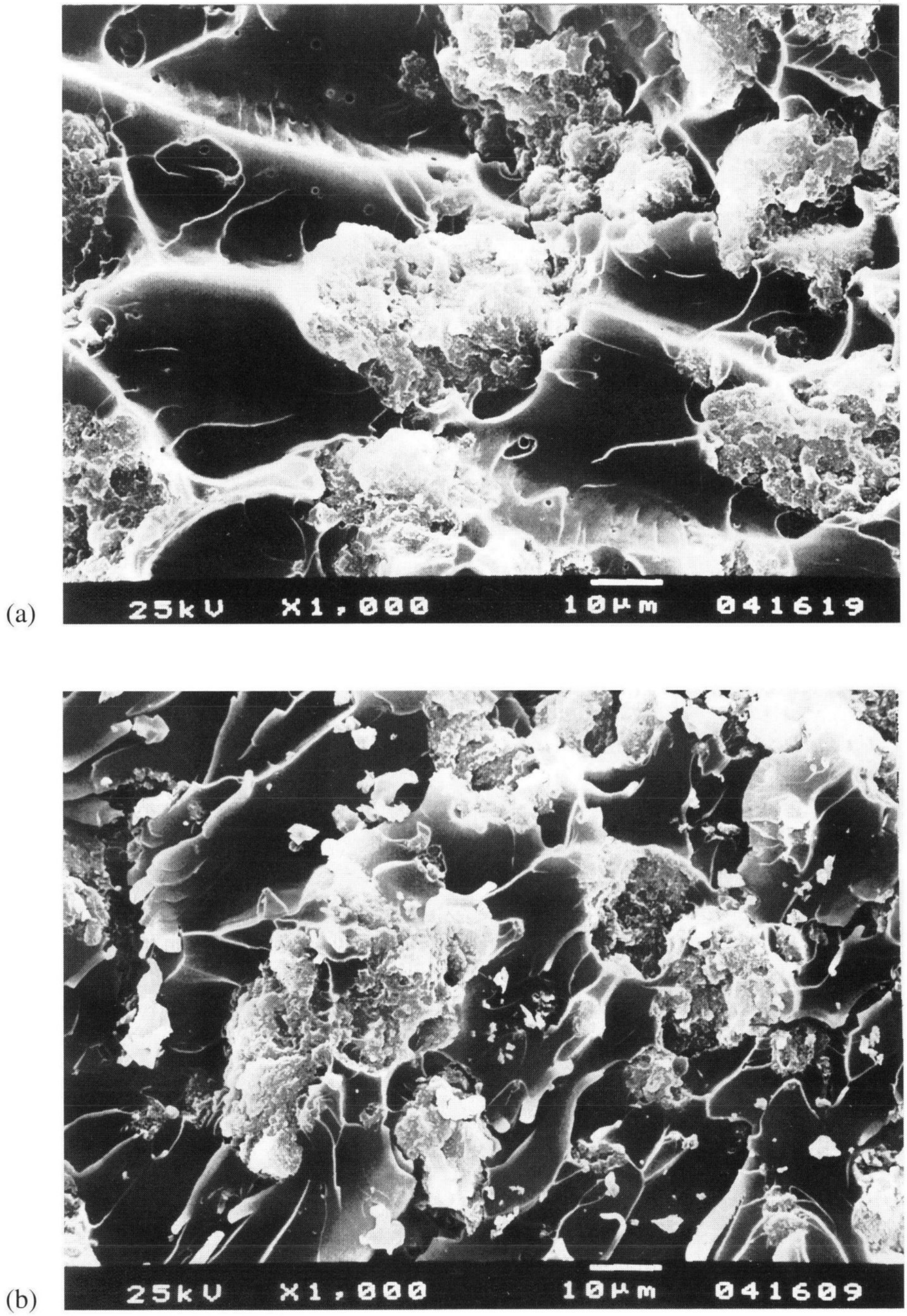

Figure 9. SEM photographs of the fractured surface of composites filled with polyimide powder: (a) epoxy-silicone alloy composites, volume fraction of the filler is 0.18; (b) epoxy resin composites, volume fraction of the filler is 0.17.

Table 1.
Density of composites of epoxy resin and epoxy-silicone alloy with polyimide filler

Sl. No.	Volume fraction of filler	Density of epoxy-silicone composites		Density of epoxy composites	
		Calculated	Measured	Calculated	Measured
1	0	1.154	1.155	1.156	1.156
2	0.01	1.155	1.155	1.158	1.158
3	0.04	1.161	1.159	1.164	1.162
4	0.09	1.170	1.170	1.171	1.170
5	0.17/0.18	1.185	1.182	1.187	1.180
6	0.36	1.219	1.198	—	—

discrepancy of the epoxy resin composite is larger than that of the epoxy-silicone alloy composite which accords with the SEM observation.

4. DISCUSSION

The composites of the both epoxy resin and epoxy-silicone alloy exhibit a higher T_g than that of the respective control samples by 7 to 20°C. It has been shown [13] that T_g of the epoxy resin composites depends not only on the characteristics of the matrix but also on the interaction between the filler and the matrix. Thus increase in T_g suggests an interaction between the matrices and the polyimide particles.

The decrease in T_g at high volume fraction of the filler is attributed to the residual voids between the agglomerates of filler particles and the matrices as shown in Fig. 9.

As Fig. 1 shows, the epoxy-silicone alloy and its composites have a lower T_g than that of epoxy resin. This fact accords with the result shown in Fig. 7 that the α-relaxation peak of the $\tan\delta$ curve for the epoxy-silicone alloy has a lower temperature and a slightly less intensity than that for the epoxy resin. This result indicates that the epoxy resin (DGEBA) react with amino terminated silicone with lower T_g. However, the small relaxation peak in the $\tan\delta$ curve of the epoxy-silicone alloy composite at -124°C suggests the occurrence of phase separation because this temperature corresponds to T_g of the silicone polymer. This is confirmed by the SEM photographs shown in Figs 8 and 9. It implies that not all the silicone has reacted with epoxy resin (DGEBA).

In general, the E' of the polymer alloy system [14] is decreased the component with low E' in the system. This is the case in E'_r of control samples and low ϕ_f (0.01) composite sample where the silicone-epoxy alloy has a lower E'_r that the epoxy resin as shown in Fig. 2. On the contrary, the E' enhances E'_g of the epoxy-silicone alloy and its composite is higher than that of the epoxy resin. Thus silicones with low E' enhance E'_g of the composite system. This effect is attributed to promotion of epoxy-molecular rearrangement induced by presence of silicone below T_g [15, 16]. The epoxy resin (DGEBA) in the epoxy-silicone alloy undergoes a molecular rearrangement to a high extent during the cooling from the curing temperature below T_g, resulting in a high packed molecular arrangement and a high E'_g. The fact that

E_r' of the epoxy-silicone alloy composite exceeds that of the epoxy resin composites at high ϕ_f may be the result of complicated effects of the characteristics of matrix and interaction parameter between matrix and filler. The order of the magnitude of the relative storage modulus is also reversed at T_g as indicated in Fig. 3. The relative storage modulus reflects the interaction between matrix and filler as well. It is inferred that the high thermal stability of the silicone strengthens the interaction between matrix and filler above T_g because of the higher relative storage modulus of the epoxy-silicone alloy composites.

Figure 4 indicates that the ratio $\tan\delta_c/\tan\delta_m$ is described by equation (1) fairly well. The equation has been proposed by Nielsen and co-workers [12] assuming that $\tan\delta$ of unfilled resins and composites is determined by the same mechanisms. The ratio decreases with increasing ϕ_f because the deformation of matrix is restricted by the filler. Accordingly the fact that the value of epoxy-silicone alloy composite is lower than the theoretical one suggests a higher restriction of the deformation of matrix resulting from the stronger interaction between matrix and filler.

Figure 5 shows that the flexural strength decreases with increase in ϕ_f. Here, the epoxy-silicone alloy composite has a larger flexural strength than that of epoxy resin composite at ϕ_f above 0.09. As revealed in Fig. 9 and Table 1, the addition of silicone to the epoxy resin accelerates the removal of the voids during the degassing process, resulting in the higher flexural strength silicone alloy composite.

Both α_g and α_r decrease with increase in ϕ_f (Fig. 6). The decrease in α_g is very low while that of α_r is much higher. The difference in α_g between the matrix and the filler is very slight below 70°C (α of polyimide is 0.55×10^{-4} up to 200°C). Therefore, the addition of the filler does not affect α_g so much. On the other hand, the difference between them is considerably greater above T_g; hence, a noticeable decrease of α_r was observed as the volume fraction of imide (ϕ_f) increased.

5. CONCLUSIONS

The dynamic mechanical properties and the morphologies of composites of epoxy or epoxy-silicone alloy with thermoplastic polyimide powder were studied.

Incorporation of the imide powder enhanced the T_g of the composite. The storage modulus increased with increasing volume fraction of imide. The imide polymer particle did not enhance the flexural strength of epoxy or epoxy-silicone alloy. The DMA data and SEM observations revealed the phase separation in alloy and its composites. It was also observed that the interaction between filler and matrix is more pronounced for epoxy-silicone alloy composites compared to that for epoxy. The presence of silicone enhanced the ease of composite preparation at higher volume fractions.

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