P6 球状シリカ粒子充填エポキシ樹脂複合材料の熱粘弾性挙動の 粒子充填モデルによる考察

Thermo-viscoelastic Behavior of Spherical Silica Particulate Filled Epoxy Composites: Considered in terms of the particle packing model

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The effect of two-silica-particle compositions on the thermo-viscoelastic properties of epoxy composites was studied according to Lewis and Nielsen's mixture law and particle packing model. The composite specimens varied with different compositions of two-silica-particle (240 nm and 1.56 μm) were prepared at the constant volume fraction, 0.30. The thermo-viscoelastic properties for neat epoxy and the composites were measured in the temperature ranges from 123 K to 523 K and compared to theoretical results according to Lewis and Nielsen's law with the maximum packing fraction of particles, ϕ_{max} of Ouchiya and Tanaka's model. Consequently, thermo-viscoelastic properties of two silica particulates filled epoxy composites were definitely dependent on maximum packing fraction of particles below glass transition temperature T_g , and on mobility of matrix resin above T_g .

Key Words: Polymer-matrix composite; Silica particle; Thermo-viscoelastic property; Maximum packing fraction of particles; Mixture law

1. INTRODUCTION

Mechanical properties of epoxy resin can be improved by reinforcing particles due to the effects of particle's volume fraction, size and shape, and surface characteristics, and the degree of particle dispersion¹⁾. Generally, the effects of particles on the viscoelastic properties of composites were discussed based on the maximum packing fraction of particle, ϕ_{max} ²⁾. Because the parameter ϕ_{max} of particulate composites specifically depends on the particle size distribution. However, the reinforcement of two different particles into a matrix could vary the particle size dispersion, distance between adjacent particles, and the degree of particle packing, which differ to mono-dispersed particles.

The purpose of this study is to clarify the effect of two-silica-particle composition on thermo-viscoelastic properties of epoxy composites based on experimental results obtained with the particle packing model in the Lewis and Nielsen's mixture law.

2. EXPERIMENTAL

2.1 Materials and specimen preparation

The matrix was prepared with epoxide type resin Epikote 828 (bisphenol-A, Japan Epoxy Resins), hardener type HN-2200R (methyl-tetrahydro-phthalic anhydride, Hitachi Chemical) and accelerator type DMP 30 (2,4,6-Tris (dimethyl amino-methyl) phenol, Kayaku Akuzo) in the proportion of 100: 80: 0.5 wt%. The reinforcing particles were spherical silica particles (not chemically treated at the surface) with a median diameter of 240 nm (1-FX, Tatsumori) and 1.56 μm (SO-C5, Tatsumori). Both particles showed relatively same particle distribution. The composite specimens were prepared where total particles volume fraction, V_f was 0.30, while the composition ratio, Φ_{SP} of small (1-FX) and large particles (SO-C5) ranged from 0 to 1.0. These mixing/blending processes were conducted at room temperature, and cured in two steps with a constant heating rate of 72 K/h: 353 K for 3 hours as pre-curing, and 413 K for 15 hours as post-curing.

2.2 Thermo-viscoelasticity

The thermo-viscoelastic properties were measured using a dynamic viscoelastometer (Orientec, Rheovibron DDV-III-EA) in nonresonance tensile method. The temperature dependencies of storage modulus E' , loss modulus E'' and $\tan \delta$ ($= E'' / E'$) measured

in the temperature ranges from 123 K to 523 K with 1.5 K/min heating rate by applying tensile oscillation at 3.5 Hz. In this study, glass transition temperature, T_g was determined from the peak of the $\tan \delta$ curve.

2.3 Maximum packing fraction

Lewis and Nielsen's mixture law known to agree well with the measured moduli of the composites is expressed as follows:

$$\frac{E'_{\text{comp}}}{E'_{\text{epoxy}}} = \frac{1 + ABV_f}{1 - BV_f}, \quad \psi = 1 + \left(\frac{1 - \phi_{\text{max}}}{\phi^2_{\text{max}}} \right) \quad (1)$$

where

$$A = \frac{7 - 5\nu_m}{8 - 10\nu_m}, \quad B = \frac{E_p/E'_{\text{epoxy}} - 1}{E_p/E'_{\text{epoxy}} + A}$$

V_p and E_p are total volume fraction and Young's modulus of the particles. ν_m is Poisson's ratio of the matrix.

The maximum packing fraction of particles ϕ_{max} for the composites with different sized particulate dispersions was calculated by using Ouchiya and Tanaka's model³⁾.

$$\phi_{\text{max}} = \frac{\sum D_i^3 f_i}{\sum (D_i \approx D_{\text{ave}})^3 f_i + \frac{1}{\beta} \sum \left\{ (D_i + D_{\text{ave}})^3 - (D_i \approx D_{\text{ave}})^3 \right\} f_i} \quad (2)$$

where

$$\beta = 1 + \frac{4}{13} (8\Phi_M^0 - 1) \left\{ \frac{\sum (D_i + D_{\text{ave}})^2 \left(1 - \frac{3D_{\text{ave}}}{8(D_i + D_{\text{ave}})} \right) f_i}{\sum (D_i^3 - (D_i \approx D_{\text{ave}})^3) f_i} \right\}$$

$$f_i = \frac{\frac{V_p}{D_i^3}}{\sum \frac{V_p}{D_i^3}},$$

$$(D_i \approx D_{\text{ave}}) = \begin{cases} 0 & \text{for } D_i \leq D_{\text{ave}} \\ D_i - D_{\text{ave}} & \text{for } D_i > D_{\text{ave}} \end{cases}$$

D_{ave} is the average diameter ($D_{\text{ave}} = \sum D_i f_i$) of the different sizes of particles, and D_i is the median diameter of two particles ($D_1 = 0.24 \mu\text{m}$, $D_2 = 1.56 \mu\text{m}$). Then, Φ_M^0 denotes the mono-dispersed packing fraction of spheres as 0.632.

3. RESULTS

Figure 1 shows the temperature dependence of storage modulus E' and $\tan \delta$ for the neat epoxy and the composites. The storage modulus of each composite was slightly larger with Φ_{SP} in orders of $1.0 > 0.8 > 0 > 0.5 > 0.2$ at 300 K, and $1.0 > 0.8 > 0 > 0.5 > 0.2$ at 500 K, while having the same total volume fraction of particles in each composite. The moduli of both epoxy and composites dropped and decreased in a narrow temperature range where the $\tan \delta$ peak reached the maximum, i.e. glass transition temperature, T_g . In addition, maximum peak values of $\tan \delta$ decreased gradually as Φ_{SP} reached 0 to 0.8, while the rapidly decreased and broadened peak of $\Phi_{SP} = 1.0$ was found at low temperature.

Fig. 1 Temperature dependence of E' and $\tan \delta$

4. DISCUSSIONS

Figure 2 shows the composition ratio Φ_{SP} dependence of relative storage modulus ($E'_r = E'_{comp}/E'_{epoxy}$) and T_g at 188 K, 300 K, and 500 K ($T < T_g$), and 500 K ($T > T_g$). At 188 and 300 K, the composites of $\Phi_{SP} = 0.2$ and 0.5 showed a relatively decrease in modulus compares to $\Phi_{SP} = 0$, and then brings about an increase in $\Phi_{SP} = 0.8$ and 1.0. However, when temperature elevated to 500 K the modulus in all Φ_{SP} increases dramatically. On the other hand, the composites with Φ_{SP} from 0 to 0.5 showed an approximately constant T_g , but gradually decreased with an increase in Φ_{SP} exceeds 0.8. Generally, the T_g of particulates-filled composites shifts to higher temperature due to the immobility of polymer molecules by local adsorption onto the particle⁴⁾. In our results, however, T_g decreased at high Φ_{SP} . It is considered that the

decrease in T_g is caused by a increase in the interaction between adjacent particles due to increasing Φ_{SP} narrows interspaces. By this reason, high Φ_{SP} is expected to an increase in modulus. The variation of modulus and T_g could be depended on their particle size dispersion. So the ϕ_{max} for each Φ_{SP} was calculated from Lewis-Nielsen's equation with experimental results and Ouchiya-Tanaka's model, as shown in Fig. 3. At $T < T_g$, maximum packing fractions were higher than $\Phi_{SP} = 0$, especially showing a maximum value at $\Phi_{SP} = 0.2$. It verifies that the composition of two particles gives relatively well-packed particle dispersion due to smoothly embedding small particles in the interspaces between large particles, and results in lower modulus. However, suddenly increasing in modulus of $\Phi_{SP} = 1.0$ at 188 K can be explained by lower ϕ_{max} . And from Fig. 3, unvaried ϕ_{max} is observed at 500 K, indicates as $T > T_g$ the modulus is more strongly depended on the mobility of polymer matrix instead of the particle composition.

REFERENCES

- 1) Perrin-Sarazin F, Ton-That MT, Bureau MN, Denault J, *Polymer* **46** (2006) 11624.
- 2) Pal R, *Comp. Part B: Eng.* **36** (2005) 513.
- 3) Ouchiya N, Tanaka T, *Ind. End. Chem. Fundam.* **23** (1984)490.
- 4) Dabak T, Yucel O, *Powder Technol.* **52** (1987) 193.

Fig. 2 Particle composition dependence of E'_r and T_g

Fig. 3 Particle composition and temperature dependence of ϕ_{max}