

Dynamic Viscoelastic Properties and Thermal Properties of Ni Powder–Epoxy Resin Composites

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ABSTRACT: The composite materials containing metal Ni powder of 5–15 μm in size were prepared by use of the matrix epoxy resin of glycidyl amine crosslinked with bis-4-amino-3-methylcyclohexyl methane and 2,4-diamine 3,5-dimethyltoluene. Dynamic viscoelastic properties of the composites at various volume fraction (Φ_p) of Ni powder have been measured over the temperature range from 30 to 300°C. The peak temperatures in dynamic loss modulus–temperature diagrams of the composite increased with increasing Φ_p , although the peak position was abruptly shifted to lower temperatures in the range of Φ_p more than 0.245. At this high concentration of Φ_p , agglomeration of the particles occurring in the composite lead to reduction of the interaction between Ni particle and epoxy resin. Parallel studies on the thermal conductivity (λ) of the composites materials showed that the value of λ at $\Phi_p = 0.245$ increased by approximately 7 times that of the original epoxy resin. The shape of Ni particles also affected the thermal durabilities of the composites; the rough surface of Ni powder yields a higher storage modulus of the composite than that of the materials containing the powder with a smooth surface, which had been brought through a ball-milling process. The finding suggested that the increasing in specific surface area of the powder improved the thermal durability of the composites as well as their mechanical properties.
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Key words: composite materials; metal powder; epoxy resin; dynamic viscoelasticity; surface treatment

INTRODUCTION

In this past decade, particle-filled polymer composites with high thermal conductivity are required in various industries particularly to release thermal energies outside during molding processes.¹ The composites with thermal durabilities are also needed to maintain the stiffness of materials at elevated temperatures. Mixing various kinds of inorganic or metallic powder with matrix epoxy resin is a well-known technique to

improve both the thermal durabilities of the resultant materials.^{2–5} Numerous studies on mechanical properties of epoxy composite materials have been published in variety of powder, including glass⁶ or ceramic beads.^{6–11} Sizes and volume fraction of the particles (Φ_p) are important factors to govern their mechanical properties as well as the effect of the crosslinking agent for matrix epoxy resin. For example, the storage modulus of the composites is expressed by an appropriate equation as a function of Φ_p .^{12,13} Specifically, the mechanical properties of composites depend on various chemical interactions between the particles and matrix polymers.^{14,15}

In the present study, we examine the dynamic

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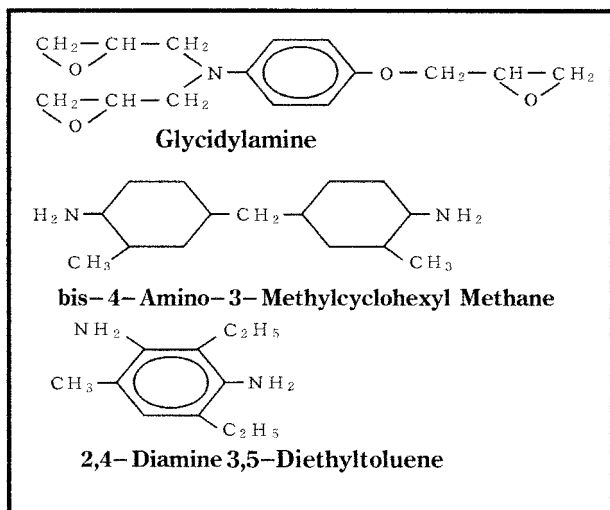


Figure 1 Chemical structure of epoxy resin and crosslinking agents.

viscoelasticity and the thermal conductivity of Ni particle-epoxy composites with various Φ_p and 2 types of particle shapes to improve their thermal durabilities.

EXPERIMENTAL

Materials

Chemical structure of epoxy resin and crosslinking agent used in this work are shown in Figure 1. The crosslinking agent was prepared by the blending of 2 kinds of amine compounds, bis-4-amino-3-methylcyclohexyl methane (6 parts) and 2,4-diamine 3,5-dimethyltoluene (4 parts). The Ni powder used was dried in a vacuum oven for 48 h before mixing with the matrix materials. The average size of the Ni particle (Inco. Ltd.) used was 10.75 μm , and its density was 8.85 g/cm^3 .

Surface Treatment of Ni Powder by Ball Milling

The Ni powder of 40 g was placed into a cylindrical vessel inner radius, 24.5 mm; length, 105 mm) with 3-mm stainless balls and then ground by a vibration ball mill (Red Devil Mill) for 2 h. After the milling procedure, the Ni powder was taken out of the vessel and passed through a metal screen of 20 mesh. We call this sample the surface-treated powder.

Distribution of Particle Size

The particle size of Ni powder was measured at 25°C by a centrifugal particle-size distribution analyzer (Horiba, CAPA-700). Silicone oil (Toshiba Silicone, TSF451-50; density, 0.96 g/cm^3 ; viscosity, 50 cp) was employed for the dispersion medium in the measurement.

Preparation of Ni Powder-Epoxy Resin Composite

Epoxy compound was prepared to contain 100 parts of epoxy resin and 53.5 parts of crosslinking agents by weights (see Table I) and a required amount of Ni powder. The calculated amount of amine group equivalent to the epoxy group was thereby added. The volume fraction (Φ_p) of the Ni powder in the composites was calculated using the following equation:

$$\Phi_p = \frac{N_w/\rho_2}{(E_w + C_w)/\rho_1 + N_w/\rho_2} \quad (1)$$

where N_w , E_w , and C_w indicate the weights of Ni powder, epoxy resin, and crosslinking agent, respectively. The symbols of ρ_1 and ρ_2 express the densities of the epoxy resin (1.192 g/cm^3) after the curing process described below and that of the Ni powder (8.85 g/cm^3), respectively. These moieties were hand-blended at first and then stirred by the use of a small mixer until the particles were completely dispersed. This mixture was then degassed under a vacuum for 4 min. The epoxy resin with Ni powder was poured into a vessel with 1 mm thickness, followed by curing to crosslink the epoxy resin, as in the following programmed process: 60°C/4 h \rightarrow 100°C/2 h \rightarrow 120°C/2 h \rightarrow 140°C/2 h \rightarrow 180°C/2 h.

The volume fraction of surface-treated Ni powder in the composites materials was fixed to 0.245, as shown in Table I. For dynamic viscoelastic measurements, the sheet material obtained was cut into small pieces by a diamond cutter, then the edge of specimen was polished using an abrasive paper. The final size of the specimen was 25 \times 5 \times 1 mm^3 .

Measurement of Dynamic Viscoelasticity

The temperature dependence of storage modulus (E') and loss modulus (E'') were measured by a FT-Rheospectra DVE-V4 (Rheology Co.) at 100 Hz in the temperature range from 30 to 300°C.

Table I Preparation of Ni Powder-Epoxy Resin Composites at Various Volume Fractions of Ni Powder

Cord No.	Epoxy Resin (g)	Crosslinking Agents (g)	Ni Powder (g)	Weight (wt %)	Volume Fractions ^a
B0	10.00	5.35	0	0	0
U1	10.06	5.35	12.76	45.30	0.100
U2	10.40	5.60	20.65	56.34	0.148
U3	10.04	5.35	28.50	64.94	0.200
U4	10.10	5.35	35.83	69.87	0.238
U5	10.10	5.35	37.32	70.72	0.245
U6	10.02	5.35	40.00	72.25	0.260
U7	10.05	5.35	50.00	76.45	0.304
T1	10.10	5.35	37.32	70.72	0.245

^a Obtained by use of eq. (1).

The heating rate and applied displacement were 2°C/min and 1 μm, respectively.

Measurement of Thermal Conductivity

Thermal diffusivity (*D*), specific heat capacity (*C_p*), and thermal conductivity (*λ*) of the samples were measured by means of a laser flash method¹⁶ using a laser flash thermal analyzer (Shinku-Riko: TC-7000; see Fig. 2). The size of specimen was 8 mm diameter and 0.6 mm thick. The source of the energy pulse was a ruby laser with 7 J of energy in each flash, and the flash time was 1 ms. The measurements were made in the temperature at 23°C and atmosphere, respectively. For monitoring the temperature response of the back surface of the specimen, a Chromel-Alumel thermocouple was used. Then, a surface of specimen was not treated and the back surface temperature was increased by about 5°C in each flash. Generally,

the thermal conductivity can be calculated by the following equation:

$$\lambda = \rho \times D \times C_p \tag{2}$$

where *ρ* is the density of the sample. In this case, the values of *ρ* can be calculated from eq. (1). Then the quantities of *D* and *C_p* were obtained by the relationships between the temperature of the back surface of the specimen and the passage of time from the laser flashing.¹⁷

Surface Examination Composite of Materials

Surface structures of the composite materials were observed by scanning electron microscopy (SEM) (JSM-5300, JEOL Co. Ltd.) at 25 kV. The tilt angle of the sample was fixed at 30°.

The samples were coated with Au by an ion sputtering apparatus (JFC-1100E, JEOL Co. Ltd.); coating time and ion current were 150 s and 10 mA, respectively.

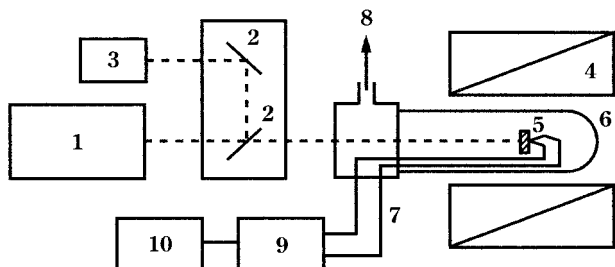


Figure 2 Schematic representation for the thermal constant analyzer utilized in the present study: (1) ruby laser head; (2) beam splitter; (3) Si photoelectric cell; (4) electric furnace; (5) specimen; (6) fused silica tube; (7) thermocouple; (8) rotary pump; (9) amplifier; (10) transient recorder.

RESULTS AND DISCUSSION

Characterization of Ni Powder

Figure 3 shows the scanning electron micrographs of the Ni powder. Many thorns are observed on the Ni particles surface, indicating the characteristic shapes probably produced by a carbonyl reduction method. In that reduction process, the Ni carbonyl compound was produced by the reaction of both hydrogen and carbon monoxide on the surface of nickel oxide and was then reduced during the suc-

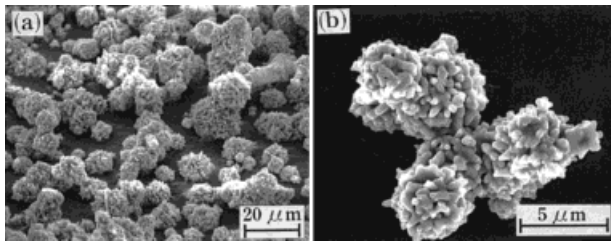


Figure 3 SEM photographs of Ni powder with magnifications of (a) 1000 and (b) 7500.

cessive heating process. The shape of Ni powder is thus influenced by that of nickel oxide crystals. The particle size distribution for the Ni particles, as received, is shown in Figure 4. The average size of the particle is calculated as $10.75 \mu\text{m}$, approximately equal to that observed in the SEM pictures.

In general, the oxidation of metallic surface influences the affinity of metal powder with matrix resin. It is necessary to confirm whether or not the nickel oxide exist on the surface of Ni powder. Although the experimental results are not shown, powder X-ray diffraction data (XRD), for the Ni particles indicated good agreement of d-spacings in comparison with those of the nickel metal itself. Therefore, if any, there exist extremely small amounts of nickel oxide on the surface of Ni particle used.

Dynamic Viscoelastic Properties of the Composite Materials

Figure 5 displays the variations of E' and E'' as a function of temperature. The value of E' of the epoxy resin begins to decrease at 240°C . This cor-

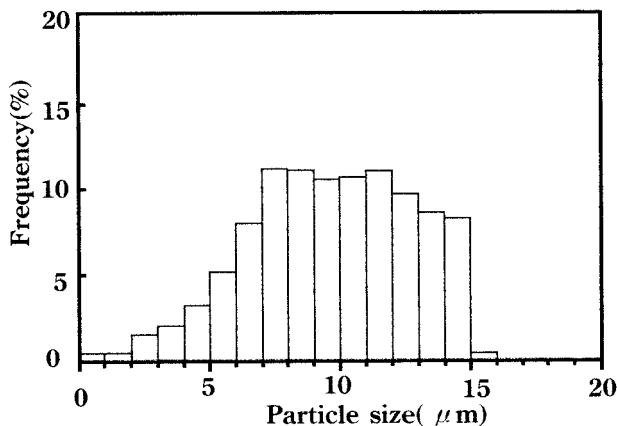


Figure 4 Particle size distribution of Ni powder as received in a silicone oil.

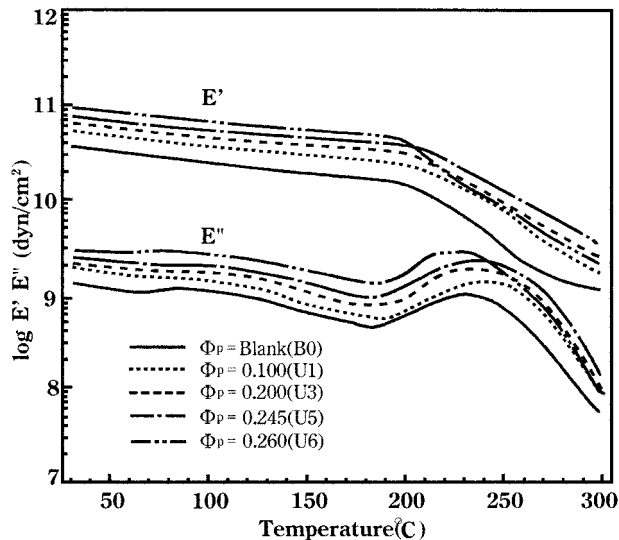


Figure 5 Temperature dependence of dynamic viscoelasticity for various Ni-epoxy resin compounds.

responds to the glass transition temperature (T_g) of the matrix epoxy resin itself. The Φ_p dependence of E' at 30°C and the peak temperature of E'' is shown in Figure 6. The magnitude of the E' at 30°C increases with an increase in Φ_p .

This result comes from that the higher modulus of the Ni particle than the epoxy resin. On the other hand, T_g increased with an increase in Φ_p , though they decreased more rapidly than $\Phi_p = 0.245$.

Generally, the filler has an effect to shift the T_g of composites to higher temperature since the mobility of polymer molecules are restricted by their partial adsorption onto the filler.¹⁸ In this

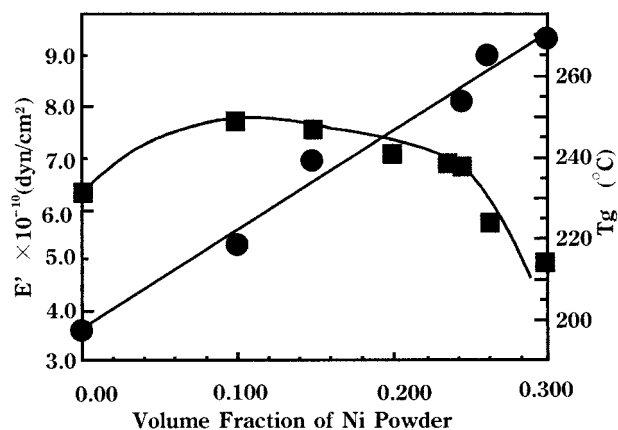


Figure 6 Changes in the peak temperature of T_g (■) and storage modulus values at 30°C (●) as a function of Ni powder concentration.

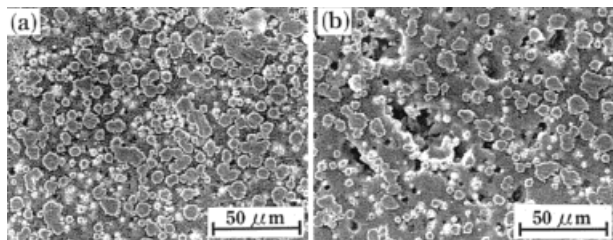


Figure 7 SEM photographs of the fracture surfaces for samples (a) U5 and (b) U6.

case, however, T_g decreases at high Φ_p . We consider that the decrease of T_g is caused by a decrease in the interaction between Ni particle to epoxy resin due to the Ni particle agglomeration.

The SEM photographs of the composites of $\Phi_p = 0.245$ and 0.345 are shown in Figure 7(a). There were no cavities around the Ni particle at $\Phi_p = 0.245$. This result indicates excellent affinity of Ni powder with epoxy resin. However, a small amount of agglomeration of particles or voids are observed in higher Φ_p [Fig. 7(b)]. Fu and Wang¹⁹ suggested that the agglomeration of CaCO_3 brought to reduce both impact strength and heat distortion temperature in the composite material formed of CaCO_3 -polyethylene. In our case, T_g of composites decreased due to the particle agglomeration at a high concentration of the Ni powder.

Changes in Thermal Conductivity of Composite Materials

Figure 8 shows the thermal properties of composite materials with various Φ_p measured by the laser flash thermal analyzer. The value of C_p de-

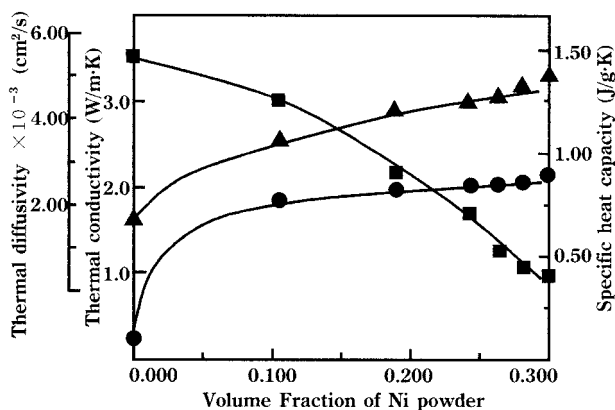


Figure 8 Changes in various thermal properties of Ni powder-epoxy resin composites materials: thermal conductivity (●), specific heat capacity (■), and thermal diffusivity (▲).

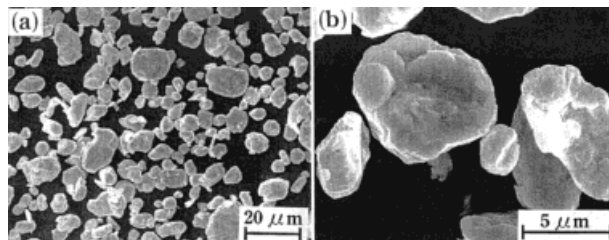


Figure 9 SEM photographs for the surface-treated Ni powder by ball milling with magnifications of (a) 1000 and (b) 7500.

creased with increasing Φ_p ; on the contrary, D and λ increased. The λ value was about 7 times as large as that of the original epoxy resin when they are compared at $\Phi_p = 0.245$. The increase in λ of the composite material with increasing Φ_p is reasonable since the λ values for Ni powder⁹ and epoxy resin are 29.4 and $0.3 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. However, the increase of λ ranges from $\Phi_p = 0.1$ to 0.3 is little. It seems that the Ni powder is well dispersed in the composites. Thus, λ values depended on Φ_p and was influenced by the dispersed state and the packing density of Ni particles within the composites.

Shape Effect of Particle in the Dynamic Viscoelastic Properties of Composites

The SEM photograph of the surface-treated Ni powder is shown in Figure 9. The surface of the particle was smooth, and the thorn could not be observed on untreated Ni particles. The smooth surface of the treated Ni powder were caused by grinding during the ball milling process. Figure 10 shows the particle size distribution of the sur-

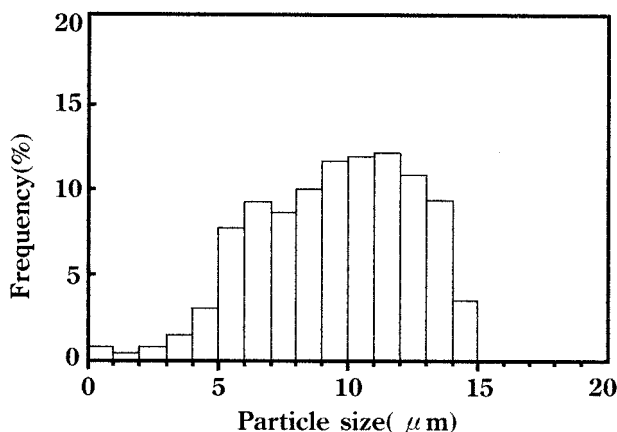


Figure 10 Particle size distribution of the surface-treated Ni powder by ball milling measured in a silicone oil.

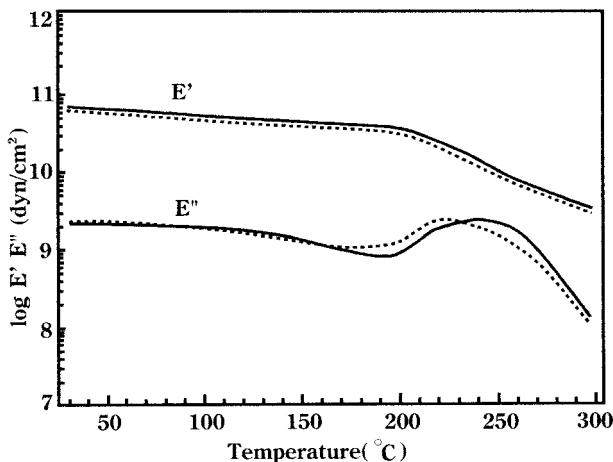


Figure 11 Temperature dependence of dynamic viscoelasticity for Ni-epoxy resin compounds: Untreated Ni powder (U5) (—) and surface-treated Ni powder by ball milling (T1) (---).

face-treated Ni powder. There is little difference in the particle size distribution between the surface treated particle and untreated particle, as illustrated in Figure 4.

Figure 11 shows the comparison of E' and E'' of the composite material containing the treated Ni powder with those of the as-received Ni powder. T_g of the composite material containing with the treated Ni powder is lower than that of the untreated Ni powder. The rough surface of Ni powder gives higher T_g of the composite due to excellent affinity between the untreated Ni particle and epoxy resin as compared with the treated powder.

CONCLUSIONS

Dynamic viscoelastic properties of the Ni powder-epoxy resin composites at various Φ_p have been studied.

The peak temperatures in dynamic loss modulus-temperature diagrams of the composite increased with increasing Φ_p , although the peak position was abruptly shifted to lower temperatures in the range of Φ_p more than 0.245. At this high concentration of Φ_p , agglomeration of the particles occurring in the composite led to a reduction of the interaction between the Ni particle and epoxy resin. The value of λ at $\Phi_p = 0.245$ increased by

approximately 7 times that of the original epoxy resin. The shape of Ni particles also affected the thermal durabilities of the composites; the rough surface of Ni powder yields a higher storage modulus of the composite than that of the materials containing the powder with a smooth surface, which had been brought through a ball-milling process. The finding suggests that the increase in the specific surface area of the powder improved the thermal durability of the composites as well as their mechanical properties.

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