

## Dynamic Mechanical Properties of Three-Component Composites (Acrylic Polymer/Epoxy/SiO<sub>2</sub>) in the Glass-Transition Region

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**ABSTRACT:** In previous studies, we reported the linear and nonlinear rheological properties of three-component composites consisting of acrylic polymer (AP), epoxy resin (EP), and various SiO<sub>2</sub> contents (AP/EP/SiO<sub>2</sub>) in the molten state. In this study, the dynamic mechanical properties of AP/EP/SiO<sub>2</sub> composites with different particle sizes (0.5 and 8 μm) were investigated in the glass-transition region. The EP consisted of three kinds of EP components. The α relaxation due to the glass transition shifted to a higher temperature with an increase in the volume fraction (φ) for the AP/EP/SiO<sub>2</sub> composites having a particle size of 0.5 μm, but the α relaxation scarcely shifted for the composite having a particle size of 8 μm as a general result. This result suggested that the SiO<sub>2</sub> nanoparticles that were 0.5 μm in size adsorbed a lot of the low-glass-transition-temperature (T<sub>g</sub>) component because of their large surface area. The AP/SiO<sub>2</sub> composites did not exhibit a shift in T<sub>g</sub>; this indicated that the composite did not adsorb any component. The modulus in the glassy state (E'<sub>g</sub>) exhibited a very weak φ dependence for the AP/EP/SiO<sub>2</sub> composites having particle sizes of 0.5 and 8 μm, although E'<sub>g</sub> of the AP/SiO<sub>2</sub> composites increased with φ. The AP/EP/SiO<sub>2</sub> composites exhibited a peculiar dynamic mechanical behavior, although the AP/SiO<sub>2</sub> composites showed the behavior of general two-component composites. Scanning electron microscopic observations indicated that some components in the EP were adsorbed on the surface of the SiO<sub>2</sub> particles. We concluded that the peculiar behavior of the AP/EP/SiO<sub>2</sub> composites was due to the selective adsorption of the EP component. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40409.

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### INTRODUCTION

In the semiconductor industry, integrated circuit (IC) chips are three-dimensionally integrated to increase the capacity of their memory without a change in their size. IC chips are stacked on a substrate with an adhesive material. This stacking process is carried out at a temperature (*T*) above the glass-transition temperature (*T<sub>g</sub>*) of the adhesive material and cured completely at a higher *T* to enhance the interfacial adhesion. An adhesive film consists of three components: (1) an acrylic polymer (AP) having a low *T<sub>g</sub>* for elasticity and toughness at room *T*; (2) an epoxy resin (EP) to exert the adhesion strength and the heat resistance, and (3) SiO<sub>2</sub> particles to keep the linear expansion coefficient low. Inada and coworkers<sup>1,2</sup> reported the effect of SiO<sub>2</sub> particles on the adhesion strength between an AP/EP film and an IC chip. Suzuki and coworkers<sup>3–5</sup> studied EP/mesoporous composites and reported that a low expansion coefficient of EP was often achieved by the addition of mesoporous SiO<sub>2</sub> with a high volume fraction (φ).

Rheological properties are very important for the stacking process of IC chips/adhesion films. However, the properties of AP/EP/SiO<sub>2</sub> adhesion films have been scarcely reported. Therefore, we studied the linear and nonlinear rheological properties of AP/EP/SiO<sub>2</sub> suspensions having various contents of SiO<sub>2</sub> particles with an average diameter of 0.5 μm in the molten state, and we discuss the processability of the stacking of IC chips.<sup>6–9</sup> In the linear viscoelastic measurements, the AP/EP/SiO<sub>2</sub> systems exhibited a critical gel behavior characterized by a power law relationship between the storage shear modulus (*G'*) and loss shear modulus (*G''*) and the frequency (*ω*):<sup>7</sup>

$$G' = G'' / \tan(n\pi/2)\alpha\omega^n$$

where *n* is the critical relaxation exponent between 0 and 1.

The reversible *T*-induced gelation was interestingly found at φ = 35 vol %. This gelation was considered to be due to a change in the affinity of AP and/or EP toward the SiO<sub>2</sub> particles with increasing *T*. The nonlinear stress relaxation and

elongational viscosity suggested that the nonlinear behavior was attributable to the strain-induced disruption of the network structure formed by the SiO<sub>2</sub> particles in the gel state.<sup>8,9</sup> Thus, the processability of stacking was established from the relationship between the rheological behavior and the structure of the AP/EP/SiO<sub>2</sub> suspensions.

It is also important to prevent crack and keep handling easy for adhesive films at room  $T$  because the films are shifted to a stacking apparatus and fitted to the shape of IC chips. The handling of the films depends on the chemical species and the content of each component and is generally determined by trial and error. Therefore, the linear viscoelasticity near room  $T$  is very important to control the glass transition of the films. However, the glass-transition behavior of adhesion films has never been reported, although the viscoelasticity of adhesion films in the molten state has been reported already.<sup>6–9</sup> Thus, the  $T$  dependence of the internal structure and the physical properties of the AP/EP/SiO<sub>2</sub> composites might be very interesting in the glassy–rubbery state because the AP/EP media have a sensitive affinity toward SiO<sub>2</sub> depending on the  $T$  stimulus.<sup>7</sup>

The modulus of two-component polymer/filler composites depends on those of each component and the  $\phi$  value of filler. The theoretical modulus of the polymer/filler composites was proposed by Neilsen<sup>10</sup> and Halpin and Kardos<sup>11</sup>. In general, it is well-known that the dynamics of the polymer component in a simple composite is not affected by the filler component.<sup>12–15</sup> Therefore, many researchers have focused on the improvement of the affinity between the polymer chain and the filler. Improvements in the heat resistance, handling, and stiffness have been made by surface treatments of the filler,<sup>16,17</sup> the use of compatibilizing agents such as surfactants,<sup>18–20</sup> and chemical reactions.<sup>21–24</sup> In these reports, Zia et al.<sup>24</sup> showed that the tensile strength of bionanocomposites synthesized with chitin–bentonite clay and polyurethane was effectively improved. Thus, we found that chemical reactions are one of the most effective methods for controlling the physical properties of composites. So far, the thermophysical properties of multicomponent materials (polymer blend/rigid filler systems) strongly depend on the nanostructure/microstructure and the affinity of each component. However, studies of the effect of rigid fillers on the physical properties and morphology of polymeric materials containing multicomponents have been very few and have compared the properties of polymer/rigid filler two-component systems. It is necessary to investigate multicomponent materials because materials that consist of a number of components are usually used in industry.

In the stacking process of IC chips, the handling of adhesion films (AP/EP/SiO<sub>2</sub> composites) is basically controlled by the size and content of SiO<sub>2</sub> particles without any changes in AP/EP component because it is easy method. However, the mechanism of control by SiO<sub>2</sub> particles has been scarcely clarified, and the material design of adhesion films has been left as an unsolved problem. Therefore, the thermophysical properties of AP/EP/SiO<sub>2</sub> composites are very important in the design of these materials and in determining the processing conditions without trial and error. It is also interesting to investigate the structure–property relationship of AP/EP/SiO<sub>2</sub> composites from an academic point of view because the AP/EP matrix has a sensitive affinity toward SiO<sub>2</sub>.

Thus, we focused our attention on the effects of the size and content of the SiO<sub>2</sub> particles on the dynamic mechanical properties near the glass transition temperature ( $T_g$ ) values of the composites. The details of these results are presented in this article.

## EXPERIMENTAL

### Materials

A blend of a linear AP and a low-molecular-weight EP was used as the matrix phase. Both the AP and EP were provided by Hitachi Chemical Co., Ltd. The weight-average molecular weight ( $M_w$ ) and heterogeneity index ( $M_w/M_n$ , where  $M_n$  is the number-average molecular weight) of the AP were 360,000 and 2.2, respectively. The EP component consisted of bisphenol A diglycidylether (L-epo), cresol novolac type EP (S-epo), and bisphenol A novolac (CA). The composition ratio of L-epo to CA was unity, and that of S-epo to L-epo was one third in volume. The content of EP in the AP/EP blend was 70 vol %. The  $\phi$  of the SiO<sub>2</sub> particles (which were provided by Admatechs Co., Ltd.) ranged from 0 to 40 vol %. The SiO<sub>2</sub> particles were produced by a vaporized metal combustion method. Two kinds of SiO<sub>2</sub> particles with different diameters, 0.5 and 8  $\mu\text{m}$ , were used. The surface of the SiO<sub>2</sub> particles was treated with an epoxy silane coupling agent to prevent the agglomeration of SiO<sub>2</sub> particles. Each of the components was dissolved homogeneously in cyclohexanone. The total content of the AP and EP components in the solution was about 20 vol %. Cyclohexanone in the solutions was evaporated at 120°C for 30 min. It was confirmed by thermogravimetric analysis (TGA) that the cyclohexanone in the sample disappeared. The material with SiO<sub>2</sub> particles with a diameter of 0.5  $\mu\text{m}$  was named AP/EP/Si05, and the content of SiO<sub>2</sub> particles was described after an underscore, such as AP/EP/Si05\_20 for the material with SiO<sub>2</sub> with a  $\phi$  of 20 vol %.

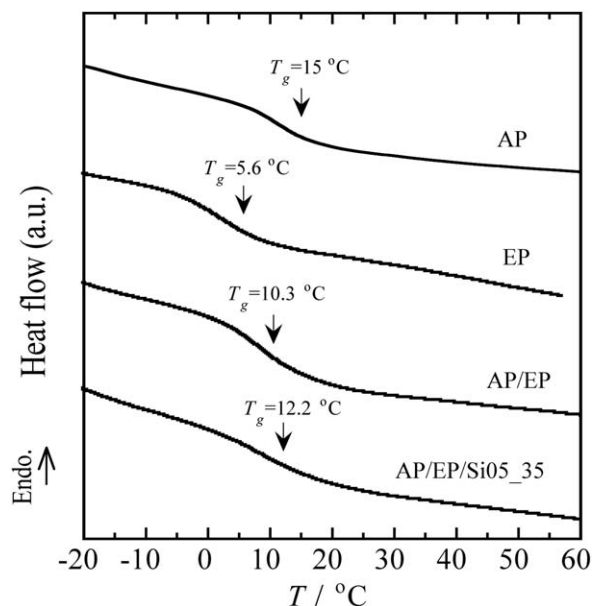
### Measurements

The  $T_g$ 's of the composites and their components were measured with a differential scanning calorimeter (TA Instruments DSCQ100) at a heating rate of 10°C/min. The  $T_g$  was taken as the  $T$  corresponding to half of the heat capacity change; that is,  $T_g$  was the midpoint of the glass transition. Dynamic mechanical analysis was performed with a viscoelastic spectrometer (TA Instruments RSA II) at a heating rate of 2°C/min and an  $\omega$  of 5 Hz. The samples with dimensions of 30 × 5 × 0.5 mm<sup>3</sup> were used in the dynamic mechanical analysis test. Measurements were begun at –20°C and continued until the sample became too soft to be tested. The measurements were performed two or three times for each sample. The morphologies of the samples were observed with scanning electron microscopy (SEM; Hitachi High-Technologies Corp. S-3400N) to investigate the dispersed state of the SiO<sub>2</sub> particles in the matrix. All of the samples were coated with platinum for 5 min to make the material conductive. The morphological observation was carried out under the standard high-vacuum mode, and the voltage was kept at 10 kV throughout the analysis. The morphology of each sample was imaged at a variety of magnifications.

## RESULTS AND DISCUSSION

### Glass Transition Temperature

The differential scanning calorimetry (DSC) curves for AP, EP, AP/EP, and AP/EP/Si05\_35 are shown in Figure 1. The  $T_g$  values



**Figure 1.** DSC thermograms of AP, EP, AP/EP, and AP/EP/SiO<sub>5\_35</sub>.

of the AP and EP were 15.0 and 5.6°C, respectively. In Table I, the  $T_g$ 's of each component in the EP are shown. A single endothermic transition was exhibited in EP like in a homogeneous material, although the EP consisted of three components with different  $T_g$ 's. Therefore, we concluded that the components in the EP were miscible each other. The AP/EP blend also exhibited a single endothermic transition. The  $T_g$  of AP/EP was decided to be 10.3°C. The  $T_g$  of AP/EP/SiO<sub>5\_35</sub> was 12.2°C and was slightly higher than that of AP/EP.

The  $T_g$  of pure L-epo was determined with a linear extrapolation of the  $T_g$  of the AP/L-epo blends with several blend ratios and was estimated to be -48.4°C. We found that L-epo had a lower  $T_g$  than the other components in the EP. Another interesting result was that the  $T_g$  of the AP/EP blend was hardly affected by the SiO<sub>2</sub> particles because the  $T_g$  of the AP/EP blend was almost the same as that of the AP/EP/SiO<sub>2</sub> composite.

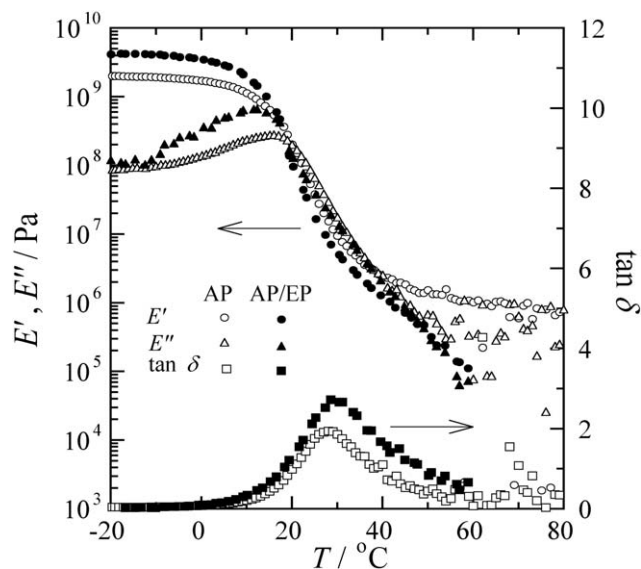
### Dynamic Mechanical Properties

**Effect of the EP and SiO<sub>2</sub> on the Dynamic Mechanical Properties of the AP.** The  $T$  dependence of the storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta = E''/E'$ ) of the AP and AP/EP (30/70 v/v) blend is shown in Figure 2. With elevating  $T$ , the  $E'$  of the AP decreased gradually up to 20°C, then

**Table I.**  $T_g$  Values for Each Component as Determined by DSC

Component	$T_g$ (°C)
L-epo	-48.4 <sup>a</sup>
S-epo	50.9
CA	54.4
EP	5.6
AP	15.0

<sup>a</sup>Estimated from the extrapolation of the  $T_g$  value of the AP/L-epo miscible blends.

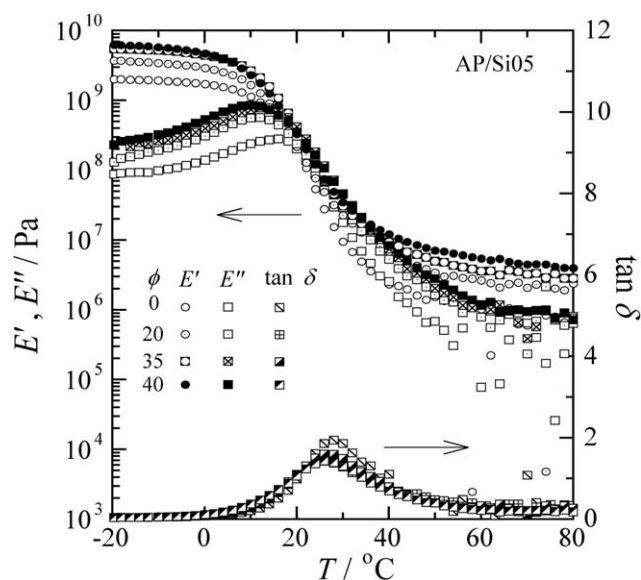


**Figure 2.**  $E'$ ,  $E''$ , and  $\tan \delta$  as a function of  $T$  for AP and AP/EP at 5 Hz and a heating rate of 2°C/min.

decreased steeply above 20°C, and decreased gradually again above 50°C. Corresponding to the  $E'$  behavior, the  $E''$  had a peak around 25°C. These results mean that the primary relaxation ( $\alpha$  relaxation) due to the glass–rubber transition of the AP chains was seen near 25°C. The AP chain exhibited the same behavior as those of typical amorphous polymers. Here, we define the representative  $T$  of  $\alpha$  relaxation as the peak temperature of  $\tan \delta$  ( $T_p$ ).  $T_p$  was 29°C for AP. On the other hand,  $T_p$  of the AP/EP blend was observed at 30°C, although the AP/EP blend contained 70 vol % EP. It was interesting to note that the glassy modulus of the AP/EP blend was higher than that of the AP. The result implies that the glassy modulus of EP was higher than that of AP. At  $T$ s above  $T_g$  the  $E'$  of the blend was lower than that of AP.

The  $T$  dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  of AP and AP/SiO<sub>5</sub> with various particle contents is shown in Figure 3. The  $E'$  values of both AP and AP/SiO<sub>5</sub> gradually decreased from about 15°C, and the  $\alpha$  relaxation of each sample was observed in the same  $T$  range, regardless of the content of SiO<sub>2</sub> particles. In other words, the dependence of the  $\tan \delta$  of AP/SiO<sub>5</sub> was almost the same as that of AP regardless of the SiO<sub>2</sub> particles. The magnitude of  $\tan \delta$  of AP/SiO<sub>5</sub> decreased slightly with increasing content of SiO<sub>2</sub> particles. The glassy and rubbery moduli of AP increased with the addition of SiO<sub>2</sub> particles. We concluded that the mobility of AP in the AP/SiO<sub>2</sub> composites was independent of the particles, although the modulus of the AP/SiO<sub>2</sub> composites was enhanced by the rigid SiO<sub>2</sub> particles. This means that the interaction between the AP chains and SiO<sub>2</sub> particles was extremely weak. Therefore, the  $\alpha$  relaxation of AP was not affected by the SiO<sub>2</sub> particles.

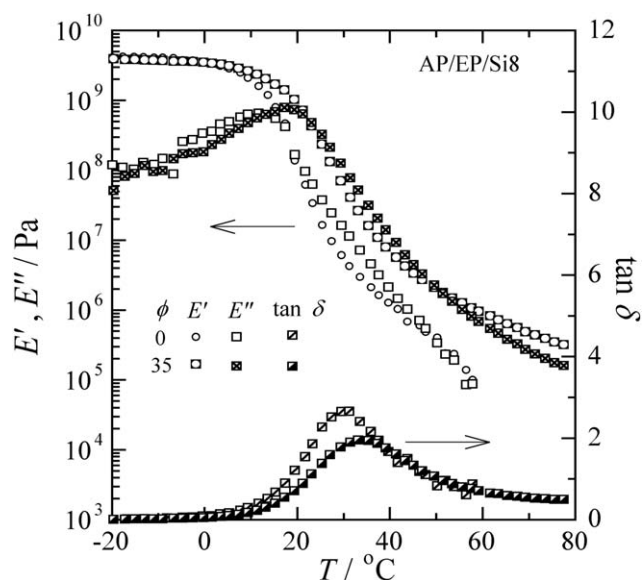
**Effect of SiO<sub>2</sub> on the Dynamic Mechanical Properties of AP/EP.** The  $T$  dependence of the  $E'$ ,  $E''$ , and  $\tan \delta$  values of AP/EP, AP/EP/SiO<sub>8\_35</sub>, is shown in Figure 4. The glassy modulus of AP/EP hardly changed with the SiO<sub>2</sub> content. The transition from the glassy state to the rubbery one of AP/EP/SiO<sub>8</sub> was observed



**Figure 3.**  $E'$ ,  $E''$ , and  $\tan \delta$  as a function of  $T$  for AP and AP/SiO<sub>5</sub> with various  $\phi$  values at 5 Hz and a heating rate of 2°C/min.

in the  $T$  range from about 20 to 40°C. The magnitude of  $\tan \delta$  decreased, and the peak of  $\tan \delta$  shifted slightly to a higher region with the addition of SiO<sub>2</sub> particles in the AP/EP matrix. The values of AP/EP and AP/EP/Si<sub>8\_35</sub> were 30 and 32°C, respectively. Therefore, the  $\alpha$  relaxation of the AP/EP/SiO<sub>2</sub> composites shifted slightly to a higher  $T$  by the addition of SiO<sub>2</sub> with a size of 8.0  $\mu\text{m}$ . Figure 5 shows the  $E'$ ,  $E''$ , and  $\tan \delta$  values for AP/EP/SiO<sub>5</sub> with various particle contents ( $\phi = 0, 20, 35,$  and 40 vol %). The glassy modulus hardly depended on the content of SiO<sub>2</sub>. The transition from the glassy state to the rubbery one was observed above 10°C. The  $\tan \delta$  of AP/EP/SiO<sub>5\_20</sub> decreased slightly compared with that of AP/EP. On the other hand, the peak of  $\tan \delta$  of AP/EP/SiO<sub>5</sub> with more than 35 vol % SiO<sub>2</sub> drastically decreased, and  $T_p$  clearly shifted to a higher  $T$ . Interestingly, the  $\tan \delta$  at a low  $T$  region (20°C <  $T$  < 30°C) decreased prominently above 35 vol %. Figure 6 shows  $T_p$  as a function of the SiO<sub>2</sub> content. The standard deviations of the  $T_p$  values are denoted as bars in Figure 6. As shown in Figure 6,  $T_p$  hardly changed for both the AP/SiO<sub>2</sub> and AP/EP/SiO<sub>2</sub> composites having an SiO<sub>2</sub> size of 8  $\mu\text{m}$ . On the contrary, the  $T_p$  of the AP/EP/SiO<sub>2</sub> composites with an SiO<sub>2</sub> size of 0.5  $\mu\text{m}$  increased drastically above 35 vol % SiO<sub>2</sub>.

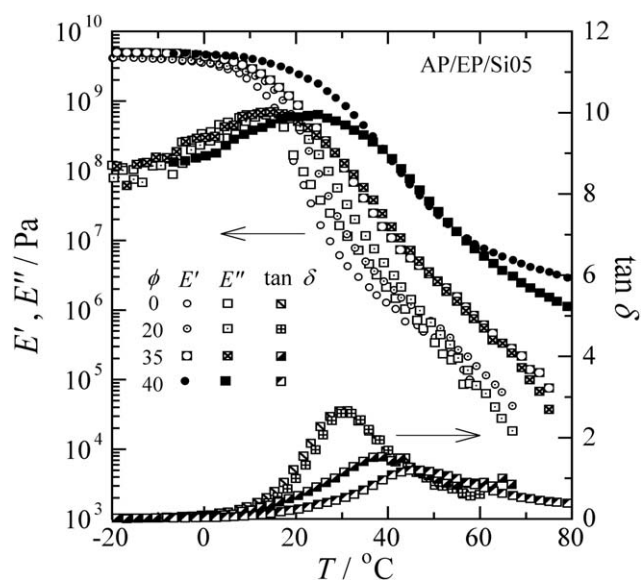
It was reported that the  $T_g$  and  $\alpha$  relaxation were changed by a chemical reaction between the polymer chain and a rigid filler.<sup>22</sup> This implied that the mobility of the polymer chain might be prevented by the filler because the affinity of the filler toward the polymer chain could be improved by the chemical reaction. Hence, we checked the chemical reaction of AP and EP with the SiO<sub>2</sub> surface by TGA after the rheological measurements. The TGA results verified that neither AP nor EP reacted with SiO<sub>2</sub> because the weight loss was less than 0.003% for the SiO<sub>2</sub> particles after centrifugation. Gel permeation chromatography with multiangle laser light-scattering measurements showed that the  $M_w$  and radius of gyration of AP were the same, regardless of the SiO<sub>2</sub> content, before and after the rheological measure-



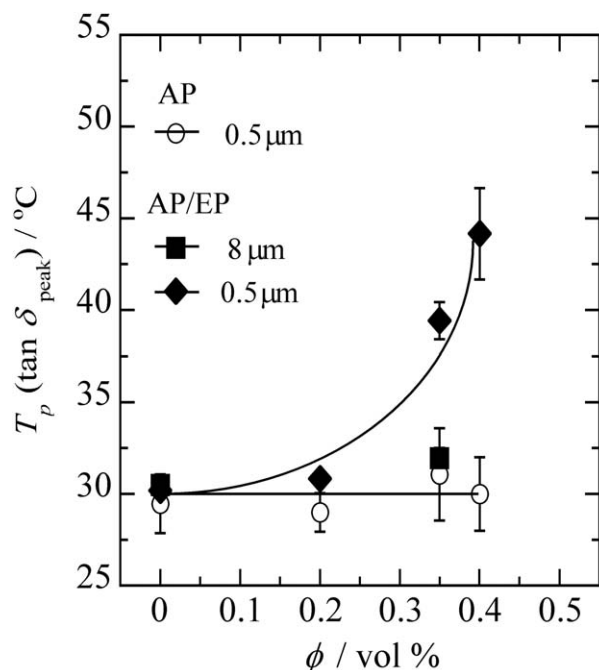
**Figure 4.**  $E'$ ,  $E''$ , and  $\tan \delta$  as a function of  $T$  for AP/EP and AP/EP/Si<sub>8\_35</sub> at 5 Hz and a heating rate of 2°C/min.

ments, although the measurement of  $M_w$  of EP was difficult because of the lower detection limit of gel permeation chromatography ( $M_w = 3000$  g/mol). Thus, we concluded that no chemical reactions occurred in the AP/EP/SiO<sub>2</sub> composites. In other words, it was impossible to interpret the enhanced mechanism of dynamic relaxation in terms of the chemical reaction.  $T_p$  shifted to a higher  $T$  above 35 vol %, as shown in Figure 5, without chemical reaction.

The previous results led to our presumption that the compatibility between the AP chain and SiO<sub>2</sub> particles was improved by the presence of the EP. In other words, the AP or EP might have adsorbed on the SiO<sub>2</sub> surface locally. If this presumption was correct, it would be possible to interpret the effect of the



**Figure 5.**  $E'$ ,  $E''$ , and  $\tan \delta$  as a function of  $T$  for AP/EP and AP/EP/SiO<sub>5</sub> with various SiO<sub>2</sub>  $\phi$  values at 5 Hz and a heating rate of 2°C/min.



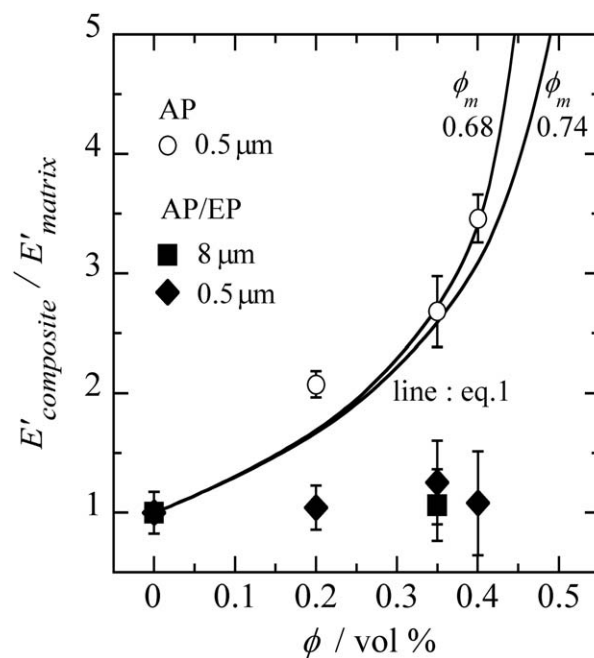
**Figure 6.**  $T_p$  as a function of  $\phi$  of  $\text{SiO}_2$  for AP/Si05, AP/EP/Si8, and AP/EP/Si05.

size of  $\text{SiO}_2$  on the  $\alpha$  relaxation of the AP/EP/ $\text{SiO}_2$  composites. A specific surface area of the  $\text{SiO}_2$  particles increased with a decrease in the particle size. Then, the adsorption amount of the AP or EP on the surface of particles must have increased with a decrease in the particle size. Under such a situation, the  $\alpha$  relaxation of the matrix phase would shift to higher  $T$ .

To clarify the effect of  $\text{SiO}_2$  on the glassy modulus of the matrix ( $E_{\text{matrix}}$ ; AP and AP/EP), the glassy modulus of the composite ( $E_{\text{composite}}$ ) was normalized with  $E_{\text{matrix}}$  at  $-10^\circ\text{C}$ . Figure 7 represents the normalized glassy modulus ( $E_{\text{composite}}/E_{\text{matrix}}$ ) as a function of the  $\text{SiO}_2$  content. The bars indicate the standard deviations. As shown in Figure 7, the  $E_{\text{composite}}$  of the AP/ $\text{SiO}_2$  composites increased monotonically with increasing  $\text{SiO}_2$  content and became three times larger than that of the AP matrix at an  $\text{SiO}_2$  content of 40 vol %. On the other hand, the  $E_{\text{composite}}$  values of the AP/EP/ $\text{SiO}_2$  composites scarcely increased with increasing  $\text{SiO}_2$  content. It is worth noting that the  $E_{\text{composite}}$  values of the AP/EP/ $\text{SiO}_2$  composites hardly changed, regardless of the content of rigid filler, although the modulus of the composites increased in an exponential manner with the content of rigid filler with far higher moduli than the polymeric material.<sup>12–14,16,20</sup> Nielsen<sup>10</sup> proposed the following equation [eq. (1)] for two-component composites. This equation is one of the most general theoretical equations used to estimate the modulus of two-phase composites:

$$\frac{E_c}{E_m} = \frac{1 + ABV_f}{1 - B\phi V_f} \quad (1)$$

where  $E_c$  and  $E_m$  are the moduli of the composite and the matrix, respectively;  $A$  is a constant that depends on the geometry of filler and the Poisson ratio of the matrix (i.e.,  $A = k_E - 1$ ,



**Figure 7.** Relative modulus ( $E_{\text{composite}}/E_{\text{matrix}}$ ) of AP/Si05, AP/EP/Si8, and AP/EP/Si05 versus  $\phi$  of  $\text{SiO}_2$  in the glassy state ( $-10^\circ\text{C}$ ). The solid lines represent the moduli calculated with the generalized Nielsen prediction [eq. (1)].

where  $k_E$  is the Einstein coefficient);  $B$  is a constant related to the ratio of the filler modulus ( $E_f$ ) to  $E_m$ ; and  $V_f$  is the volume fraction of the filler;  $\phi$  is a reduced concentration term.  $B$  takes into account the relative moduli of the filler and the matrix phase. It is defined by

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \quad (2)$$

The value of  $B$  is near 1.0 for fillers that are much more rigid than the polymer matrix. The factor  $\phi$  is a reduced content term, which depends on the maximum packing fraction ( $\phi_m$ ) of the particles. It is generally given by the following function, which fulfills the necessary boundary conditions:

$$\phi = 1 + \left( \frac{1 - \phi_m}{\phi_m^2} \right) V_f \quad (3)$$

The theoretical curves calculated by eq. (1) are shown in Figure 7 as a solid line, with values of  $\phi_m = 0.68$  and  $0.74$  ( $\phi_m$ ) taken for the body-centered cubic and hexagonal closest packing) and  $k_E = 2.50$  (the value of  $k_E$  for dispersed spheres), and the modulus in the glassy state ( $E'_g$ ) of the AP/EP matrix (experimental data at  $-10^\circ\text{C}$ ). We found that the modulus of the AP/ $\text{SiO}_2$  composites was in good agreement with the values calculated with eq. (1). However, it was obvious that the moduli calculated by eq. (1) did not fit the experimental moduli of the AP/EP/ $\text{SiO}_2$  composites. We considered this to be the reason why the experimental moduli hardly increased with the content of  $\text{SiO}_2$  particles for the AP/EP/ $\text{SiO}_2$  composites. If L-epo was adsorbed on the  $\text{SiO}_2$  surface, as explained previously, the modulus of the

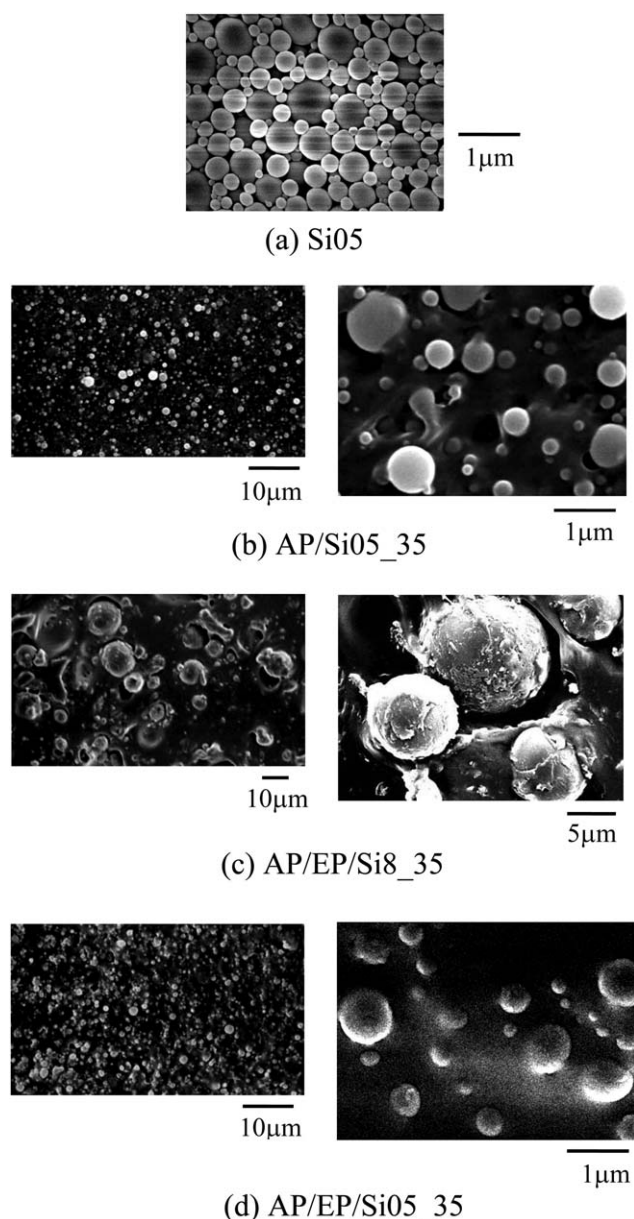
AP/EP/SiO<sub>2</sub> composites would have become lower because the modulus of L-epo must have been lower than that of the SiO<sub>2</sub> particles. In other words,  $B$  in eq. (2) was less than 1 because of the low modulus component adsorbed on the SiO<sub>2</sub> particles. On the other hand, the modulus of the AP/SiO<sub>2</sub> composites became higher with increasing SiO<sub>2</sub> content. If two factors canceled each other, the modulus of the composites hardly changed with the SiO<sub>2</sub> particles. It was likely that the selective adsorption of L-epo on the SiO<sub>2</sub> must have led to the specific thermophysical properties of the AP/EP/SiO<sub>2</sub> composites.

**Morphology of the AP/SiO<sub>2</sub> and AP/EP/SiO<sub>2</sub> Composites.** To confirm the adsorption of medium material on the SiO<sub>2</sub> surface, the morphologies of the three composites were investigated. The SEM photographs of Si05, AP/Si05\_35, AP/EP/Si8\_35, and AP/EP/Si05\_35 are shown in Figure 8. As shown in Figure 8(a), we found that the SiO<sub>2</sub> particles were spherical, and the surface of the particles was smooth like that of a general SiO<sub>2</sub> particle. The SiO<sub>2</sub> particles in these composites were regularly dispersed without remarkable agglomeration in the matrix, regardless of the diameter of the SiO<sub>2</sub> particles. The smooth and spherical shape of the SiO<sub>2</sub> particles were clearly observed in the AP/Si05\_35 composite. On the other hand, this shape of the SiO<sub>2</sub> particles was not observed for AP/EP/Si8\_35 and AP/EP/Si05\_35. In particular, we found that the surface of the SiO<sub>2</sub> particles was covered by some material, probably AP and/or EP components, for AP/EP/Si8\_35 and AP/EP/Si05\_35. The local and general selective adsorptions of the AP and EP components on the surface of the SiO<sub>2</sub> particles were found in AP/EP/Si8 and AP/EP/Si05, respectively. In observation of AP/EP/Si05, getting a clear image of the SiO<sub>2</sub> particles was very difficult. This result implied that the L-epo component, which behaved in a liquid state at room  $T$ , was adsorbed on the surface of the SiO<sub>2</sub> particles.

When the particles were randomly dispersed, the average distance between surfaces of the neighboring particles was several dozen nanometers at 35 vol % with diameter of 0.5  $\mu\text{m}$ . The micro-Brownian motion of AP might be suppressed when the average distance of SiO<sub>2</sub> particle is smaller than the radius gyration of AP chain. In other words, it is likely that  $\alpha$  relaxation shifted to high  $T$  region because the S-epo and CA with high  $T_g$  component eccentrically located at the size of radius gyration of AP chain. Therefore, we have to clarify the selective adsorption and eccentric location of the EP. However, a change in the thermophysical properties of a polymer by the addition of rigid particles without a chemical reaction is a scarce phenomenon. That is, it should be emphasized that the specific thermophysical properties appear in multicomponent systems without any chemical reaction. We concluded that the specific thermophysical properties were shown in the multiple composite, which had a sensitive affinity toward the rigid filler.

## CONCLUSIONS

We measured the  $T$  dependence of the  $E'$ ,  $E''$ , and  $\tan \delta$  values of AP/EP/SiO<sub>2</sub> composites with various SiO<sub>2</sub>  $\phi$  values to study the effects of the SiO<sub>2</sub> particles on the dynamic mechanical properties of the composites. Three kinds of EPs were used in



**Figure 8.** SEM micrographs of (a) Si05, (b) AP/Si05\_35, (c) AP/EP/Si8\_35, and (d) AP/EP/Si05\_35.

this study as EP components. Two kinds of SiO<sub>2</sub> particles with different sizes (0.5 and 8  $\mu\text{m}$ ) were used to investigate the dependence of the particle size. The  $\alpha$  relaxation due to the  $T_g$  shifted to a higher  $T$  with increasing  $\phi$  value for the AP/EP/SiO<sub>2</sub> composites having an SiO<sub>2</sub> particle size of 0.5  $\mu\text{m}$  but scarcely shifted for the composite having an SiO<sub>2</sub> particle size of 8  $\mu\text{m}$ . This suggested that the 0.5- $\mu\text{m}$  SiO<sub>2</sub> nanoparticles adsorbed lots of low- $T_g$  components compared to the 8  $\mu\text{m}$  microparticles because the nanoparticles had a large surface area.  $E'_g$  exhibited a very weak  $\phi$  dependence for the AP/EP/SiO<sub>2</sub> composites, although  $E'_g$  of the AP/SiO<sub>2</sub> composites increased with  $\phi$ , which was the same behavior as that of general two-component polymer/filler composites. The theoretical values of  $E'_g$  were calculated with the Nielsen equation and compared with our experimental values. The experimental

values of the AP/SiO<sub>2</sub> composites were in good agreement with the calculated ones. However, those of the AP/EP/SiO<sub>2</sub> composites exhibited a very weak  $\phi$  dependence and did not agree with the calculated ones. The SEM observations suggested that the EP component physically adsorbed on the surface of the SiO<sub>2</sub> particles. These peculiar results demonstrated that the dynamic mechanical properties of the AP/EP/SiO<sub>2</sub> composites were due to the selective adsorption of the EP component. We concluded that specific properties were found for the three-component composites having a sensitive affinity toward the rigid filler.

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