

# Influence of Polarity of Polymer on Inorganic Particle Dispersion in Dielectric Particle/Polymer Composite Systems

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## SYNOPSIS

The influence of the polarity of polymers on the degree of dispersion of BaTiO<sub>3</sub> particles in BaTiO<sub>3</sub>/polymer composite systems was investigated. The BaTiO<sub>3</sub>/polymer composite systems were prepared from BaTiO<sub>3</sub> particles and low-density polyethylene (LDPE) or ethylene vinyl acetate copolymer (EVA) with 7 and 15 wt % vinyl acetate. Scanning electron microscopy observation showed that BaTiO<sub>3</sub> particles aggregated in the polymer matrices and dispersed more readily into the EVA matrix than into LDPE. The shift of the  $\beta$ -peak temperature by ca. +5°C in the temperature dispersion of the loss modulus was observed for EVA–BaTiO<sub>3</sub> composite systems in dynamic mechanical property measurement. On the other hand, the  $\beta$ -peak temperature of the polymers filled with graphite particles, which have hydrophobic surfaces, was almost constant in a volume fraction region of 0–0.3. The ellipsoidal axes' ratios given by comparison of experimental dielectric constant values and theoretical ones using the Maxwell equation were 4.2, 3.6, and 3.1 for LDPE/BaTiO<sub>3</sub>, EVA(7%)/BaTiO<sub>3</sub>, and EVA(15%)/BaTiO<sub>3</sub> composite systems, respectively. The axes' ratio decreased by the introduction of polar vinyl acetate groups into nonpolar LDPE. The results confirmed that the polarity of the polymers was one of the key factors governing the dispersibility of BaTiO<sub>3</sub> particles in the polymer matrix. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Composite systems of polymers and dielectric inorganic particles are expected to be useful dielectric materials since they might show superior mechanical and fabrication properties as well as excellent dielectric properties. It is well known that dielectric properties of composite systems depend strongly on the degree of dispersion of inorganic dielectric particles in a polymer matrix. Many theoretical investigations have been performed on the dielectric constants,  $\epsilon$ , in various composite systems. In this context,  $\epsilon$  for the composite systems consisting of a continuous polymer phase and a dielectric particle phase has been expressed by the Maxwell [eq. (1)]

and Bruggeman formulas.<sup>1,2</sup> Yamada et al.<sup>3</sup> and Das-Gupta and Doughty<sup>4</sup> reported that the  $\epsilon$  for the composite system consisting of a polar polymer such as poly(vinylidene fluoride) and ellipsoidal dielectric particles were in good agreement with the theoretical values derived from eq. (1):

$$\epsilon_C = \epsilon_1 \left[ 1 + \frac{n\phi(\epsilon_2 - \epsilon_1)}{n\epsilon_1 + (\epsilon_2 - \epsilon_1)(1 - \phi)} \right] \quad (1)$$

where  $\epsilon_C$ ,  $\epsilon_1$ , and  $\epsilon_2$  are the dielectric constant for a composite system, a polymer, and a particle, respectively;  $\phi$ , the volume fraction of the particle, and  $n$ , the parameter attributed to the shape of the ellipsoidal particles. Many researchers have investigated the dielectric properties of the several composite systems and found that the dielectric properties changed discontinuously at the loading content of particles, beyond which the particles formed

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a continuous phase in the composite system.<sup>5-7</sup> The connectivity model was proposed by Newnham et al.<sup>5,8</sup> in interpreting the discontinuous change in the  $\epsilon$  value as a function of loading content.

Various polymers such as poly(vinylidene fluoride), poly(vinyl chloride), polystyrene, polyethylene, poly(methyl methacrylate), and epoxy are used as a matrix polymer of dielectric composites. Dielectric particles used in the composites are hydrophilic inorganic particles such as barium titanate ( $\text{BaTiO}_3$ ), lead titanate ( $\text{PbTiO}_3$ ), and lead zirconate titanate. However, many researchers have not considered the influence of the polar groups of the matrix polymers on the hydrophilic inorganic particle dispersion. This influence has not been fully understood, but it is important for the application of dielectric composite materials to clarify this influence.

In this study, the influence of the polarity of the polymers on the degree of dispersion of dielectric inorganic particles in  $\text{BaTiO}_3$ /polymer composite systems and their dielectric constants is discussed. We used nonpolar and polar polymers which were low-density polyethylene (LDPE) and ethylene-vinyl acetate-co-polymer (EVA) containing vinyl acetate of 7 or 15 wt %. The degree of dispersion of  $\text{BaTiO}_3$  particles was investigated by SEM observation, X-ray diffraction analysis, dynamic mechanical properties, and ac impedance measurement. The introduction of polar vinyl acetate groups into nonpolar LDPE improved the degree of dispersion of  $\text{BaTiO}_3$  particles in the polymer matrices through dipole-dipole interaction and/or hydrogen bonding and resulted in the decrease in the  $\epsilon$  values above  $\phi$  of 0.3. The particle dispersion could be explained on the basis of Maxwell equation that expressed the  $\epsilon$  of a dielectric particle-polymer composite system. It was clearly shown that the polarity of the polymers was one of the key factors governing the degree of dispersion of the dielectric particles.

## EXPERIMENTAL

### Preparation of Composite Systems

Polymers used in this work were low-density polyethylene (LDPE: Mitsubishi F121) and ethylene-vinyl acetate copolymer (EVA: Showa Denko CL12-3, CL12-5) which contained 7 or 15 wt % vinyl acetate. The dielectric powder was  $\text{BaTiO}_3$  (Fuji Titanium), which had an average particle size of 1.2  $\mu\text{m}$  and a specific surface area of 1.9  $\text{m}^2/\text{g}$ . For comparison, spherical graphite with an average particle size of 5.0  $\mu\text{m}$  and a specific surface area of 2.4  $\text{m}^2/\text{g}$

was used as a hydrophobic particle. The LDPE and EVA were dissolved, respectively, in cyclohexane at 85°C. The  $\text{BaTiO}_3$  or graphite particles were mixed with the respective polymer solutions in a particle volume fraction range of 0–0.6 using a rotary evaporator. The  $\text{BaTiO}_3$  and graphite particles were dried at 150°C for 24 h under vacuum conditions. The cyclohexane of the compounded materials was evaporated under vacuum conditions at 85°C. Subsequently, the compounded materials were mixed in a hot roll for 10 min in the temperature range of 90–120  $\pm$  5°C. The composites obtained were pressed into a sheet with 1 mm thickness at 160°C under a pressure of 184  $\text{kg}/\text{cm}^2$  and were then quenched at 15°C.

### Characterization of Composite Systems

The dispersion of the  $\text{BaTiO}_3$  particles in the composite system were observed by a scanning electron microscopy (SEM, Hitachi S-310A) on the surface fractured under liquid  $\text{N}_2$ . X-ray diffractions of the LDPE and EVA matrices were measured using an automated X-ray diffractometer (Rigaku RINT1300) with  $\text{CuK}\alpha$  radiation in order to examine the variation of a crystallite size and a crystallinity of polyethylene with the loading powder.

Dynamic mechanical properties were measured using a rheometer (Seiko Instruments SDM5600) at a heating rate of 1°C/min, with a frequency of 5 Hz, at temperature ranges from –100°C to 60, 70, or 80°C for EVA(15%)-particle, EVA(7%)-particle, and LDPE-particle composite systems, respectively.

### Characterization of Particles

Surface areas of the particles were determined by the BET method. Adsorption isotherms for water on the particles were measured at 25°C and at relative pressure of 0.001–1.0 by a volumetric apparatus (Japan Bell BELSORP 18). Prior to all measurement, the particles were treated at 150°C under vacuum conditions.

### Dielectric Constant of Composite Systems

Dielectric constants of the composite systems were monitored by inserting the sample sheet into a three-terminal parallel-plate capacitor (Hewlett Packard, HP16451B) and measuring complex impedance with an ac impedance analyzer (Hewlett Packard, HP4192A) in the frequency range from 5 Hz to 13 MHz at 25°C. The specimen was 60  $\times$  60 mm and the thickness was 1 mm. The electrode of the spec-

imen was obtained by sputtering with Pt–Pd. The electrode diameter was 40 mm.

## RESULTS AND DISCUSSION

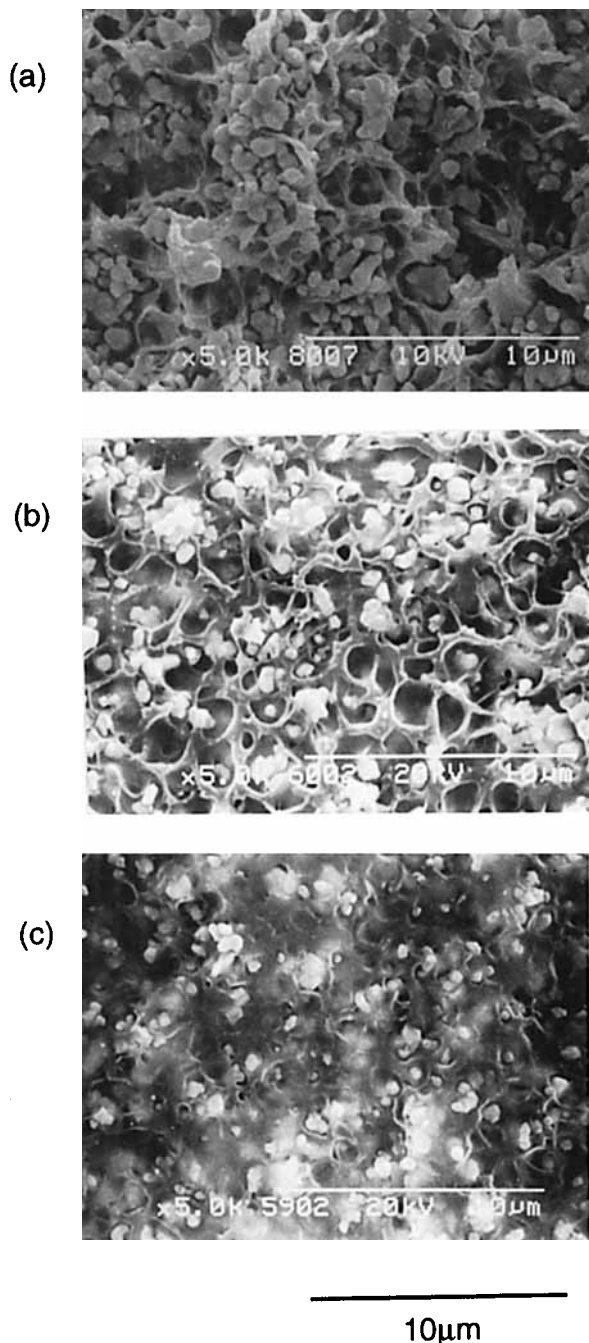
### Particle Dispersion in Polymer Matrices

The surfaces of the composite systems fractured under liquid N<sub>2</sub> were observed by an SEM in order to examine particle dispersion. Figure 1 shows the scanning electron micrographs of LDPE, EVA(7%), and EVA(15%) loading BaTiO<sub>3</sub> in a volume fraction of the particle,  $\phi$ , of 0.3. The hydrophilic BaTiO<sub>3</sub> particles easily formed small aggregates irrespective of the polymers. The BaTiO<sub>3</sub> aggregates were dispersed in the continuous LDPE and EVA matrices below of  $\phi$  of 0.25 [Fig. 2(a)]. In the  $\phi$  region above 0.3 [Fig. 2(b)], BaTiO<sub>3</sub> aggregates were in contact with each other for the LDPE composite system. To clarify these observations, we examined whether the surface of the BaTiO<sub>3</sub> particles were water-attracting. Figure 3 shows the adsorption isotherms of water vapor on BaTiO<sub>3</sub> and the graphite particle. The amounts of a monolayered water absorbed per unit area of the BaTiO<sub>3</sub> and graphite particles calculated by applying the BET method to the isotherms were 5.2 and 0.2 nm<sup>-2</sup>, respectively. The BaTiO<sub>3</sub> particle had, by far, higher adsorptive activity of the water molecule than that of the graphite particle. Therefore, it was suggested that the BaTiO<sub>3</sub> particles aggregated strongly together in the polymer matrices by means of hydrogen bonding between the particles. The BaTiO<sub>3</sub> particles were more easily dispersed in the EVA matrix than in LDPE. It was observed that introduction of the polar vinyl groups into nonpolar LDPE improved the adhesion between BaTiO<sub>3</sub> particles and the polymers. These results suggest that the degree of dispersion of the BaTiO<sub>3</sub> particles is determined mainly by the interaction based on hydrogen bonding and/or dipole–dipole interaction between the particle surfaces and vinyl acetate groups of EVA.

Figure 4 shows LDPE loading graphite at a  $\phi$  of 0.3. Graphite particles did not aggregate in LDPE and EVA matrices. This result suggests that the dispersibility of the particles was presumably improved by good affinity between hydrophobic graphite particles and nonpolar ethylene chains of the polymers.

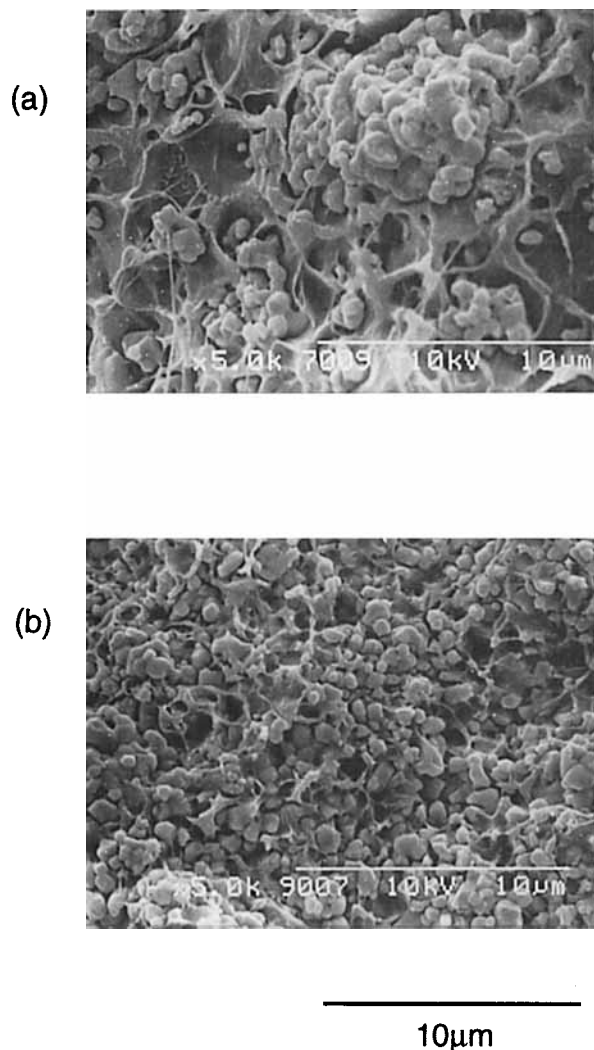
### Dynamic Mechanical Properties of Composite Systems

To discuss the interaction between particles and polymer matrices, we measured the dynamic me-



**Figure 1** SEM micrographs of the fractured surface of polymer/BaTiO<sub>3</sub> composite systems with a particle volume fraction of 0.3: (a) LDPE; (b) EVA(7%); (c) EVA(15%).

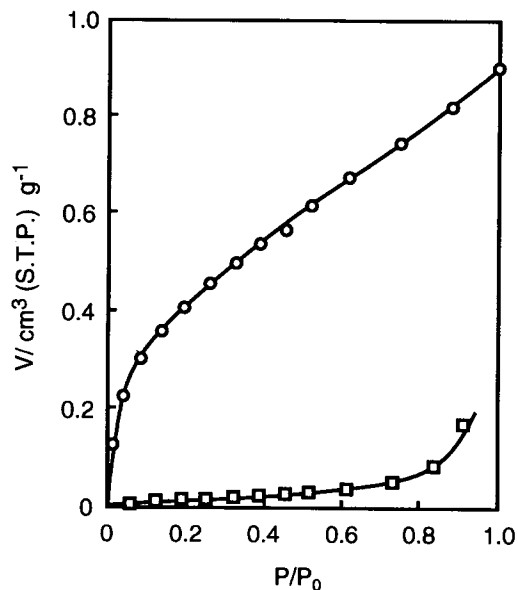
chanical properties of LDPE and EVA filled with the BaTiO<sub>3</sub> or graphite particles. Figure 5 shows the dynamic storage modulus, loss modulus, and loss tangent for LDPE, EVA(7%), and EVA(15%) as a function of temperature. The respective peaks of the loss modulus,  $E''$ , at  $-9.5^{\circ}\text{C}$  for LDPE,  $-12.9^{\circ}\text{C}$  for EVA(7%), and  $-19.1^{\circ}\text{C}$  for EVA(15%) were as-



**Figure 2** SEM micrographs of the fractured surface of LDPE/BaTiO<sub>3</sub> composite systems with a particle volume fraction of (a) 0.1 and (b) 0.5.

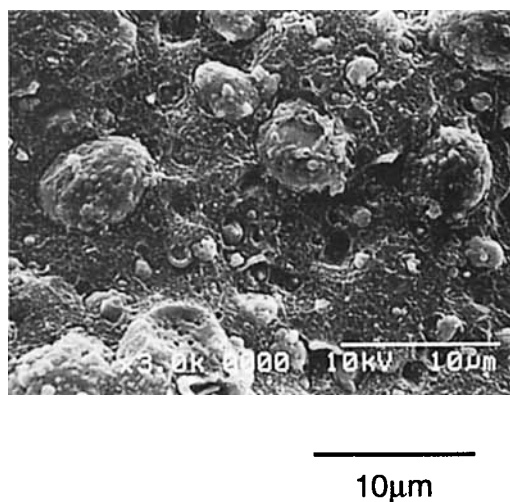
signed to the  $\beta$ -transition of the polyethylene.<sup>9-11</sup> It is known that the  $\beta$ -transition is associated with the relaxation of a main chain in the amorphous phase, the branch point of the molecular chain, or the vinyl acetate unit of the EVA copolymer.<sup>10-12</sup> The  $\beta$ -transition corresponded to the glass transition of LDPE and EVA. The temperature of the  $\beta$ -transition decreased from  $-9.5$  to  $-19.1^\circ\text{C}$  with increasing vinyl acetate contents. The crystallinity of polyethylene decreased with increasing vinyl acetate contents, as shown in Table I. These data indicated that the vinyl acetate units of EVA were distributed in the amorphous region.

Figure 6 shows the relationship between the  $\beta$ -peak temperature of  $E''$  and  $\phi$  for LDPE and EVA filled with graphite or BaTiO<sub>3</sub>. The shift of the  $\beta$ -

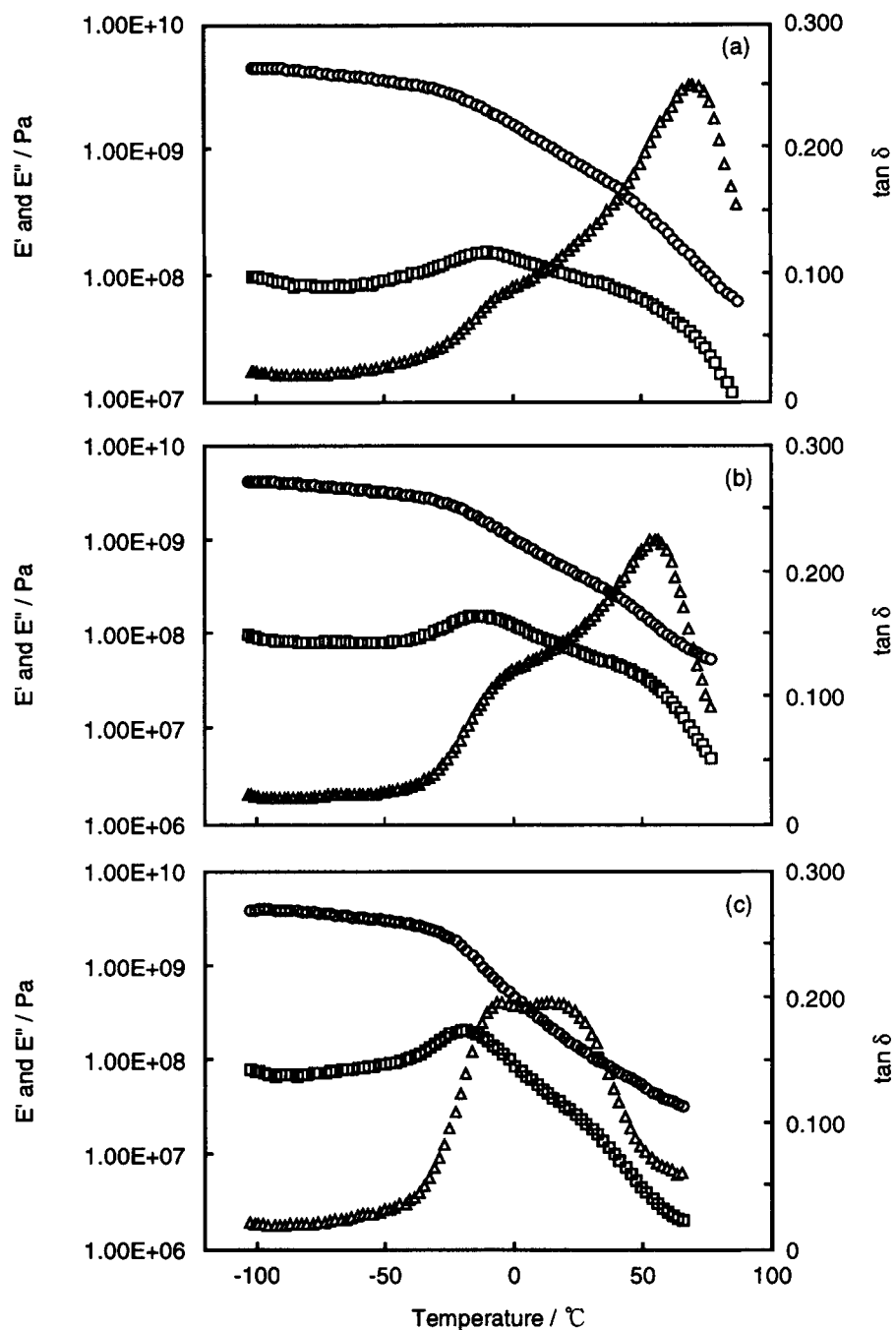


**Figure 3** Adsorption isotherms of water at  $25^\circ\text{C}$  on particles: (○) BaTiO<sub>3</sub>; (□) graphite.

peak temperature by ca.  $+5^\circ\text{C}$  was observed for the EVA/BaTiO<sub>3</sub> composite systems. On the other hand, the  $\beta$ -peak temperature for LDPE/BaTiO<sub>3</sub> and LDPE or EVA/graphite composite systems was independent of  $\phi$  [see Fig. 6(a) and (b)]. Many researchers have reported that the ascending shifts of the glass transition temperature upward with increasing  $\phi$  were observed for the composite systems consisting of inorganic particles such as TiO<sub>2</sub>, glass



**Figure 4** SEM micrographs of the fractured surface of LDPE/graphite composite systems with a particle volume fraction of 0.3.



**Figure 5** Logarithms of storage and loss modulus, and loss tangent at 5 Hz, plotted against temperature for three polymers: (○) storage modulus; (□) loss modulus; (△) loss tangent; (a) LDPE; (b) EVA(7%); EVA(15%).

beads, and mica and an amorphous polymers such as poly(vinyl chloride), polystyrene, epoxy resin, and poly(methyl methacrylate).<sup>12-16</sup> This phenomenon was explained by the interaction between hydroxyl groups on the surface of the inorganic particles and the polar groups of the polymers. This interaction is thought

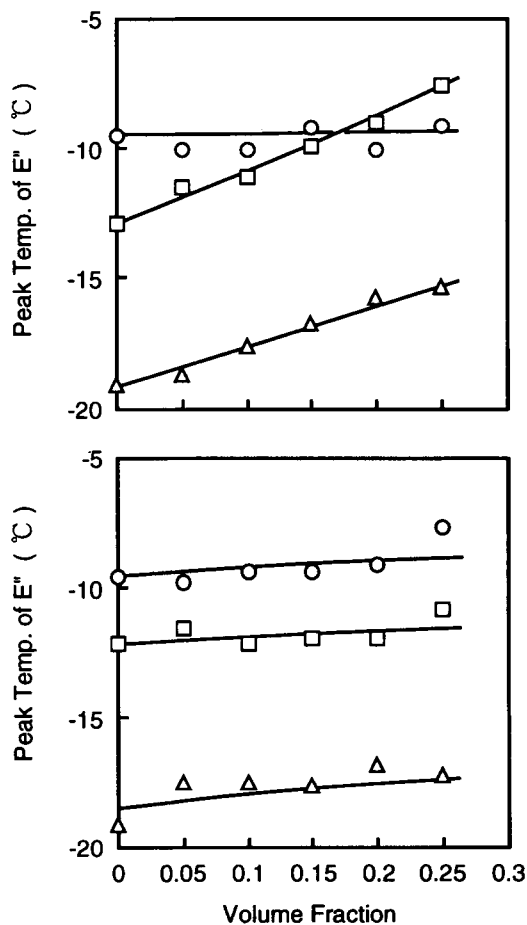
to be hydrogen bonding or dipole-dipole interaction. Therefore, the peak shift of the temperature dispersion of  $E''$  for EVA-BaTiO<sub>3</sub> composite systems was due to the presence of hydrogen bonding and/or dipole-dipole interaction between the particle surface and the acetate groups of EVA.

**Table I Crystallinity of Three Polymers**

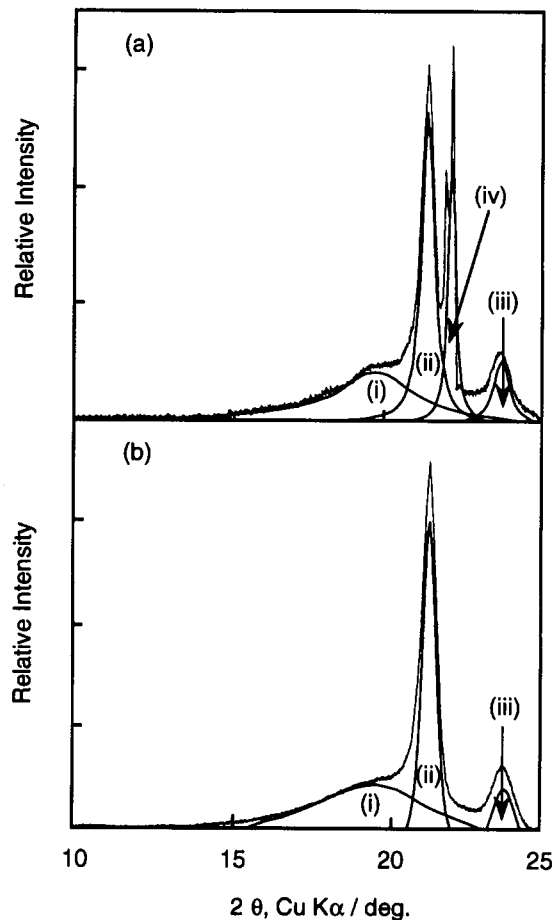
Polymers	Crystallinity (%)
LDPE	46
EVA (7%)	45
EVA (15%)	35

**X-ray Diffraction Analysis for Composite Systems**

To examine the relationship between the change of crystallite size of polyethylene with loading particles and particle dispersion, we measured the X-ray diffraction for the composite systems. Figure 7 shows the X-ray diffraction profiles of LDPE filled with the BaTiO<sub>3</sub> [Fig. 7(a)] or graphite [Fig. 7(b)] particles at  $\phi$  of 0.05. These profiles were resolved into the following components: (i) amorphous region, (ii) (110) plane of polyethylene, (iii) (200) plane of poly-

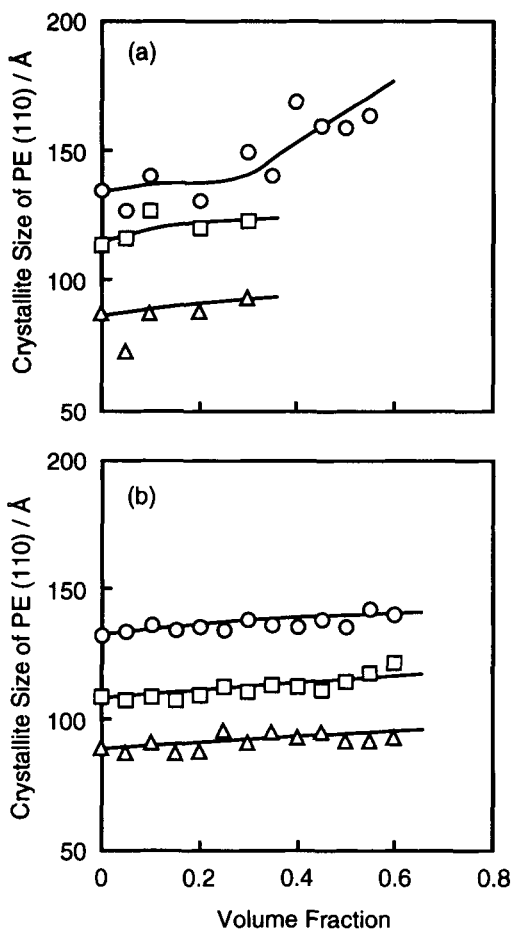


**Figure 6** Variation of peak temperature of loss modulus with particle content for composite systems: (a) polymers-BaTiO<sub>3</sub>; (b) polymers/graphite. (○) LDPE; (□) EVA(7%); (△) EVA(15%).



**Figure 7** X-ray diffraction patterns of LDPE/particles composite systems with a volume fraction range of 0.05; (a) BaTiO<sub>3</sub>; (b) graphite. (i) amorphous region; (ii) (110) plane of PE; (iii) (200) plane of PE; (iv) (100) plane of BaTiO<sub>3</sub>.

ethylene and (iv) (100) plane of BaTiO<sub>3</sub>. The crystallite size of the (110) plane was calculated on the basis of Sheer's equation. Figure 8 shows the relationship between a volume fraction of the particles,  $\phi$ , and the crystallite size of the (110) plane of polyethylene crystal for LDPE and EVA filled with the BaTiO<sub>3</sub> or graphite particles. The crystallite size for LDPE filled with BaTiO<sub>3</sub> was almost constant in the  $\phi$  region between 0 and 0.3 and increased gradually beyond  $\phi$  of 0.4 [Fig. 8(a)]. Little change in the crystallite size of EVA filled with BaTiO<sub>3</sub> was also observed in the  $\phi$  region between 0 and 0.3. We could not resolve the peak profiles exactly for the EVA/BaTiO<sub>3</sub> composite systems in the  $\phi$  region above 0.4. This is because of the following reasons: (1) the absorption coefficients of CuK $\alpha$  radiation for Ba and Ti atoms were larger than that for the C atom and (2) the crystallinity of EVA was smaller



**Figure 8** Relationship between volume fraction and crystallite size of (110) plane of PE for composite systems: (a) polymer/BaTiO<sub>3</sub>; (b) polymer/graphite. (O) LDPE; (□) EVA(7%); (Δ) EVA(15%).

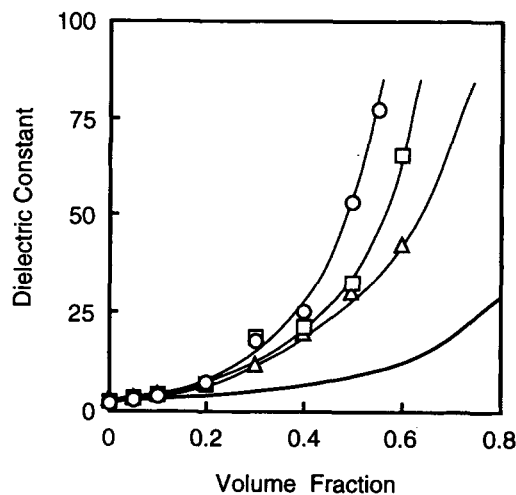
than that of LDPE. The crystallite size for polymer/graphite composite systems was also independent of  $\phi$  [Fig. 8(b)].

We already reported that polyethylene molecules crystallized around the loaded particles in both LDPE/graphite and LDPE/SnO<sub>2</sub> composite systems and that the crystallization of polyethylene was affected by the nature of the filled particles and their dispersion.<sup>17</sup> Increase in the crystallite size of the polyethylene (110) plane with  $\phi$  was interpreted as due to the orientation of polyethylene crystal along the rolling direction.<sup>17</sup> Therefore, little variation of the crystallite size with  $\phi$  indicated that polyethylene molecules crystallized isotropically around spherical particles. On the other hand, increase in the crystallite size of the LDPE–BaTiO<sub>3</sub> composite system in the  $\phi$  region above 0.3 was due to the orientation of the polyethylene crystal on the surfaces of the BaTiO<sub>3</sub> particles which were ordered along the roll-

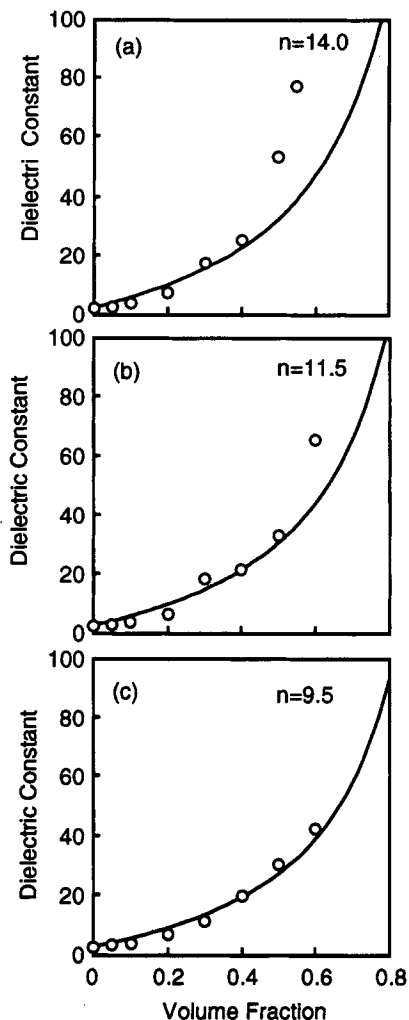
ing direction by the strong mechanical shearing force for the polymer during the roll-mixing procedure. Therefore, these results indicated that the graphite particle, which has a hydrophobic surface, dispersed randomly in the polymer matrices, while the BaTiO<sub>3</sub> particle, which has a hydrophilic surface, was ordered along the rolling direction in the nonpolar LDPE above of  $\phi$  0.3.

### Dielectric Constant of Composite Systems

The relationship between  $\phi$  and the dielectric constant at 100 kHz for LDPE and EVA filled with BaTiO<sub>3</sub> particles is shown in Figure 9. Kitayama,<sup>18</sup> Yamada et al.,<sup>3</sup> and Das-Gupta and Doughty<sup>4</sup> reported that  $\epsilon$  for binary systems consisting of polymers and dielectric inorganic particles were in good agreement with the theoretical values obtained from eq. (1). We investigated the change of the degree of dispersion of BaTiO<sub>3</sub> particles with the morphological parameter derived from eq. (1). The solid line in Figure 9 is the theoretical curve when  $n$  is 3. This curve was calculated as the homogeneous dispersion of spherical particles in the polymer matrix.  $n$  reflects the shape of the particles. The  $\epsilon$  for the LDPE or EVA/BaTiO<sub>3</sub> composite systems deviated markedly from the theoretical curve when  $n$  is 3. These results suggested that BaTiO<sub>3</sub> particles aggregated with each other in the matrix owing to hydrogen bonding and/or dipole–dipole interaction between the particle surfaces. Figure 10 shows the comparison of experimental data and theoretical values derived by data-fitting procedure using eq. (1), where



**Figure 9** Relationship between volume fraction and dielectric constant for polymer/BaTiO<sub>3</sub> composite systems: (O) LDPE; (□) EVA(7%); (Δ); EVA(15%); (—) theoretical curve when  $n$  is 3.



**Figure 10** Comparison of experimental data and theoretical values for polymer/BaTiO<sub>3</sub> composite systems: (a) LDPE; (b) EVA(7%); (c) EVA(15%); (—) theoretical values.

$n$  was estimated to be 14.0, 11.5, and 9.5 for LDPE/BaTiO<sub>3</sub>, EVA(7%)/BaTiO<sub>3</sub>, and EVA(15%)/BaTiO<sub>3</sub> composite systems, respectively. The  $\epsilon$  values of the EVA(15%)/BaTiO<sub>3</sub> composite system were best-fitted with the theoretical ones [Fig. 10(c)]. On the other hand, the  $\epsilon$  values for the LDPE–BaTiO<sub>3</sub> composite system in the  $\phi$  region above 0.4 remarkably deviated from the theoretical values, suggesting that a continuous medium changed from the polymer to the BaTiO<sub>3</sub> particles beyond  $\phi$  of 0.4. Similar results were obtained with the EVA(7%)/BaTiO<sub>3</sub> composite system in the  $\phi$  region above 0.5.

The ellipsoid axes' ratios calculated on the basis of Maxwell's equations were 4.2, 3.6, and 3.1 for the LDPE/BaTiO<sub>3</sub>, EVA(7%)/BaTiO<sub>3</sub>, and EVA(15%)/BaTiO<sub>3</sub> composite systems, respectively. Therefore,

for the EVA(15%)/BaTiO<sub>3</sub> composite system, the BaTiO<sub>3</sub> particles were dispersed as ellipsoidal aggregates with the axes' ratio of 3.1 in the matrix. The axes' ratio decreased with increasing the vinyl acetate contents of EVA. This was probably due to appreciable interaction between the surface of the BaTiO<sub>3</sub> particles and the vinyl acetate groups of EVA, and the dispersibility of BaTiO<sub>3</sub> particles was clearly improved by the introduction of the vinyl acetate groups. Moreover, the dispersing state of the BaTiO<sub>3</sub> particles could be interpreted by the statistical comparison of experimental  $\epsilon$  values and theoretical ones derived from the Maxwell equation.

## CONCLUSION

The influence of the polarity of polymer matrices on the degree of dispersion of BaTiO<sub>3</sub> particles was successfully investigated by the SEM observation, X-ray diffraction analysis, dynamic mechanical properties, and dielectric measurement. The introduction of vinyl acetate groups into nonpolar polyethylene improved the degree of dispersion of BaTiO<sub>3</sub> particles in the polymer matrix. The degree of dispersion of the BaTiO<sub>3</sub> particles was largely determined by the attractive interaction based on hydrogen bonding and/or dipole–dipole interaction at the BaTiO<sub>3</sub>/polymer interfaces. This is illustrated by the following phenomena: (i) the BaTiO<sub>3</sub> particles, which have hydrophilic surfaces, were more easily dispersed in the EVA matrix with a polar vinyl acetate groups than they were in the LDPE matrix. (ii) The shift of the  $\beta$ -peak temperature by ca. +5°C in the temperature dispersion of  $E''$  was observed for the EVA–BaTiO<sub>3</sub> composite systems. On the other hand, the  $\beta$ -peak temperature for LDPE/BaTiO<sub>3</sub> and LDPE or EVA/graphite composite systems was not correlated with  $\phi$ . (iii) Polyethylene molecules crystallized isotropically around aggregates of the graphite particles which dispersed randomly in the polymer matrices. The aggregates of BaTiO<sub>3</sub> particles, which have a hydrophilic surface, were ordered along the rolling direction in nonpolar LDPE. (iv) The ellipsoidal axes' ratios given by the comparison of experimental  $\epsilon$  values and theoretical ones using the Maxwell equation decreased with the introduction of the polar vinyl acetate groups into nonpolar LDPE.

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