Effect of ceramics/polymer heterointerface on dielectric property of self-assembled BaTiO3/poly-L-lactic acid composite materials

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The dispersion state of barium titanate (BT) particle groups in self-assembled BT/poly-L-lactic-acid (PLLA) composites prepared under different fabrication conditions was investigated. In particular, the BT/PLLA/BT heterointerface in the BT aggregates by the self-assembly process was analyzed and the effect of the BT/PLLA/BT heterointerface and the BT/PLLA interface on the dielectric properties of BT/PLLA composites was investigated. BT/PLLA composites were fabricated by adding BT particles and BT granules with low and high-speed kneading conditions. The volume fraction of BT in composites varied from 5 to 20 vol.%. The BT aggregates having a BT/PLLA/BT heterointerface were formed under the low-speed kneading condition and the BT agglomerates having a BT/PLLA interface were formed under the high-speed kneading condition within the self-assembly process. The tan δ of the BT/PLLA composite of self-assembled BT aggregates having the BT/PLLA/BT heterointerface was lower than that of the BT granules having the BT/PLLA interface. The dielectric constant (ε') of the self-assembled composite was increased by growing an average secondary particle area of BT fillers. In contrast, the average secondary particle area of BT granules was increased, as compared with 5 vol.% of BT. However, the change in ε' was saturated. The slopes of the change in the ε' depending on the secondary particle area of BT fillers were different between the self-assembled BT aggregates having the BT/PLLA/BT heterointerface and the BT granules having the BT/PLLA interface. Thus, it was suggested that it was an important role in improving the dielectric properties to form ceramic secondary particle groups having the ceramics/polymer/ceramics heterointerface by the self-assembly process.

Key-words : BaTiO3/PLLA, Polymer composite material, Ceramics/polymer heterointerface, Dielectric property, Self-assembly

1. Introduction

In general, the dielectric constant of a polymer is relatively low, less than 10.1,3 In order to increase dielectric constant for energy storage in polymers, ceramic powder fillers with a high dielectric constant such as barium titanate (BaTiO3, BT) with a dielectric constant of 1000 or more are added to the polymer matrix.1,3 However, 50 vol.% or more of ceramics with a high dielectric constant are applied to the polymer matrix to achieve a high dielectric constant. Thus, the mechanical properties of these composites are extremely poor and are not suitable for using dielectric materials such as capacitors. In ceramics/polymer composite material, a composite of two components is added; each component and volume fraction determine the total energy density, and the dispersion state of the ceramic filler in the polymer matrix plays a vital role in the energy density during energy storage.1,3 Furthermore, while controlling the degree of dispersion of a ceramic filler in the polymer matrix, both ceramic and polymer are chemically modified for dispersing the ceramic filler to a higher degree.3

Previously, Robertson and Varlow2 showed that size, shape, and aggregation of BT particles influence an effective bulk dielectric constant of BT filler or polymer composites with a high dielectric constant. They suggested forming agglomerations, which reduces impedance due to the lower ratio of resin to filler across the shortest impedance

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Researchers proposed a more considerable electrical flux for the agglomerated particles to move rather than for the non-agglomerated particles, which would result in a higher permittivity for the per unit sample. Akimune et al. showed an analysis of mechanical and electrical properties of TiN/Si3N4 in which a particle shape and size of the granules in ceramics play an important role in network formation. They highlighted that formation of agglomerates leads to an improvement in function. Researchers have also shown that the average secondary particle area of BT filler aggregates of BT filler/poly-L-lactic acid (PLLA) composites is related to dielectric constant, regulating the microstructure of aggregates. Phan et al. reported the effect of controlled BT nanoparticle aggregates on the dielectric properties of epoxy nanocomposites for various experimental parameters, such as frequency, ceramic content, and temperature. They suggested that the nature of an interphase region depends not only on the chemical bonding at the filler interface but also on the network confinement between nanoparticles.

Heterointerface of ZnO with Bi2O3 or Pr–Co Oxide has been investigated. The insulating region, such as Bi2O3 and Pr–Co, is essential for controlling electrical properties, whereas an insulator zone exists between the grain boundaries. Previously, Yano et al. fabricated multilayered composites with Ni/ZnO/PrCoOxide/Au structure to investigate electrical properties at junctions. They found a depletion region formed in ZnO films near the ZnO/PrCoOxide interface. Matsuoka reported nonohmic properties of ZnO ceramics with five additives, such as Bi2O3, Nb2O5, MnO, Cr2O3, and Sb2O3, and proposed a microstructure model that surround each of ZnO grains with a segregation layer responsible for the nonohmic property. In their model, the electrical capacitance of ZnO ceramic was primarily attributed to segregation layers. The electrical properties are therefore controlled by a microstructure with grain boundaries such as ceramics/intergranular material.

Munakata et al. highlighted that the dielectric constant of the BT/PLLA composites and the size of the self-assembled BT secondary particle groups. In a previous report, the morphology of the self-assembled BT secondary particle groups was affected by the kneading speed. Therefore, it was assumed that the BT secondary particle groups under the different processes were different. In this paper, the dispersion state of BT secondary particle groups in self-assembled BT/PLLA composites prepared by changing the fabrication conditions was investigated. In particular, the BT/PLLA/BT heterointerface in the BT aggregates by the self-assembly process was analyzed, and the effect of the BT/PLLA/BT heterointerface and the BT/PT interface in the BT secondary particle groups on the dielectric properties of BT/PLLA composites was investigated.

2. Experimental procedures

2.1 Sample preparation

BT powder was prepared using a conventional solid-state synthesis technique. BaCO3 (99.95%, High Purity Chemical Co., Japan) and TiO2 (99%, High Purity Chemical Co., Japan) were used as the starting materials. Powders used for the experiments were ground and properly mixed. The powder mixture was fired at 1373 K for 4 h. The sintered BT was ground to get a BT powder. The resultant BT powder had an average particle diameter of approximately 1 μm. The powder exhibited a single phase, which was determined using powder X-ray diffraction. BT granules were made using the same method and had average particle diameters of over 20 and 150 μm. BT/polymer composites were generated from BT powder and granular poly-L-lactic acid (PLLA, Nature Work, Japan). PLLA was melted at a temperature of 473 K, and BT powder was added to PLLA to form mixtures. The volume fractions of BT were 0, 5, 10, and 20%. Two different processes have been adopted during the mixing: (1) slow-speed hand mixing for 30 min with approximately 10 rpm and (2) high-speed mixing via a kneader [TOYOSEIKI, Labo Plastomill (4C150)] for 10 min with 30 rpm. After the mixing was over, each sample was cooled in the air. In order to homogenize BT/PLLA composites with dispersion, both BT powder and Tegomer® P121 (polyolefin type, Evonik, U.S.A.) were mixed and kneaded under the same conditions, as described earlier. The amount of additive Tegomer® P121 in the mixture was approximately 4.0 wt% in BT powder. The required dosage level is 2.0–4.0%, and the added amount of Tegomer® P121 was decided by a preliminary experiment. 4.0 wt% of Tegomer® P121 was slight for PLLA. BT powders with two different diameters (average particle diameters: over 20 μm and over 150 μm) and PLLA were mixed under low kneading speed to prepare BT/PLLA composites by adding BT granules, respectively. The volume fraction of the BT granule was 5%.

2.2 Measurement method

The dielectric constant and loss tangent of BT/PLLA composite at the frequency range from 100 Hz to 100 MHz were measured at 298 K using an Agilent 4294 A precision impedance analyzer; lead wires were made of platinum. Each sample was a rectangle with a surface area of 64 mm² and a thickness of 0.3 mm. Gold was deposited on electrodes with square faces.

The cross-sections of samples were analyzed using a field emission scanning electron microscope, FE-SEM (Hitachi Co., Japan: S-4100 and SU-8230, JEOL Ltd.: JSM-7001F). FE-SEM images have been converted to binary images to estimate an average secondary particle area of BT fillers for each sample.

3. Results

Figure 1 presents the images of FE-SEM micrographs of BT/PLLA composites with and without Tegomer® P121 under high-speed kneading, low-speed kneading, and the presence of BT granules (particle size of BT: 20 and 150 μm, 5 vol%). Figures 1(a) and 1(b) shows samples with 5 vol% fraction of BT prepared under high-speed kneading conditions with and without Tegomer® P121. Samples
with 5, 10, 20% volume fraction of BT prepared under low-speed kneading conditions with Tegomer® P121 are shown in Figs. 1(c)–1(e). Samples with 5, 10, 20% volume fraction of BT prepared under low-speed kneading conditions without Tegomer® P121 are presented in Figs. 1(f)–1(h). Figure 1(i) depicts a sample with 5% volume fraction of small BT granules prepared under low-speed kneading conditions without Tegomer® P121, whereas Fig. 1(j) shows a sample with 5% volume fraction of large BT granules prepared under low-speed kneading without Tegomer® P121. The binary images based on Fig. 1 are shown in Fig. 2. The result showed that BT fillers were highly dispersible in the presence of Tegomer® P121 under high-speed kneading. BT aggregates produced under low-speed kneading conditions. Comparing samples with and without Tegomer® P121 under low-speed kneading conditions, it was observed that BT aggregates were better promoted with Tegomer® P121 than without Tegomer® P121. The starting material (BT powder) was aggregated by van der Waals.4) BT secondary particle groups were formed in the presence of BT granules additive, having a particle size of 20μm [see Fig. 1(i)]. However, BT aggregates were not formed by adding BT granules when particle size is close to 150μm [see Fig. 1(j)].

Figure 3 presents the result of the volume fraction of BT and dielectric constant (ε′) at 1 kHz. The addition of Tegomer® P121 had a negligible effect on the dielectric constant of pure PLLA materials. However, the dielectric constant of BT/PLLA composites increased by the addition of BT powder. In order to evaluate the effects of the filler, the Bruggeman model is used to composite materials wherein the fillers are homogeneously dispersed in the matrix, as shown in Fig. 3.9) The model shows as follows:10)

\[
1 - V = \left( \frac{\varepsilon'_{\text{composite}}}{\varepsilon'_{\text{matrix}}} - \frac{\varepsilon'_{\text{filler}}}{\varepsilon'_{\text{filler}}} \right) \left( \frac{\varepsilon'_{\text{matrix}}}{\varepsilon'_{\text{filler}}} \varepsilon_{\text{composite}} \right)^{1/3}
\]

(1)

Where V refers to the volume fraction of BT; ε'_{matrix} refers to the dielectric constant of PLLA (ε'_{matrix} = 3.2); ε'_{filler} is the dielectric constant of BT (ε'_{filler} = 1000);
\(\varepsilon'_{\text{composite}}\) is the dielectric constant of BT/PLLA composite.

The dielectric constant of BT/PLLA composites with Tegomer® P121 under low-speed kneading was higher than that of the Bruggeman model. Earlier, researchers found a higher dielectric constant in the coarse (agglomeration) particle samples, which could be explained by considering the number of particles along the agglomerated low-impedance path.\(^2\) Comparing composites of 5 vol.%, the dielectric constant of (1) a sample with large granules, (2) a sample with small granules, and (3) a sample prepared under a low-speed kneading condition with Tegomer® P121 was higher than the Bruggeman model. 

The data related to the average secondary particle area, average dielectric constant, and \(\tan\delta\) are shown in Table 1.

In order to investigate the formation of interface for the BT secondary particle groups, the extended FE-SEM images of samples with Tegomer® P121 under high-speed kneading and low-speed kneading are shown in Fig. 4.

Figures 4(a)–4(a’) and 4(b)–4(b’) show samples with 5 vol.% fraction of BT prepared under high-speed and low-speed kneading with Tegomer® P121, respectively. Figure 5 depicts magnified FE-SEM images of samples with large granules and small granules under low-speed kneading. Figures 5(a) and 5(a’) presents a sample with 5% volume fraction of BT prepared with small granules under low-speed kneading without Tegomer® P121, whereas 5b and 5b’ shows a sample with 5% volume fraction of BT prepared with large granules under low-speed kneading without Tegomer® P121. BT powder indicates a blue arrow and PLLA as a red arrow. The images of a and b in Figs. 4 and 5 present BT secondary particle groups. The images of a’ and b’ in Figs. 4 and 5 are the magnified images of BT secondary particle groups. BT particles of a sample with Tegomer® P121 prepared under high-speed kneading were dispersed, and BT agglomerates were small. It is observed that a sample with Tegomer® P121 prepared under high-speed kneading has a small BT/BT interface. 

The dielectric constant of the samples with Tegomer® P121 under the high-speed kneading condition was lower than the Bruggeman model (see Fig. 3). The dielectric constant of air is lower than PLLA and BT. Therefore, it was suggested that the voids affected the dielectric properties. BT aggregates having the BT/polymer/BT heterointerfaces of a sample with Tegomer® P121 under low-speed kneading condition were found [see Figs. 4(b) and 4(b’)]. Researchers suggested BT aggregates were formed by a repetition of dispersion and aggregation between particles under low-speed kneading.\(^4\) This model explains an outcome of the present experiment. The BT/PLLA/BT heterointerface was formed under the low-speed kneading condition within the self-assembly process. It was confirmed that BT and PLLA were not partially contacted. However, the dielectric constant of the samples with Tegomer® P121 under the low-speed kneading condi-

**Table 1. The characteristic of BT/PLLA composites**

| Kneading speed | BT Volume fraction | Dielectric constant, \(\varepsilon'\) | Loss tangent, \(\tan\delta\) | Average secondary particle area of BT fillers, \(S/\mu m^2\) |
|----------------|-------------------|-------------------------------|-------------------|-----------------|
| High kneading (30 rpm, 10 min) | 5 Without Tegomer P121 | 3.62\(^4\) | — | 23.62\(^4\) |
| | 5 With Tegomer P121 | 3.58 | 0.0047 | 16.06\(^4\) |
| | 6 Without Tegomer P121 | 3.65\(^4\) | — | 28.52\(^4\) |
| Low kneading (10 rpm, 30 min) | 5 With Tegomer P121 | 3.91 | 0.0030 | 47.75\(^4\) |
| | 5 Without Tegomer P121 | 4.34\(^4\) | — | 39.83\(^4\) |
| | 6 Without Tegomer P121 | 5.18\(^4\) | — | 74.22\(^4\) |
| | 5 With Tegomer P121 | 6.99\(^4\) | — | 115.58\(^4\) |
| | 5 Small granules | 10.16\(^4\) | — | 183.06\(^4\) |
| | 5 Large granules | 4.23 | 0.0054 | 90.43 |
| | 5 Without Tegomer P121 | 5.16 | 0.0472 | 1541.67 |
tion was higher than the Bruggeman model (see Fig. 3). Therefore, it was suggested that the dielectric constants of the BT/PLLA composite with Tegomer® P121 under the low-speed kneading condition were not sufficiently affected by the voids. The spherical voids were confirmed in the sample with Tegomer® P121 under the low-speed kneading condition in Figs. 4(b) and 4(b’). It was suggested that the BT particles were eliminated when the samples were cut to prepare for the cross-sections of the samples. Therefore, the spherical voids in the BT aggregates did not affect the dielectric constant of the sample. In order to clarify the BT/BT interface and the BT/PLLA/BT heterointerface in the BT secondary particle groups, BT granules with a BT/BT interface were added to PLLA. BT aggregates of small granules had polymer, suggesting the formation of BT/BT and BT/polymer/BT interfaces [see Figs. 5(a) and 5(a’)]. The distance between BT particles of the sample with Tegomer® P121 under low-speed kneading was closer than

Fig. 4. Cross-sectional FE-SEM images and magnified images of samples with 5% volume fraction of BT prepared under a) high and b) low-speed kneading conditions with Tegomer® P121.

Fig. 5. Cross-sectional FE-SEM images and magnified images of samples with 5% volume fraction of BT prepared with a) small and b) large granules under low-speed kneading conditions without Tegomer® P121.
the small granules sample. BT agglomerates with large granules had BT/BT interface and had a coarse [see Figs. 5(b) and 5(b')] Hence, the formation of BT/polymer/BT heterointerface was different depending on the production of BT/PLLA composites.

Figure 6 presents results of the dielectric constant and tan δ, depending on the frequency used to examine the effects of the BT secondary particle groups prepared under the different processes. Figure 6 1 and 1' shows a sample with 5 % volume fraction of BT prepared by adding large granules under low-speed kneading without Pegomer P121, whereas 6 2 and 6 2' shows a sample with a 5 % volume fraction of BT prepared by adding small granules under low-speed kneading without Tegomer P121. Furthermore, Fig. 6 3 and 6 3' and Fig. 6 4 and 6 4' depicts a sample with 5 % volume fraction of BT formed under low-speed and high-speed kneading with Tegomer P121, respectively. The relationship between tan δ and ε' is shown in Fig. 7. Figures 6 and 7 present the results of a sample of 5 vol.% of BT particles, which is higher than the Bruggeman model and a sample of 5 vol.% of BT with Tegomer P121 under high-speed kneading condition. The ε' of these samples with large granules was highest at all frequencies, as shown in Fig. 6. In contrast, the ε' of a sample under high-speed kneading was lowest at all frequencies. The value of tan δ of BT/PLLA composites with Tegomer P121 under low-speed kneading and high-speed kneading is almost similar. The tan δ of the sample by adding BT large granules was the highest, and it was considered that a loss at the interface was large as the BT particles were not bonded; thus, delaying the dielectric response [see Figs. 5(b) and 5(b')]. According to Fig. 7, the tan δ of the samples with Tegomer P121 under low-speed kneading condition was lower than the tan δ of the sample by adding BT large granules. It was considered that the voids at the BT/PLLA interface of the BT aggregates with Tegomer P121 under the low-speed kneading condition did not efficiently reflect the dielectric properties. Based on the results of small granules, samples with Tegomer P121 under low-speed kneading and high-speed kneading condition, ε' were increased without raising the tan δ (see Fig. 7).

**4. Discussion**

Figure 8 shows that a dielectric constant (ε') of the self-assembled BT/PLLA composites is increased with an increase of average secondary particle area of BT fillers. Robertson and Varlow suggested that a low-impedance path formed BT agglomerations, resulting in an improvement of dielectric constant. In addition, researchers suggested that the dielectric constant of self-assembled BT/PLLA composites was increased with increasing the BT
secondary particle groups. This is, they investigated the size of BT secondary particle groups. In this paper, in order to clarify the BT/BT interface and the BT/PLLA/BT heterointerface in the BT secondary particle groups, the BT/PLLA composite was prepared by adding BT granules with a BT/BT interface. Comparing the results of BT volume fraction (5%), the change in $\varepsilon''$ was saturated with an increase in the average secondary particle area of BT fillers. The slopes of the change in $\varepsilon''$ depending on the secondary particle area of BT fillers were different between the sample having the BT/PLLA/BT heterointerface and the sample having the BT/BT interface. That is, it was suggested that the interface effect was different and the BT/PLLA/BT heterointerface improved the $\varepsilon''$ more efficiently than the BT/BT interface.

The self-organization processes in a non-equilibrium chemical system have been studied in a solution system described by the Belousov-Zhabotinsky reaction. The self-organization process is seen in the reaction-diffusion system, which is assumed to occur due to a competitive reaction between an inhibitor and a promoter within a diffusion process. The reaction is shown in the following Eq. (2),

$$\frac{\partial u}{\partial t} = u - v + D_v \nabla^2 v$$  \hspace{1cm} (2)

Where $u$ is the active term; $v$ is the inhibitive term; $D_v$ is the diffusion coefficient. The self-assembly process of solid particles is assumed to be driven by both condensing and dispersing forces. The self-assembly process of a solid is shown as the reaction-diffusion system with technical terms as follows.

Aggregation $\Leftrightarrow$ Decomposition + Diffusion process

This reaction corresponds to a process of aggregation and decomposition. That is, BT aggregates are formed by the competitive reaction of dispersion and aggregation. Van der Waals force acts as a cohesion force. The shear stress by the stirring speed acts for decomposition. The kneading process can indicate the diffusion process in the reaction-diffusion system. As a result of self-assembly progress, the secondary particle group of BT particles can be formed by reactions of both condensation and dispersion forces. In order to homogenize BT fillers in PLLA, Tegomer® P121 was added to BT/PLLA composites. After BT fillers were homogeneity, the shear stress is high under the high-speed kneading condition, and the BT fillers were dispersed. In the low-speed kneading condition, the shear stress is low, and the BT aggregates were formed within the self-assembly process. Therefore, a material texture was depended on the shear stress. As a consequence, BT aggregates with BT/PLLA/BT heterointerface have been developed within the self-assembly process, wherein grain boundaries play an essential role in electrical properties. From the magnified images in Figs. 4(b) and 4(b’), it is considered that the self-assembled BT aggregates had a BT/polymers/BT heterointerface by adding Tegomer® P121 under low kneading speed. In general, a depletion layer is formed at the interface between semiconductor and insulator. In this experiment, it was suggested that the BT/PLLA/BT heterointerface in which PLLA acts as an insulating layer of the semiconductor–insulator–semiconductor (n-i-n) model was formed in the BT aggregates. The schematic drawing the model of the electronic structure was shown in Fig. 9. $E_c$ is the conduction band, $E_F$ is the Fermi level, and $E_v$ is the valence band. It was considered that the electric structure of the BT/BT interface related to the double Schottky barrier model [see Fig. 9(a)]. On the other hand, as the BT/PLLA/BT heterointerface, the BT particles were surrounded by PLLA, and the depletion layers were formed [see Fig. 9(b)]. That is, in the BT/PLLA/BT heterointerface, it was considered that the electric dipoles were increased. Thus, the electric dipole of a BT/PLLA/BT heterointerface was induced to improve the dielectric constant (see Fig. 8). In addition to small BT granules, the polymer also contained BT aggregates. In contrast, the composite with large BT granules had developed BT/PLLA/BT heterointerface. However, the BT/BT interface was dominantly formed, as shown in Figs. 5(b) and 5(b’). For the sample with Tegomer® P121 by high kneading speed, BT/PLLA/BT heterointerface was not formed. Therefore, it is proposed that the dielectric properties significantly improved by the formation of BT/PLLA/BT heterointerface in the BT aggregates within the self-assembly process.

5. Conclusions

BT/PLLA composites were prepared under different process based on three conditions: (1) low-speed kneading, (2) high-speed kneading, and (3) granules (particle sizes: 20 and 150μm) to investigate the dispersion state of BT secondary particle groups. In particular, the BT/PLLA/BT heterointerface in the self-assembled BT aggregates and the effect of the BT/PLLA/BT heterointerface and the BT/BT interface in the BT secondary particle groups on the dielectric properties of the BT/PLLA composites were investigated.
According to FE-SEM images, it was confirmed that the process of preparing composite materials affected the formation of BT aggregates and agglomerates. In particular, BT agglomerates having BT/BT interfaces were formed under high-speed kneading condition, and BT aggregates having BT/PLLA/BT heterointerfaces were formed under low-speed kneading condition. It was suggested that BT aggregates having the BT/PLLA/BT interface were formed under the low-speed kneading condition and the self-assembly process was driven.

Comparing BT granules having the BT/BT interface with the self-assembled BT aggregates having the BT/PLLA/BT heterointerface, the tan δ of the self-assembled BT aggregates having the BT/PLLA/BT heterointerface was lower than that of BT granules having the BT/BT interface, and the dielectric constant of the self-assembled BT aggregates having the BT/PLLA/BT heterointerface was higher than that of the BT granules having the BT/BT interface.

Hence, it was suggested that it was an important role in improving the dielectric properties to form ceramic secondary particle groups having the ceramics/polymer/ceramics heterointerface by the self-assembly process. It is expected that the dielectric properties can be improved by controlling the formation of ceramics aggregates with a ceramics/polymer/ceramics heterointerface.

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