Particle Alignment Condition and Size Influence on the $d_{33}$ of the Pseudo-1–3 Piezoelectric Ceramic/Rubber Composite

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Abstract A piezoelectric ceramic/rubber composite comprising linearly aligned Lead Zirconate Titanate (PZT) particles as pillars in a silicon rubber matrix was fabricated. The optimum fabrication conditions of pseudo 1–3 composites (referred to as “aligned-type” composites) were evaluated as the functions of the electric field strength and the piezoelectric particle size. The piezoelectric strain constant $d_{33}$, which represents the value of the electric charge per unit force generated from a piezoelectric material, and the ratio of the number of particles involved in the alignments (RPIA) to all particles in an RPIA sample were used to quantitatively evaluate the composites. The $d_{33}$ exhibited linear dependence on the piezoelectric particle size and a non-linear dependence on the RPIA. The RPIA depended on both the electric field strength and particle size. The electric field strength dependency of the RPIA exhibited a maximum at approximately 2 kV/mm. The optimum condition for the fabrication of the aligned-type piezoelectric rubber composite was achieved an electric field strength of 2.0 kV/mm with larger PZT particles.

Keywords Piezoelectric ceramic/rubber composite, Pseudo-1–3 composite, Particle alignment, Direct electric field, Dielectric constant, Piezoelectric strain constant

Introduction

Recently, the flexible piezoelectric materials have become the center of attention as materials which can overcome the brittleness of piezoelectric ceramics1–2). These materials are expected as a sensor which can be adopted at various places. In these materials, the “pseudo-1–3 piezoelectric ceramics/polymer composite” is one of the candidates to realize the flexible piezoelectric materials having high flexibility and piezoelectricity3–4). One of the features of pseudo-1–3 piezoelectric composite is forming pillars consisting of piezoelectric particles aligned linearly in the soft matrix. Therefore, the force applied to the piezoelectric particles and the electric charge generated from the particles is easy to transfer. The piezoelectricity of the pseudo-1–3 piezoelectric composite becomes higher than that of the 0–3 piezoelectric composites5–7) in which the pillars of piezoelectric particles are connected in the matrix, because in case of “the pseudo-1–3 composite”, the piezoelectric particles are connected each with other and the flexibility of the matrix polymer is retained.

The pseudo-1–3 composite is prepared under the alternating or direct electric field so as to form the piezoelectric particle pillars in the liquid matrix. Under the alternating field, the particle size is limited, e.g., 1–10 μm, because the particles must disperse homogeneously in the uncured matrix3). In our previous study, the alignment of piezoelectric particles was prepared under the direct (static) electric field4). In case of the direct electric field, larger particles are available to form one dimensional pillar because the piezoelectric particles need not disperse in the matrix6–12). In our investigation, the pseudo-1–3 piezoelectric ceramics/rubber composite, which was named “aligned-type”, was fabricated using Lead Zirconate Titanate (PZT) for the piezoelectric particles and the thermosetting silicone rubber for the matrix rubber under the direct electric field4). Then, the remarkable increase of the piezoelectric strain...
constant $d_{33}$ of the aligned-type was confirmed in comparison with the $d_{33}$ of the piezoelectric rubber which was fabricated without particle alignment using the same PZT particles with the same concentration. Here, the piezoelectric strain constant $d_{33}$, which is a representative index of the piezoelectricity of piezoelectric materials, indicates the value of electric charge per force generated from piezoelectric materials when force is applied to the piezoelectric materials and it is calculated by the following equation.

$$d_{33} = \frac{C_3}{f_3/S}$$

where, $C_3$ and $f_3$ are the generated charge and the applied force in the vertical direction, which is the direction of sample thickness, respectively. And $S$ is the surface area of the sample. In this study, to determine the optimum condition to fabricate the aligned-type manifesting the higher $d_{33}$, the influence of the particle alignment condition and the size on the $d_{33}$ of the aligned-type was investigated.

**Experimental**

**Materials**

The thermosetting silicone rubber (KE-106, Shin-Etsu Chemical Co.) and Lead Zirconate Titanate (PZT; Z-711, CERATEC Engineering Co) particles whose $d_{33}$ was approximately 610 pC/N were used as the matrix rubber and the piezoelectric particle, respectively. Five kinds of PZT particles with a different particle size (A, B, C, D and E) were used to analyze the effect of the particle size on the $d_{33}$ of the aligned-type. The size distribution of PZT particles used for the experiment was shown in Figure 1, and the mean sizes of particles A, B, C, D, and E are 0.46, 0.55, 0.65, 0.82, and 1.05 mm, respectively.

**Sample Fabrication**

Figure 2 shows the fabrication apparatus of the aligned-type. Firstly, the sample holder was prepared by a 50-mm-diameter hole bored at the center of a 2-mm-thick Bakelite plate placed on a steel grounding electrode. After PZT particles were inserted into the sample holder, the uncured silicone rubber was poured over the PZT particles. Then, a vacuum dryer was used to remove the air at voids between the particles in the sample. After degassing, the positive electrode was placed on the sample holder. Then the whole kit was placed in a thermostatic oven for 1 hr at 100°C to cure the silicone rubber while applying a direct electric field between the positive and grounding electrodes. Once a solid composite was obtained, the positive electrode was removed and the aligned-type with 50 mm in diameter and 2 mm in thickness was pulled out of the sample holder.

Another aim of this investigation was to evaluate the influence of the particle alignment condition on the $d_{33}$ of the aligned-type. It was assumed that the particle alignment condition varied according to the strength of the electric field. Therefore, the electric field was changed from 0 to around 3 kV/mm. And the PZT particle concentration of all the aligned-types was fixed at 10 Vol% as the common condition of the sample fabrication. Figure 3 shows the flexibility of the aligned-type fabricated using the particle C at 1.5 kV/mm in electric filed.

**Method of the Evaluation of Properties**

**Particle Alignment condition**

The particle alignment condition was evaluated by the projection image by using a digital microscope (VH8000, KEYENCE Co.). The projection image was observed by the light transmission in the composite thickness direction. In addition, the cross-sectional observation using a digital
microscope was also carried out to evaluate the particle alignment condition.

Piezoelectric Strain Constant $d_{33}$

As above mentioned, the $d_{33}$ was defined as the amount of the generated electric charge per unit force, when the force applied in the direction of sample thickness. Therefore, the measurement of $d_{33}$ was made by applying the force to the sample in the thickness direction by a fatigue testing machine (KC-V-2, Saginomiya Seisakusho, Inc., Japan). The samples were placed between the electrodes which were made of steel, and were set on the machine in the measurement. Then, the vibration force which was a sine wave with control values of $2\pm 1 \text{kN}$ at 100 Hz, was applied. The $d_{33}$ was calculated as the quotient of the amplitude of generated electric charge divided by the value of the vibration force.

Results and Discussion

Particle Alignment Condition

Figure 4 shows the projection images of the aligned-types using the particle C obtained under the different electric field condition during the fabrication process. The black parts were “PZT parts” where PZT particles existed.

The area of PZT parts was varied with the electric field strength. Then, in order to estimate the particle alignment condition quantitatively using the area of PZT parts, the ratio of the number of particles involved in the alignments to that of all particles in the sample named “RPIA”, was defined. RPIA was calculated by the following procedure.

Firstly, the ratio of PZT parts area to the sample surface area, $X$, was defined as follows.

$$x r^2 (a + b) \frac{100}{S} \times = X$$

$$b = z - ac$$

where, $r$, $a$, $b$, $S$, $z$ and $c$ indicate the mean radius of particles, the number of particle alignments, the number of particles not involved in the alignments, the area of the sample surface, the total number of particles and the number of particles involved in one alignment, respectively. The $z$ value was calculated using the mean value of each particle weight which obtained from the image analysis. And, $c$ was calculated by dividing the thickness of the sample by the mean value of the radius of the particle.

Secondary, the RPIA ($R$) was expressed by the following equation.

$$\frac{ac}{z} \times 100 = R$$

From the equations (2) to (4), the $R$ was expressed as the following equation.

$$R = \frac{c\left(SX - 100xzr^2\right)}{xsr^2(1-c)}$$

Figure 5 shows the relationship between the RPIA and the strength of the electric field (upper) and the relationship between the $d_{33}$ and the RPIA (lower). The results of the aligned-type using particle C are shown in the figure. And Figure 6 shows the cross-sectional views of the aligned-type using particle C: (a) without the electric field, (b) at 1.5 kV/mm, and (c) at 3.5 kV/mm.

In Figure 6 (a), all PZT particles in the silicone rubber existed on the lower (ground) electrode, and no connection of particles was observed between the electrodes. In this case, the RPIA is 0%, because no particle was involved in the alignments. And, the $d_{33}$ is also 0pC/N, because no force is applied to the particles. In Figure 6 (b), most particles participated in the pillar like alignments which connected the lower and upper electrodes. In this state, the RPIA value is at its maximum with about 80%. It means that about 80% of all PZT particles are involved in the alignments. And, the $d_{33}$ indicates the maximum value. It means that charge of a large value is generated from the many pillar alignments when the force is applied. How-
ever, in Figure 6 (c), many particles dispersed on the upper positive electrode in addition to particles involved in pillar alignments. In this case, the RPIA value is lower than the state of Figure 6 (b). Because the number of pillar alignments is less than the case of Figure 6 (b). In addition, the $d_{33}$ also decreases with the decrease of the number of pillar alignments. The reason why the number of pillar alignments in the case of Figure (c) is less than the case of Figure (b) is discussed as follows. As shown in Figure 7, when the attractive force between particles and the positive electrode overcame the contact force between each particle due to the increase of the dipole moment with the increase of the electric field, particles are attracted to the positive electrode.

According to the above results, when the aligned-type was fabricated, the optimum strength of the electric field, at which the RPIA indicate the maximum value, existed. And, the aligned-type made by using the optimum strength of the electric field indicates the maximum value of $d_{33}$.

**Particle Size**

Figure 8 shows the relationship between the RPIA and the strength of the electric field for the aligned-type using particles A–E.

The RPIA value of the aligned-type using smaller particles (A, B, and C) showed a higher value at 1.5 kV/mm,
and almost a similar value at 2.0 kV/mm. For larger particles (D and E) showed a smaller value at 1.5 kV/mm, however the RPIA became larger and the maximum appeared at 2.0 kV/mm, which was significantly higher than that at 1.5 kV/mm.

This result indicated that the smaller particles moved at a lower electric field, however the larger particles had the threshold of the capability to form pillars. In order for the particles to move, the coulomb’s force between the particles and the electrode had to become larger than the gravity force and the viscous resistance produced by the uncured silicone rubber. Such force increases with the increase of the particle size. Therefore, different optimum values of the strength of the electric field required for forming pillar alignments according to the particle size were observed.

Figure 9 shows the relationship between the particle size and the $d_{33}$ of the aligned-type fabricated at 2 kV/mm.

![Figure 8](image1.png)

**Figure 8.** Relationship between the strength of the electric field and the RPIA of the aligned-type using particles A–E.

![Figure 9](image2.png)

**Figure 9.** Relationship between the particle size and the $d_{33}$ of the aligned-type fabricated at 2 kV/mm.

![Figure 10](image3.png)

**Figure 10.** Projection images of the distribution of the force applied to the aligned-type with different particle sizes.

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Figure 9 shows the relationship between the particle size and the $d_{33}$ of the aligned-type fabricated at 2.0 kV/mm which was the optimum condition to fabricate better composites using particles A–E.

The $d_{33}$ value increased with increase of the particle size. This result suggested that the applied force to the particle alignment is transmitted more efficiently in the direction of thickness with the increase of the particle size because the $d_{33}$ value of the aligned-type increased with the increase of the force applied to the particle pillar alignment. The increase of the applied force was caused by a better connection between particles in the pillar alignment, which the reduction of the contact points and defects such as the branch in the pillar were induced by the decrease of the number of particles involving in each pillar alignment with increase of particle size. In Figure 8, the RPIA of the aligned-type using the larger particles (D and E) was higher that of the aligned-type using the smaller particles (A, B, and C) at 2.0 kV/mm. This result indicated that the defects in the particle alignment decreased for the aligned-type using the larger particles.

On the other hand, the order of the RPIA is B<C<A<D<E as shown in Figure 8. Regarding the small particles (A–C), no definite relationship between the RPIA and the particle size was indicated. In addition, while the number of pillar alignments was decreased with the increase of the particle size, the $d_{33}$ was increased with the increase of the particle size. As a result of the above, it was indicated that, in case of the same particle size, the $d_{33}$ value become the maximum under the optimum condition which was achieved by the largest number of pillar alignments, but that when the particle size was different and the value of the RPIA was similar, the influence of particle size on the $d_{33}$ was predominant.

To evaluate the force applied to the pillar alignment, the distribution of the force in the aligned-type was measured by a pressure measurement film (Prescale LLW, Fujifilm Co.) placed between the sample and the electrode during the $d_{33}$ measurement. The Prescale LLW detected the force higher than 0.2 MPa by gray dots. The composite regarding particle A showed many small gray dots. Figure 10 shows the force distribution images of the aligned-types using particles A, C and E.

The size and clarity of the gray dots increased with the increase of the particle size, while the number of gray dots
decreased with the increase of the particle size. These results also provided the \( d_{33} \) was increased with the increase of the force applied to the particle alignment.

**Conclusion**

The effects of the particle alignment condition and the particle size on the piezoelectric properties of the pseudo-1–3 piezoelectric ceramics/polymer composites in which PZT particles formed one dimensional alignments, named “aligned-type”, were evaluated. The aligned-types with different alignment conditions and particle sizes were fabricated using PZT particles and thermosetting silicone rubber. From the evaluation of the particle alignment conditions and the measurement of the piezoelectric strain constant \( d_{33} \) of the fabricated aligned-types, the following conclusions were obtained.

The ratio of number of particles involved in the alignments, ‘RPIA’ value varied according to the strength of the applied electric field throughout the fabrication process. The RPIA showed the maximum at the certain strength of the applied electric field, and influenced the \( d_{33} \) of the aligned-type. Provided that the size of the particle was the same, it was proven that the \( d_{33} \) increased under the optimum condition of the particles alignment due to the decrease of the defects inside the particles alignment pillar and the large number of particles alignment pillars. In addition, the \( d_{33} \) was enhanced by the increase of the force applied to the particle alignment due to the strong connection of the particle alignment, which was causes by the increase of the particle size. On the other hand, no definite relationship between the RPIA and the particle size was proven. And in cases where the value of the RPIA was similar, the influence of the particle size on the \( d_{33} \) was larger than that of the RPIA.

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