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Matrix influence on the piezoelectric properties of piezoelectric ceramic/polymer composite exhibiting particle alignment

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ABSTRACT: This study was addressed to the influence of an electric field strength applied at fabrication process and matrix properties, such as the dielectric constant and the Young's modulus, on "pseudo-1-3 piezoelectric ceramic/polymer composite" in order to further enhance the piezoelectricity of that. The pseudo-1-3 piezoelectric ceramic/polymer composite consists of linearly ordered piezoelectric ceramic particles in polymer material. Silicone gel, silicone rubber, urethane rubber, and poly-methyl-methacrylate, which exhibit different dielectric constants and Young's modulus, were used as matrices to evaluate the matrix influence. The piezoelectricity of the pseudo-1-3 piezoelectric ceramic/polymer composite was evaluated using the piezoelectric strain constant d_{33}. The d_{33} is one of the indices of the piezoelectric properties for piezoelectric materials. As a result, it was confirmed that d_{33} of the pseudo-1-3 piezoelectric ceramic/polymer composite increased with the increase of the electric filed strength applied at fabrication process, though, it reached a constant value at a certain strength value. Further it was confirmed that dielectric constant of the matrix had a small influence on d_{33} of the pseudo-1-3 piezoelectric ceramic/polymer composite, however, in case of matrix of lower Young's modulus, d_{33} was increase. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41817.

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INTRODUCTION

Recently, flexible materials that can solve the problems associated with ceramics, such as fragility and brittleness, are expected to hold the stage in the development of piezoelectric device.[1–4] In this study, we focused on the piezoelectric ceramic/polymer composite, which is a mixture of the piezoelectric-ceramic particles in polymer.[5–9] In addition to flexibility, piezoelectric ceramic/polymer composite benefits from an easy and versatile fabrication that provides a wide range of shapes according to plasticity of polymer. However, its piezoelectric properties are generally inadequate because the ceramic particles are isolated in a polymer matrix that does not exhibit piezoelectricity. Conventional piezoelectric ceramic/polymer composites are categorized as a "0–3 composite" because piezoelectric ceramic particles are disconnected from each other, while polymer forms a three-dimensional network. Large particles, e.g., more than 2 mm, have been mixed into polymer in substantial amounts, e.g., more than 50 vol %, to enhance the piezoelectric properties of these 0–3 composites; however, this treatment reduces the materials' elasticity.[5–9] Therefore, to boost the piezoelectricity while maintaining elasticity, only a little amount of particles have been added. The resulting "1–3 composites" display high piezoelectric properties because in addition to the three-dimensional polymer matrix, the piezoelectric ceramics form one-dimensional structures that directly transmit the applied force and generate an electric charge.[10–15] However, these one-dimensional structures consist of single ceramic pillars that affect the elasticity of polymer because their Young's modulus, which is significantly higher than that of polymer, is dominant.

Therefore, "pseudo-1–3 composites" comprising aligned ceramic particles was investigated in this study.[16–20] The pseudo-1–3 composite structure is more flexible than that of the 1–3 composite because the contacts among particles occur over a small area, preserving the elasticity of polymer. The pseudo-1–3 composite is denoted as "aligned-type piezoelectric composite". An aligned-type piezoelectric composite has previously been synthesized from lead zirconate titanate (PZT) ceramic particles and a thermosetting silicone rubber matrix by applying an electric filed at the fabrication process. This material showed a remarkable increase in piezoelectricity compared with a piezoelectric composite containing the same PZT particles and matrix without alignment.[21]

Table I. The Mixing Ratio of Main Agent and Curing Agent, the Curing Condition, and the Viscosities of the Uncured Matrices

	Viscosity (Pa s)						
	Main agent		Curing agent		Mixed	Mixing ratio	Curing condition
Matrix	RT[a]	100°C	RT	100°C	100°C	(M : C)[b]	(°C, h)
Silicone gel [G]	1.0	0.6	1.0	0.5	0.5	1 : 1	100, 1
Silicone rubber [Q]	3.5	1.5	0.5	0.5	1.4	10 : 1	100, 1
Urethane rubber [U]	17	1.1	0.2	0.04	0.4	3 : 10	100, 3
PMMA [A]	0.065	-	Powder		–	100 : 1	RT, 0.5

[a] Room temperature.
[b] M, main agent; C, curing agent.

In this study, the influence of an applying electric filed strength applied at fabrication process and matrix properties on the piezoelectricity of aligned-type piezoelectric composite was investigated for further performance enhancement. For four types of matrices, the effects of the dielectric constant and the Young's modulus on piezoelectric properties were evaluated. Along with a cross-sectional examination, dielectric and piezoelectric strain constants were measured to characterize the aligned-type piezoelectric composites.

EXPERIMENTAL

Materials

The four matrices used in this study are silicone gel (G; TSE3062, Momentive Performance Materials), silicone rubber (Q; KE-106, Shin-Etsu Chemical), urethane rubber (U; MC-E19, NIPPON POLYURETHANE INDUSTRY), and poly(methylmethacrylate) (A; MACH, RYOKO). The mixing ratio of main agent and curing agent, the curing condition, and the viscosities of the uncured matrices are shown in Table I. The viscosities were measured by using a rotational viscometer (DV-I +, Brookfield Engineering Labs,). In measurement, the disc-type spindle LV-3 was put into the uncured matrices and it was rotated at 6.0 rpm. Table II shows the relative dielectric constant and the Young's modulus of cured matrices.

Lead zirconate titanate (PZT, Z-711, CERATEC Engineering) particles were selected as piezoelectric ceramic particles because of their excellent piezoelectric properties. Their particle size distribution (Figure 1) shows that PZT particle diameters are in the range of 0.4−1.6 mm and their mean diameter was approximated to be 0.9 mm. Particle size distribution was measured by magnification observation of particles by using digital microscope (VH-8000, KEYENCE).

Table II. The Relative Dielectric Constant and the Young's Modulus of Cured Matrices

Matrix	Relative dielectric constant	Young's modulus (MPa)
Silicone gel [G]	4.6	5
Silicone rubber [Q]	3.0	70
Urethane rubber [U]	6.1	180
PMMA [A]	3.4	450

Method for Aligning Particles

In a previous study, the particle alignment was achieved by dielectrophoresis in an alternating electric field.[16–20] However, the sizes of the particles, which were used in this method, were small, e.g., 0.1−10 μm because they are required to be dispersed in the uncured matrix.[16–20] In the previous study, the piezoelectricity of piezoelectric composite by using the small piezoelectric ceramic particles was low.[5–9] The d_{33} of aligned-type piezoelectric composite, which is 60 vol % of the concentration of PZT particles is almost 15 pC/N in the previous study.[20] In addition, separated processes of the alignment and poling of particles were required in fabrication procedure, because the altering electric filed was used for particle alignment and the direct electric field was used for particle poling.

Therefore, we investigated the particle alignment by ferroelectric behavior of electrorheological fluid.[22–26] This alignment was achieved by electrophoresis in a direct electric field. The behavior of PZT particle alignment was observed by using an instrument shown in Figure 2. The instrument was constructed that the lower part consisted of a grounding electrode; the upper, of a positive electrode; and the side part, of glasses. The procedure of observation is shown as follows. After the PZT particles whose concentration was 10 vol % were inserted into the grounding electrode, the silicone oil whose viscosity was 0.1 Pa s was poured on the PZT particles and deformed by vacuum dryer. Then the positive electrode was placed on the instrument,

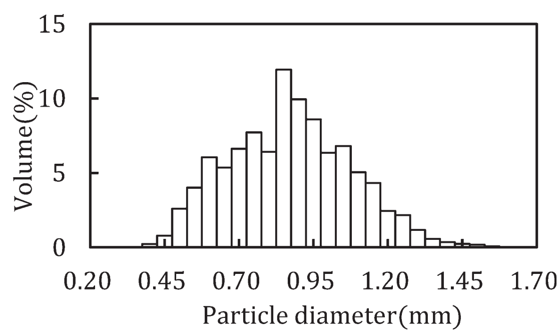

Figure 1. Particle size distribution of investigated PZT particles.

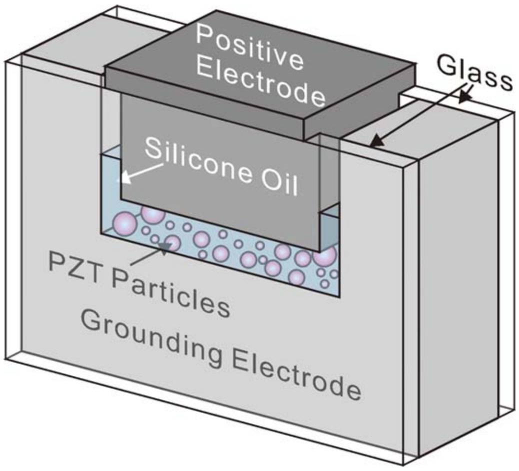

Figure 2. Schema of an observation instrument of the behavior of PZT particle aligning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and increases the strength of electric field. The behavior of PZT particle aligning was observed visually.

Fabrication of Aligned-Type Piezoelectric Composite

The fabrication process of aligned-type piezoelectric composite was shown in Figure 3. As shown in the figure, it was classified into two categories: the case for the matrices A and G adhered to the electrodes, and the case for the matrices Q and U not adhered to electrodes,

a. Fabrication of aligned-type piezoelectric composite using matrices Q and U

1. As shown in Figure 3(a), PZT particles were inserted into the sample holder of 50-mm-diameter and 2-mm-thickness.
2. After the uncured Q or U was poured over the PZT particles and degassed using vacuum dryer, the positive electrode was placed on the sample holder.
3. The sample was placed in a thermostatic oven for 1 h at 100°C to cure Q and for 3 h at 100°C to cure U, respectively, under applying a direct electric field between positive and grounding electrodes.
4. Once the solid composite was obtained, the positive electrode was removed and the composite was pulled out of the holder. This procedure generates 50-mm-diameter and 2-mm-thick aligned-type piezoelectric composite.

a. Fabrication of aligned-type piezoelectric composite using matrices A and G

1. As shown in Figure 3(b), PZT particles were inserted into the sample holder of 50-mm-diameter and 2-mm-thickness.
2. Uncured A or G was poured over the PZT particles into the sample holder. Before curing, G was degassed using a vacuum dryer. Although matrix A was difficult to degas under vacuum because of its volatility, it was not necessary to be deflated because uncured matrix A exhibits an extremely low viscosity (0.065 Pa s). The positive electrode was placed on the sample holder.
3. The sample was placed in a thermostatic oven for 1 h at room temperature for curing A or 100°C for 1 h for curing G, respectively, under applying direct electric field between positive and grounding electrodes. Here, in case of the matrix A, the electric field was applied after curing matrix A in a thermostatic oven for 1 h at 100°C.
4. Once the solid composites were formed, the spacer was removed from the grounding electrode. This procedure generates a 50-mm-diameter and 2-mm-thick aligned-type piezoelectric composite cylinder sandwiched between aluminum plates.

Property Evaluation

Cross-Sectional Examination. A cross-sectional examination was performed using digital microscope (VH-8000, KEYENCE) to evaluate the PZT particle alignment in the matrices. Samples were sliced into ~1-mm-thickness by razor.

Relative Dielectric Constant. A previous study suggested that a higher relative dielectric constant ε_r enhanced the piezoelectricity of aligned-type piezoelectric composite to a greater extent.[21] Therefore, ε_r values are measured for the newly synthesized aligned-type piezoelectric composite. The ε_r values are given as follows:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{C \times l}{s} / \varepsilon_0, \quad (1)$$

where ε is the dielectric constant of the sample, ε_0 is the dielectric constant of vacuum, C is the sample capacitance, l is the sample thickness, and s is the area of the surface at the top and the bottom of the samples.

The capacitance C was measured using a LCR meter (ZM 2353 LCR, NF) at an alternating electric voltage of 1 V and a frequency of 1 kHz. Samples were held between steel electrodes weighing approximately 1 kg. Therefore, the aligned-type piezoelectric composite containing matrix Q or U, which did not adhere to electrode surfaces, was assumed to closely contact with the electrode in the same way as the aligned-type piezoelectric composite involving matrix A and G.

Piezoelectric Strain Constant. The piezoelectric strain constant d, an index of piezoelectricity, is defined as follows:

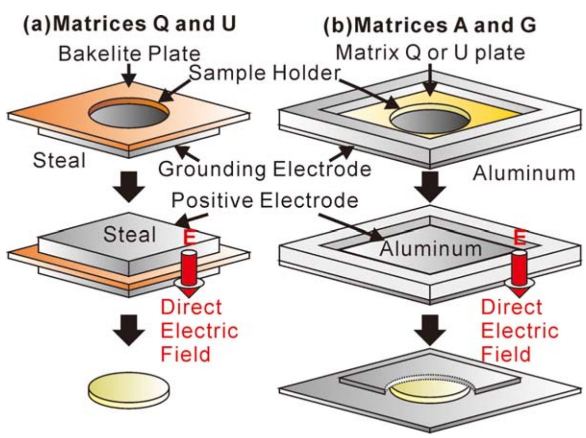

Figure 3. Fabrication process of aligned-type piezoelectric composite. (a) Matrices Q and U, (b) Matrices A and G. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

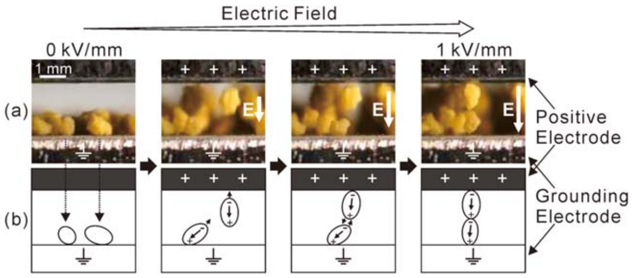

Figure 4. The observation of the behavior of PZT particle aligning. (a) Observation and (b) Schema of the formation process through the PZT particles leads to alignment, which is assumed by the observation. In (b), an arrow inside particle indicates induced electric dipole moment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$d = Q/F, \tag{2}$$

where F is the force applied to the piezoelectric materials, and Q is the generated electric charge.

In this study, a harmonic vibrating force was perpendicularly applied to the sample surface using a fatigue testing machine (KC-V-2, SAGINOMIYA SEISAKUSHO) and the d value was calculated by substituting the measured values of the force F and electric charge Q into the eq. (2). A sine wave of 100 Hz with control values of 2 ± 1 kN for aligned-type piezoelectric composite incorporating matrices A, U, and Q was applied. And a sine wave of 100Hz with control values of 0.2 ± 0.1 kN was applied for the aligned-type piezoelectric composite involving matrix G. The applied force was smaller for the matrix G-containing material because the matrix displayed a low Young's modulus and could break under high-intensity forces. In this study, d was expressed as the d_{33}, because input forces and output electric charges were vertical to the sample surface. In the previous studies, this vertical direction was denoted as "3".[10]

RESULTS AND DISCUSSION

Behavior of Particle Aligning

Figure 4(a) shows the observation of the behavior of PZT particle aligning, and Figure 4(b) shows schema of the aligning process of the PZT particles, which is presumed by the observation and its previous study.[22–26]

Inside PZT particles placed in the direct electric field, the electric charge deviation occurs by electrically induced poling, and electric dipole moment is induced. The induced electric dipole moment in the direction of the electric field is expressed as following equation;[26]

$$\mathbf{p} = 4\pi\varepsilon_{\rm rm}\varepsilon_0 \left(\frac{\varepsilon_{\rm rp} - \varepsilon_{\rm rm}}{\varepsilon_{\rm rp} + 2\varepsilon_{\rm rm}}\right) a^3 \mathbf{E}, \tag{3}$$

where $\mathbf{p}$ is the electric dipole moment, $\varepsilon_{\rm rm}$ is the relative dielectric constant of the matrix, $\varepsilon_{\rm rp}$ is the relative dielectric constant of PZT particles, $\mathbf{E}$ is the electric field vector, and a is the radius of the piezoelectric ceramic particles.

PZT particles precipitated on the grounding electrode are attracted toward the positive electrode in a stepwise manner by Coulomb's force because the electric field is applied in the vertical direction between upper and lower electrodes, which corresponded to positive and grounding electrodes. In addition, when two particles i and j are in a direct electric field, the force between each particles is defined as[26]

$$\mathbf{F}_{ij} = \frac{3}{4\pi\varepsilon_{\rm rm}\varepsilon_0}\left[p^2\frac{\mathbf{r}_{ij}}{r_{ij}^5} - 5\left(\mathbf{p}\cdot\mathbf{r}_{ij}\right)^2\frac{\mathbf{r}_{ij}}{r_{ij}^7} + 2\left(\mathbf{p}\cdot\mathbf{r}_{ij}\right)p\frac{\mathbf{r}_{ij}}{r_{ij}^5}\right], \tag{4}$$

where $\mathbf{F}_{ij}$ is the force between particles i and j, $\mathbf{r}_{ij}$ is the positional vector between particles i and j.

According to the eq. (4), the other particles are attracted and connected with tale of nearly upper particles. In this way, PZT particle alignment is formed.

This approach did not demand dispersion of particles in the uncured matrix. Therefore, available ranges of particle size and matrix type for aligned-type could be expanded. In addition, this approach simplified fabrication of aligned-type piezoelectric composite because the aligning and poling of particles can be made by same process.

Influence of Electric Field

To evaluate influence of the electric field in fabrication process, the aligned-type piezoelectric composite using matrix Q, to which 0−2.5 kV/mm of electric field was applied in fabrication process, was fabricated.

Figure 5 shows the result of the cross-sectional examination of the samples, dielectric constant, and d_{33}, to which 0−2.5 kV/mm of electric field was applied in fabrication process. The PZT concentrations of all sample were 10 vol % and the samples for the cross-sectional examination were sliced into ∼1-mm-thickness and ∼10-mm-width by razor.

By the cross-sectional examination, it was confirmed that the PZT particles, which were settled on the grounding electrode at 0 kV/mm, were aligned to the direction of electric field with increase of its strength. The number of particle alignments increased with the increase of electric field strength, and almost all of PZT particles were involved in particle alignment at 2 kV/mm. The particle alignment was formed at 1 kV/mm in silicone oil as the result of behavior of particle aligning. The reason of the difference of required strength electric field can be discussed as follows. Though the viscosity of the silicone oil was 0.1 Pa s, that of uncured matrix Q at 100°C was 1.5 Pa s. Therefore, in case of matrix Q, PZT particles were difficult to move and higher electric field was required for them to move.

The relative dielectric constant increased with the increase of the electric field up to 2 kV/mm, and the equivalent value at 2.5 kV/mm was confirmed. The relative dielectric constant increased with the increase of number of the particle alignments because the connection of PZT particle alignment between electrodes increases the relative dielectric constant. In addition, the result also indicated that number of particle alignment increased up to 2 kV/mm, and its change became small beyond 2 kV/mm. The d_{33} indicated a tendency similar to relative dielectric constant. Therefore, the increase of d_{33} was also due to the increase of number of PZT particle alignment. Though it was difficult to have an accurate comparison because of the different kind of matrix and PZT particles, 10 pC/N of d_{33} was confirmed by our study in contrast with 5 pC/N which was

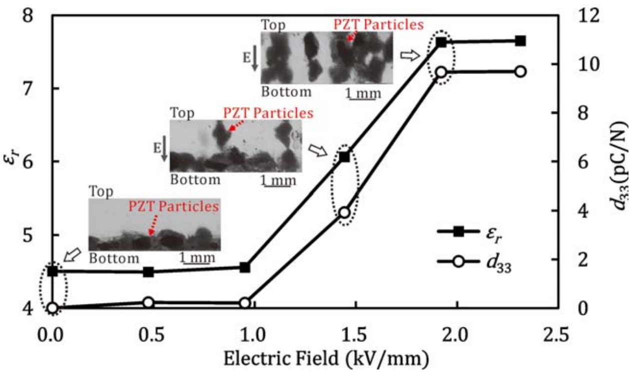

Figure 5. The result of the cross-sectional examination of samples, dielectric constant, and d_{33}, to which 0 ∼ 2.5 kV/mm of electric field was applied in fabrication process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported d_{33} value of aligned-type piezoelectric composite at the same PZT concentration of the previous study.[20]

According to those results and the viscosity under the uncured matrices at 100°C, the applied electric filed was set at 2 kV/mm for fabrication of all aligned-type piezoelectric composite.

Influence of Matrices

Particle Alignment. Figure 6 shows cross-sectional images of the aligned-type piezoelectric composite specimens for a PZT particle concentration of ∼10 vol % : (a) without electric filed, (b) applying at 2 kV/mm. The specimens for the cross-sectional image observation were sliced into ∼1-mm-thickness and ∼10-mm-width by razor. The cross section of the aligned-type piezoelectric composite using matrix G was difficult to prepare because of its low Young's modulus. However, PZT particles in matrix G were assumed to have the same linear arrangement as that in matrix Q because the viscosity of its uncured state and its curing condition, such as thermosetting temperature and time, were similar to those of Q.

The PZT particles formed a linear structure perpendicular to the specimen surface in all the matrices. This result indicated that matrix properties, such as the viscosity of the uncured state, affected the alignment of PZT particles to a small extent.

Relative Dielectric Constant. Table III shows the relative dielectric constants of the matrices G, Q, U, and A and aligned-type piezoelectric composites at a PZT particle concentration of ∼10 vol %. Matrices G and Q exhibited a larger difference between their relative dielectric constants and those of their corresponding aligned-type piezoelectric composites compared with the matrices U and A. The increased difference of the relative dielectric constants for G and Q matrices can be considered as follows.

The relative dielectric constants of the aligned-type piezoelectric composite are increased to establish PZT particles connections perpendicular to the sample surface. The particle alignment slightly influence on relative dielectric constant because the particle alignment can be observed in all the matrices by cross-sectional examination. Another reason considered is the influence of an exposed region, denoted as "Exposed-region," comprising aligned PZT particles existing outside the upper surface of the aligned-type composite. As shown in Figure 7(a), the surface of the aligned-type piezoelectric composite consists of the Exposed-region and the matrix region, denoted as "Matrix-Region." And, in the electrically expressed model of the aligned-type composite, the exposed region acts as capacitors connected in parallel [Figure 7(b)]. In this case, the capacitance of the aligned-type piezoelectric composite is the sum of the capacitance of the exposed regions and the matrix ones. Using the eq. (1), the relative dielectric constant of the aligned-type composite was given as following equation.

$$\varepsilon_r = \frac{\left(\varepsilon_{rp} A_p + \varepsilon_{rm} A_m\right)}{A} \quad (5)$$

Here, ε_{rp} is the relative dielectric constant of PZT particles, A_p is the area of the exposed region, ε_{rm} is the relative dielectric constant of the matrix, A_m is the area of the matrix region, and A is the area of the sample surface.

Since $A_p + A_m = A$, the ratio of the area of the Exposed-region to that of the sample surface (A_R) was expressed as following equation.

$$\frac{A_p}{A} = A_R = \frac{\Delta\varepsilon}{\varepsilon_{rp} + \varepsilon_{rm}} \quad (6)$$

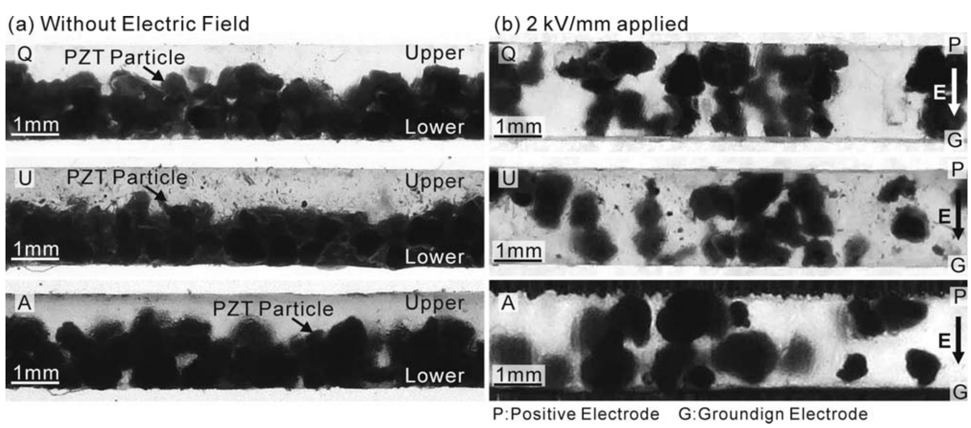

Figure 6. Cross-sectional image of aligned-type piezoelectric composite at a PZT particle concentration of approximately 30 vol %. (a) Without electric filed, (b) 2 kV/mm applied.

Table III. The Relative Dielectric Constants of Matrices and Aligned-Type Piezoelectric Composite at a PZT Particle Concentration of ~10 vol %, Along with Their Differences

	Relative dielectric constant		
Matrix	Matrix	Aligned-type (10 vol %)	$\Delta\varepsilon_r$
Silicone gel [G]	4.6	10.2	5.6
Silicone rubber [Q]	3.0	8.4	5.4
Urethane rubber [U]	6.1	8.7	2.6
PMMA [A]	3.4	4.6	1.2

Here, $\Delta\varepsilon$ is the difference between the relative dielectric constant of the aligned-type piezoelectric composite and that of the matrix.

Table IV shows the calculated A_R values using $\Delta\varepsilon$ and ε_{rm} values shown in Table III and an ε_{rp} value of 3700 in the eq. (6). The matrices U and A presented smaller A_R values than matrices G and Q. Here, Figure 8 shows scanning electron microscope (SEM; S-3400N, Hitachi High-Technologies) images of the exposed region of one particle alignment on the surface of the aligned-type piezoelectric composite involving the matrices Q and U. These exposed regions of the matrices Q and U display areas of 1.0×10^{-3} and 2.5×10^{-4} mm^2, respectively. These regions show mean areas of 7.2×10^{-4} mm^2 and 3.7×10^{-4} mm^2 for 10 alignments in the matrices Q and U, respectively. The resulting ratio of the exposed region of matrix U to that of the matrix Q amounts to 0.51, which was slightly larger than the value shown in Table IV (0.47). This confirms that the exposed region of the matrix Q exceeds that of the matrix U. It is considered that one of the reasons of the differences in A_R among the matrices is derived by the diverse affinities of these matrices for PZT particles.

Piezoelectric Strain Constant. Figure 9 shows the relation between PZT particle concentration and d_{33} value for aligned-type piezoelectric composite.

In case of the same PZT particle concentration value, the d_{33} values of matrices A, U, G, and G were in the ascending order.

Table IV. Calculated A_R Values Using $\Delta\varepsilon$ and ε_{rm} Values Shown in Table III and a ε_{rp} Value of 3700 in eq. (4)

Matrix	A_R
Silicone gel [G]	0.0015
Silicone rubber [Q]	0.0015
Urethane rubber [U]	0.0007
PMMA [A]	0.0003

Particularly, even at the PZT particle concentration of 10 vol %, d_{33} exceeded 60 pC/N and at 40 vol %, the d_{33} was enhanced over 80 pC/N. In addition, the Young's modulus of that at concentration of PZT particle of 40 vol % was ~40 MPa as shown in Figure 10. The Young's modulus was measured simultaneously measuring the d_{33}. The value of 40 MPa is lower than 70 MPa of the matrix Q itself. On the other hand, in case of matrix A, d_{33} was only 10 pC/N at the PZT particle concentration of 40 vol %. Such a difference of d_{33} values due to a difference of matrices were discussed from the viewpoint of the relative dielectric constants and Young's modulus of the matrices.

The influence of relative dielectric constant is discussed first. The relative dielectric constant of matrices (ε_{rm}) affects the induced dipole moment of PZT particles (**p**). The above-mentioned eqs. (3) and (4) suggest that a larger ε_{rm} promotes particle alignment because **p** increases with increasing ε_{rm}. As the result, it was considered that larger ε_{rm} increase the piezoelectricity of aligned-type piezoelectric composite. On the other hand, **p** varies slightly with the change of the relative dielectric constants of the selected matrices because it is extremely low compared with ε_{rp}, which equaled 3700. And, the aligned-type piezoelectric composite exhibits similar particle alignment (Figure 6) in spite of the different matrices. From these results, though the relative dielectric constant presents little effect on **p,** the influence of the relative dielectric constant on **p** is also discussed from a view of the crystal orientation of PZT particle.

The orientation degree of PZT particle crystals effects **p** which results from the crystal orientation of PZT particle. Here, the electric filed applied to PZT particles in the composite is defined as[7]

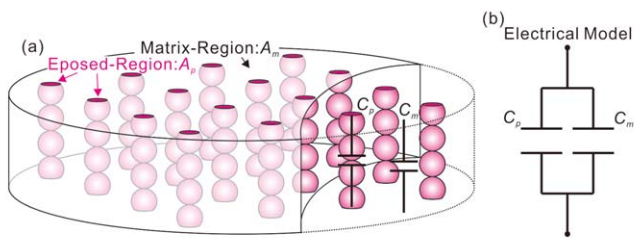

Figure 7. Schematic representations of (a) the capacitance and (b) electrical model of aligned-type piezoelectric composite. C_m and C_p represent the capacitances of the matrix and the aligned PZT particles, respectively. A_m and A_p correspond to the areas of the matrix-region and the exposed-regions, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

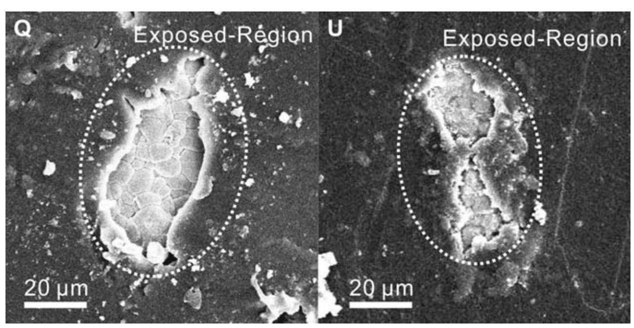

Figure 8. SEM observation of exposed-region of one PZT particle alignment on the surface of aligned-type piezoelectric composite involving matrices Q and U.

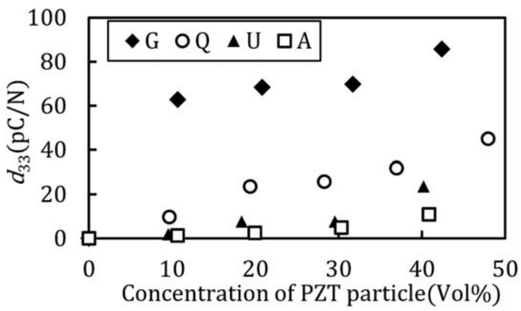

Figure 9. Relationship between PZT particle concentration and d_{33} for aligned-type piezoelectric composite.

$$E_p=\frac{3\varepsilon_{\mathrm{rm}}}{\varepsilon_{\mathrm{rp}}+3\varepsilon_{\mathrm{rm}}}E, \tag{7}$$

where E_p is the electric field applied to PZT particles and E is the electric field applied to piezoelectric composite.

According to the eq. (7), the crystal orientation of PZT particles becomes easier when the $\varepsilon_{\mathrm{rm}}$ increase because the electric field applied to PZT particles increase with the increase of these $\varepsilon_{\mathrm{rm}}$. Therefore, the orientation degrees of PZT particle crystal in the aligned-type piezoelectric composite were measured by wide angle X-ray diffraction. The X-ray diffraction was measured by X-ray diffraction instrumentation (ULTIMA IV, Rigaku). During the measurement, the X-ray was irradiated to the PZT particle without electric field and upper surface of the aligned-type piezoelectric composite, which is PZT particle concentration of 30 vol %. Figure 11 shows the measurement result of X-ray diffraction. The X-ray diffraction was not measured for the matrix G because electrodes were difficult to remove. However, the orientation degree of PZT particle crystal in the matrix G is considered to be similar to that in the matrix Q because of their similarities.

In the absence of an applied electric field, the diffraction peaks of PZT particle appeared at 44.8°. PZT presented a tetragonal crystal lattice with $a=b\neq c$, suggesting that both diffraction peaks for (020) and (200) appeared at 44.8°.[27,28] On the other hand, for the aligned-type piezoelectric composite, the PZT particle crystal displayed diffraction peaks at 44.3°, which is due to (002) diffraction peak, regardless of the matrix. This (002) diffraction peak is considered to appear because clearly the crystal tends to

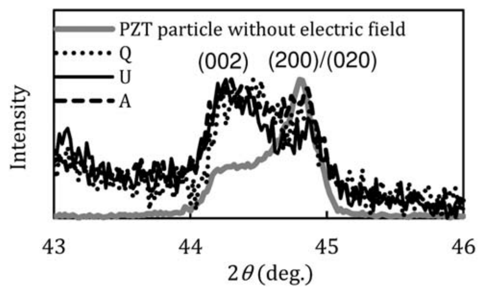

Figure 11. Wide angle X-ray diffraction spectra of PZT particle crystals without application electric field and aligned-type piezoelectric composite.

orient along the *c*-axis, similar to the direction of the applied electric field.[29–31] The measurement result presented the similar diffraction patterns of (020), (200), and (002) for all aligned-type piezoelectric composites. Therefore, it was also exhibited that the relative dielectric constant of matrices scarcely affects on electric dipole moment of PZT particles from a view of the crystal orientation of PZT particle. According to the above discussions, it was considered that the relative dielectric constant of matrices scarcely influence on electric dipole moment of PZT particles and d_{33} of aligned-type piezoelectric composite.

The influence of the Young's moduli of the matrices was discussed using a mechanical model that expresses elastic aligned-type piezoelectric composite as a spring [Figure 12(a)]. The spring constant of the aligned-type piezoelectric composite (K) is the sum of the spring constants of aligned PZT particles (K_p) and the matrix (K_p) because these springs are placed in parallel [Figure 12(b)]. In this case, the applied force is the sum of the forces applied on the aligned PZT particles and the matrix. Also, the displacements are regarded as the same for the springs K_p and K_m. In this mechanical model, using the relation between the spring constant and the Young's modulus, the force applied to the alignment PZT particles is expressed by the following equation.

$$F_p+F_m=1 \quad \text{and} \quad F_p=\frac{Y_pA_R}{Y_m+A_R\left(Y_p-Y_m\right)} \tag{8}$$

Here, F_m is the fraction of force applied to the matrix, F_p is the fraction of force applied to the PZT particle alignments, Y_p is the Young's modulus of the PZT particle alignments, and Y_m is the Young's modulus of the matrix.

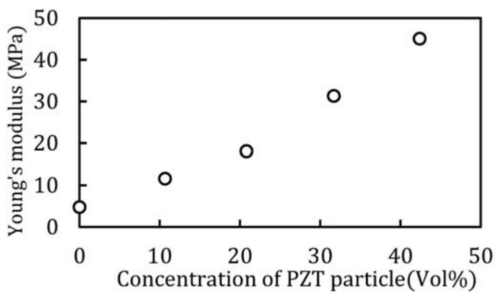

Figure 10. Relationship between PZT particle concentration and the Young's modulus for aligned-type piezoelectric composite using matrix G. The Young's modulus was measured simultaneously measuring the d_{33}.

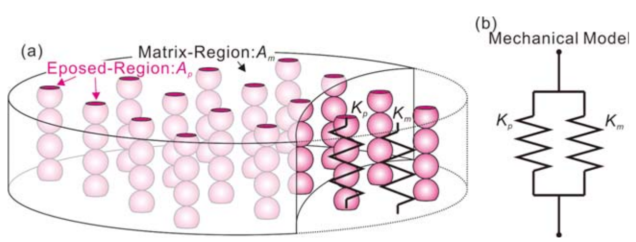

Figure 12. Schematic representations of (a) the spring constant and (b) the mechanical model of the aligned-type piezoelectric composite. K_m and K_p represent the spring constants for the matrix and the aligned PZT particles, respectively. A_m and A_p correspond to the areas of the matrix-region and the exposed-region, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

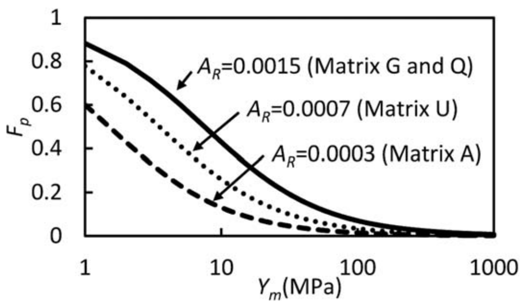

Figure 13. The calculation result of the eq. (8) indicates the change in F_p under the condition that Y_m is in the range of 1−1000 MPa, Y_p is fixed at 5 Gpa, and the A_R are 0.0003, 0.0007, and 0.0015.

Figure 13 shows the calculated F_p with the change in Y_m, which is in the range of 1−1000 MPa; the Y_p is fixed at 5 GPa and the A_R is used 0.0003, 0.0007, 0.0015 shown in Table IV. Here, the 5 GPa of the Y_p is calculated by using the Young's modulus of the aligned-type piezoelectric composite using matrix G at concentration of PZT particle of 10 vol % shown in Figure 10 and A_R shown in Table IV. The value of 5 GPa was approximately one-tenth of the Young's modulus of formed PZT Z-711. One of the causes of low Young's modulus of calculated value is thought to be due to the defect of the PZT particle alignments.

According to Figure 13, the ratio of F_p of each matrix was G : Q : U : A = 1 : 0.16 : 0.03 : 0.01 when the F_p of the matrix G equaled to 1. This result accurately matches the G : Q : U : A = 1 : 0.15 : 0.03 : 0.02, which is ratio of d_{33} of aligned-type piezoelectric composite at concentration of PZT particle of 10 vol % when d_{33} of the matrix G equaled to 1. This indicates that the assumption and mechanical model shown in Figure 12 is appropriate. As the result, the F_p increase with decreasing Y_m, indicating that the force applied to PZT particle alignments increases when the Young's modulus of the matrix decreases. The d_{33} of the aligned-type piezoelectric composite increase with the decrease of the Young's modulus of the matrices because the amount of the electric charge generated from PZT particles increase with the increase of the magnitude of the force applied on the alignment of PZT particles. In addition, the F_p also increases with increasing A_R. This is one reason that the d_{33} of the aligned-type piezoelectric composites using the matrix G and Q are larger than that of the aligned-type piezoelectric composites using the matrix U and A.

CONCLUSIONS

To enhance the piezoelectric properties of a pseudo-1–3 piezoelectric ceramic/polymer composite denoted as "aligned-type piezoelectric composite," in which the piezoelectric-ceramic particles are formed in a linear alignment, the influence of the properties of matrices on its piezoelectric properties was investigated. In this investigation, the relative dielectric constant and the Young's modulus were focused on as the properties of matrices. Therefore, aligned-type piezoelectric composite was synthesized from the PZT particles as the piezoelectric-ceramic particles and the four kinds of matrices such as Silicone gel, Silicone rubber, Urethane rubber, and poly-methyl-methacrylate, which have the different value of the dielectric constant, and the Young's modulus. As a result of the investigation, the following conclusions were confirmed.

1. As a result of the investigation of influence of an applied electric filed strength throughout the fabrication of aligned-type of piezoelectric composite, it was found out that number of PZT particle alignment increased with the increase of the electric field strength. The relative dielectric constant and d_{33} also increases with the increase of the number of particle alignment, though it reached a constant value at a certain strength value of electric field.
2. On the basis of the cross-sectional examination for the aligned-type piezoelectric composite, the PZT particle formation of linear alignment parallel to the electric field was confirmed, regardless of the type of matrices.
3. As a result of the measurement of the relative dielectric constant of the aligned-type piezoelectric composite, it was confirmed that the increased amount of relative dielectric constant of aligned-type piezoelectric composite due to PZT particles alignment was different depending on difference of matrices, even if the alignment of PZT particles was the same. The difference is considered to be due to the difference of area of exposed region of each matrix where PZT particle alignment is exposed out of the sample surface.
4. As a result of the measurement of the d_{33} and the orientation degree of the crystals of PZT particles, small influence of the relative dielectric constant of the matrix on the d_{33} of aligned-type piezoelectric composite was confirmed.
5. The increase of the d_{33} of the aligned-type piezoelectric composite with the decrease of the Young's modulus of the matrices was confirmed. The reason is considered that the force applied on the alignment of PZT particles in aligned-type piezoelectric composite increases with the decrease of the Young's modulus of the matrices. In addition, it was confirmed that the force also increased with the increase of the area of exposed region.

From the results of this investigation, it was confirmed that the desired properties of the matrices for enhancing the d_{33} of the aligned-type piezoelectric composite have a low Young's modulus. By using silicone gel, whose Young's modulus was the lowest in the selected matrices, the d_{33} was enhanced over 80 pC/N in the case where PZT particles of only 40 vol % was mixed despite of low Young's modulus of ∼40 MPa. Therefore, the aligned-type piezoelectric composite using the matrix with low Young's modulus can be used as the vibration isolation material. In addition, it is expected to use the aligned-type piezoelectric composite as a sensor, which can detect the trouble of machine placed on it by using its piezoelectricity.

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