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Partially stabilized zirconia–polymer composites fabricated with an ultrasonic cutter

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Piezoelectric transducers have been made of partially stabilized zirconia (PZT) ceramics with composition close to $PbZr_{0.5}Ti_{0.5}O_3$. Compared with other piezoelectrics, however, the piezoelectric voltage constant $g_{33}(= d_{33}/\varepsilon_{33}$, where d_{33} and ε_{33} are the piezoelectric charge constant and dielectric constant, respectively) of PZT is small. This problem can be solved by combining PZT and polymer in a composite with 1–3 connectivity [1, 2]. This type of composite consists of PZT rods embedded in a polymer matrix, in which the rods are oriented perpendicular to the transducer electrodes.

Several different techniques to make the composites have been reported in the literature [3]. A practical and simplified method for the fabrication (diamond saw dicing) of 1–3 composites was developed by Savakus *et al.* [4] and Takeuchi *et al.* [5], but their process to cut the ceramics with a diamond saw is rather delicate and time-consuming. Safari *et al.* [6] fabricated composites by drilling holes in sintered PZT blocks using an ultrasonic cutter. Ceramics can be carved into various shapes and patterns using various kinds of tools by this method.

This letter describes an alternative processing method, in which narrow grooves are carved in poled solid PZT discs with an ultrasonic cutter and are then back-filled with epoxy resin, urethane rubber or silicone rubber. The piezoelectric properties of the composites thus obtained are presented.

Ceramic discs of poled PZT (Honda Electronics Co., Japan) were prepared by a conventional powder processing method and sintered to a density of 7.58 $g\,cm^{-3}$. The basic characteristics of the studied material are shown in Table I. The PZT disc was mounted on an ultrasonic cutter (UM5000-DA; Nihon Densi Kogyo Co., Japan). Ultrasonic cutting is a machining method which is designed to cut materials a little at a time using a combination of ultrasonic vibration generated from the tool with abrasives and adequate pressure. Steel saw blades ranging in width from 0.5 to 1.0 mm were used in cutting the ceramic. Parallel grooves about 4 mm deep were made in the ceramic, leaving a 1 mm solid base for support.

TABLE I Basic characteristics of PZT ceramics

Electromechanical coupling coefficient	
k_p (%)	58
k_{31} (%)	31
k_{33} (%)	62
Piezoelectric constant	
d_{31} ($pC\,N^{-1}$)	105
d_{33} ($pC\,N^{-1}$)	330
g_{31} ($mV\,m\,N^{-1}$)	11
g_{33} ($mV\,m\,N^{-1}$)	33
Relative dielectric constant	
$\varepsilon_{33}/\varepsilon_0$	1110
Elastic modulus	
C_{11}^{E} ($\times 10^{10}\,N\,m^{-2}$)	8.2
C_{33}^{E} ($\times 10^{10}\,N\,m^{-2}$)	6.6
Elastic compliance	
S_{11}^{E} ($\times 10^{11}\,m^2\,N^{-1}$)	1.22
S_{33}^{E} ($\times 10^{11}\,m^2\,N^{-1}$)	1.51
Curie temperature	
T_c (°C)	315

Next, a second set of parallel grooves normal to the first set were made, again leaving a 1 mm solid base. An array of square pillars was formed by cutting deep grooves into a ceramic block, using the ultrasonic cutter (Fig. 1).

The grooves were filled with polymer as low-viscosity embedding medium. The polymers employed in this work were epoxy resin (EP828; Yuka Shell Co., Japan), urethane rubber (SU21539; Sanyu Resin Co., Japan) and silicone rubber (TSE388; Toshiba Silicone Co., Japan; and KE12; Sinetu Chemical Co., Japan). After cutting into 4 mm-thick discs, the composites were electroded with air-dried silver paint (6290-0275; Deguza, Co., Japan).

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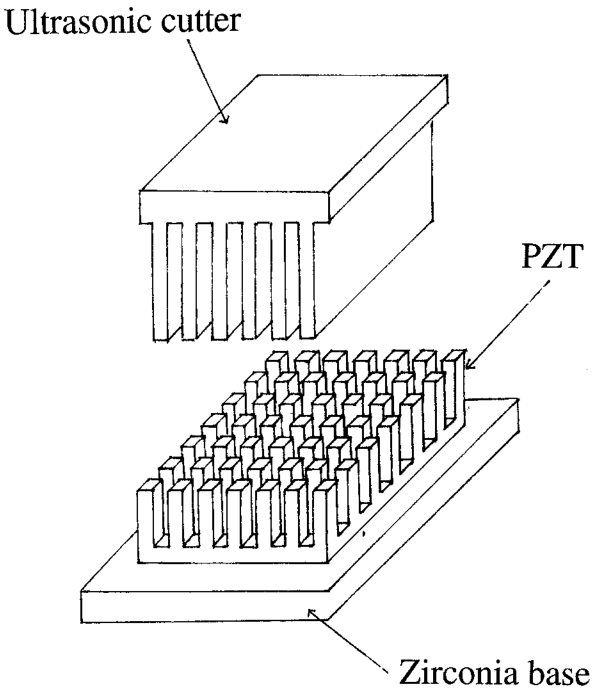

Figure 1 Schematic diagram of the ultrasonic cutter and the processed PZT.

The electric properties of the composites were measured using an impedance analyser (4194A; YHP, Japan). The tensile test was conducted using a tensile testing machine (Tensilon UCT-10TPL; Orientec Co., Japan) at a crosshead speed of 10 mm min^{-1}.

Ultrasonic cutting can make rods with various shapes and patterns. By this method PZT rods can be processed non-destructively in a very short time. Moreover, the piezoelectric properties of poled PZT do not disappear during shaving. Therefore, several composites were fabricated by this new method in this study.

The dielectric constants, $\varepsilon_{33}/\varepsilon_0$, for PZT–silicone rubber composites are shown in Fig. 2. The value of $\varepsilon_{33}/\varepsilon_0$ ranged from 100 for the sample containing 14% PZT to 380 for the sample containing 35% PZT. Since $\varepsilon_{33}/\varepsilon_0$ of PTZ is 1110 and that of silicone rubber is 7, the value of $\varepsilon_{33}/\varepsilon_0$ may be approximated as

$$\varepsilon_{33}/\varepsilon_0 = 1110 \times V \qquad (1)$$

where V is the volume fraction of PZT. The experimental values of $\varepsilon_{33}/\varepsilon_0$ agree with the calculated values.

In Figs 3 and 4 the measured d_{33} and g_{33} are plotted as functions of the PZT volume fraction for PZT–silicone rubber composites. As shown in Fig. 3, the d_{33} of the composite with 35% PZT is comparable with that of the solid PZT because of the stress transfer from the polymer to PZT. The g_{33} for the 1–3 composites (Fig. 4) are extremely large because of their relatively low dielectric constants. It can be seen in the figure that the g_{33} can be improved in 1–3 composites for the PZT–silicone rubber to four-fold (PZT 14 vol%) the value for solid PZT. By decoupling the PZT elements with polymer it is possible to suppress the radial vibration

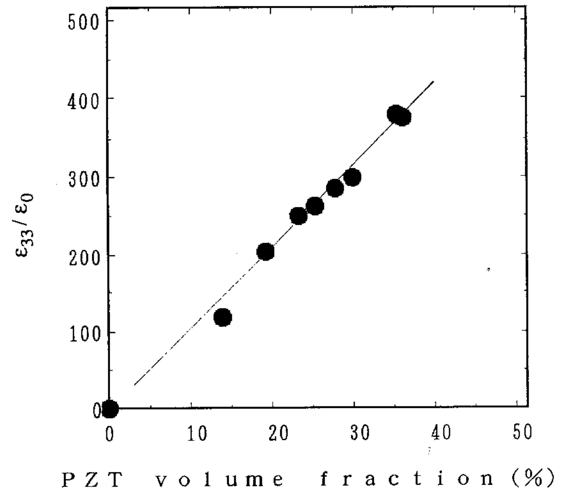

Figure 2 Dielectric constant ($\varepsilon_{33}/\varepsilon_0$) plotted as a function of the volume fraction of PZT for PZT–silicone rubber (KE12) composites.

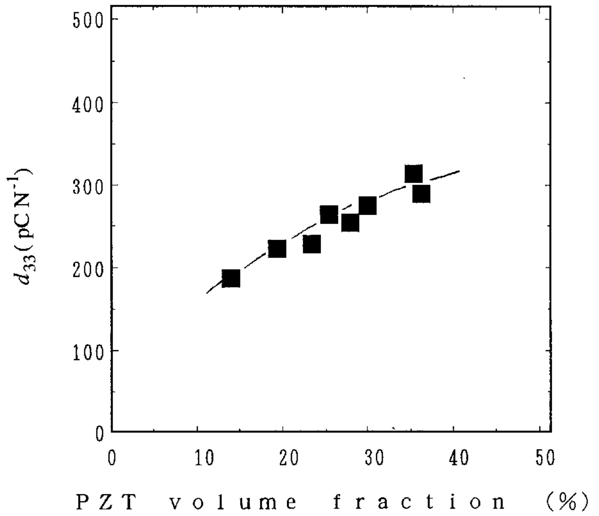

Figure 3 Piezoelectric charge constant (d_{33}) plotted as a function of the volume fraction of PZT for PZT–silicone rubber (KE12) composites. For solid PZT d_{33} = 330 pC N^{-1}.

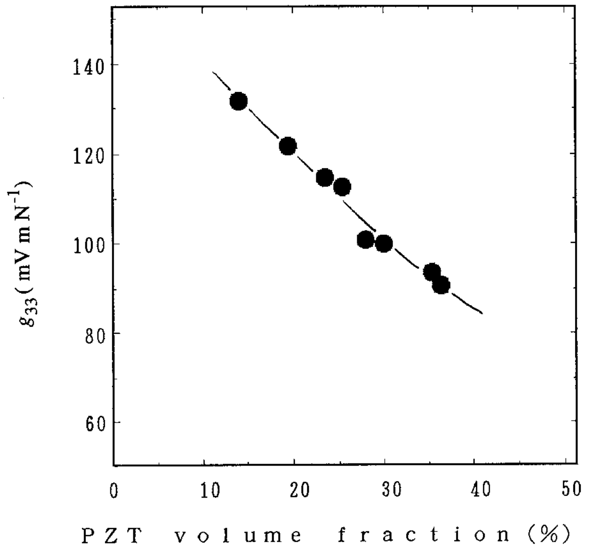

Figure 4 Piezoelectric voltage constant (g_{33}) plotted as a function of the volume fraction of PZT for PZT–silicone rubber (KE12) composites. For solid PZT g_{33} = 30 × 10^{-3} V m N^{-1}.

mode without appreciably affecting the longitudinal mode.

We fabricated 1–3 composites of ultrasonically diced PZT rods embedded in an epoxy resin matrix. The elastic modulus of the epoxy resin was 1.03×10^9 N m^{-2}. Fig. 5a shows the frequency dependence of impedance for the PZT–epoxy resin composite. It is seen that the resonance frequency of the thickness mode vibration was larger than that of the radial mode vibration, and harmonic vibration of the radial mode was never observed. This result suggests that the radial mode vibration of the composite was damped, because the elastic modulus of epoxy resin was much smaller than that of the solid PZT (6.6×10^{10} N m^{-2}).

However, to enhance the g_{33} of 1–3 composites we had to use a polymer matrix with much lower elastic modulus. We selected silicone and urethane rubbers for the polymer matrix, as their elastic moduli are very low (10^5–10^6 N m^{-2}). Fig. 5b and c shows the frequency dependence of impedance for the PZT–urethane rubber and the PZT–silicone rubber composites, respectively. It is seen that the radial mode vibration completely disappeared in both cases.

In Figs 6 and 7 the observed d_{33} and g_{33} are plotted as functions of the elastic modulus of the polymer for PZT–polymer composites. As shown in Fig. 7, g_{33} of the composite increased with decreasing tensile elastic modulus of the polymer matrix until it reached approximately 10^6 N m^{-2}. The elastic polymers, i.e. silicone and urethane rubber, were very soft and were effective for damping the radial mode vibration. The predicted g_{33} of a composite increases with decreasing elastic modulus of the polymer until it reaches about 10^9 N m^{-2}. However, below 10^9 N m^{-2}, g_{33} saturates with decreasing elastic modulus of the polymer. According to Fig. 7, a much lower elastic modulus of polymer is needed to obtain larger g_{33}. The broken curves in the figures represent the d_{33} and g_{33} constants for the composites calculated using the theory of Newnham *et al.* [7].

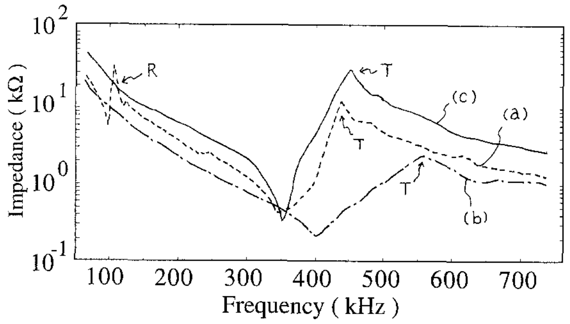

Figure 5 Frequency dependence of impedance for (a) PZT–epoxy resin composite, (b) PZT–silicone rubber composite and (c) PZT–urethane rubber composite. T and R denote thickness mode vibration and radial mode vibration, respectively.

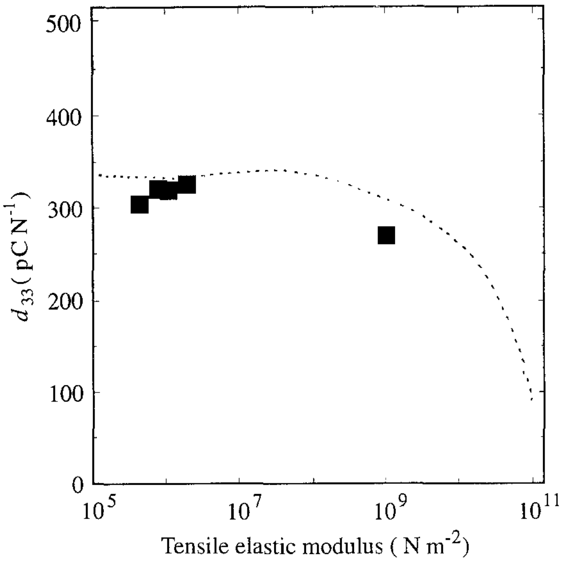

Figure 6 Piezoelectric charge constant (d_{33}) plotted as a function of the tensile elastic modulus for the polymers. The broken curve is the predicted curve.

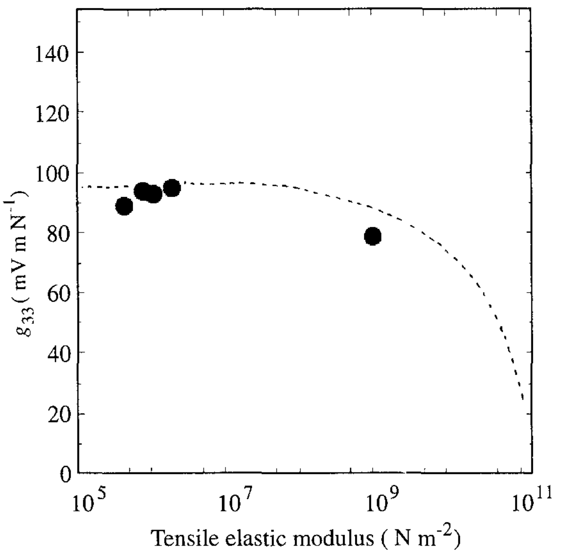

Figure 7 Piezoelectric voltage constant (g_{33}) plotted as a function of the tensile elastic modulus for the polymers. The broken curve is the predicted curve.

Some typical values of $\varepsilon_{33}/\varepsilon_0$, k_{33}, d_{33} and g_{33} are given in Table II. It should be noted that only g_{33} depends markedly on the elastic modulus of the polymer matrix. There is a critical elastic modulus for which g_{33} becomes a maximum. Composites with

TABLE II Piezoelectric properties of PZT–polymer composites containing 35 vol % PZT

Composite	Polymer	Elastic modulus[a] (N m^{-2})	Density (g cm^{-3})	$\varepsilon_{33}/\varepsilon_0$	k_{33} (%)	d_{33} (pC N^{-1})	g_{33} (V m N^{-1})
PZT rods in an epoxy resin	EP828	1.03×10^9	3.20	343	66.3	240	71.1×10^{-3}
PZT rods in a urethane rubber	SU21539	1.94×10^6	3.26	425	65.2	376	95.5×10^{-3}
PZT rods in a silicone rubber	KE12	1.08×10^6	3.49	381	63.6	316	93.6×10^{-3}
PZT rods in a silicone rubber	TSE399	6.10×10^5	3.43	393	68.8	329	94.4×10^{-3}
PZT rods in a silicone rubber	TSE388W	4.30×10^5	3.32	366	66.4	290	89.6×10^{-3}

[a] Tensile elastic modulus of various polymers.

35 vol % PZT and urethane rubber showed values of g_{33} which were three-fold larger than the value for solid PZT. Klicker *et al.* [2] and Savakus *et al.* [4] fabricated 1–3 composites of PZT rods embedded in an epoxy resin matrix. Composites with 40 vol % PZT showed d_{33} and g_{33} which were, respectively, comparable with (380–420 $\mathrm{pC\,N^{-1}}$) and 2.5 times (66–74 $\mathrm{mV\,m\,N^{-1}}$) larger than the solid PZT values (400 $\mathrm{pC\,N^{-1}}$ and 28 $\mathrm{mV\,m\,N^{-1}}$). As shown in Table II, the g_{33} of PZT–elastomer composites were larger than that of a PZT–epoxy resin composite. These results indicate that to obtain higher values of g_{33} it is necessary to fill the perforated PZT with elastomer.

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