



Piezoelectric Properties of Novel Oriented Ceramic-Polymer Composites with 2-2 and 3-3 Connectivity

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Abstract. The processing of novel 2-2 and 3-3 PZT ceramic-polymer composites with various orientation of the ceramic phase with respect to the poling direction is presented. The volume fraction of the ceramic was chosen to be 30 percent for both types of composites. The orientation angle (θ) of the ceramic phase varied between 0° and 75° for both types of composites with 15° increments. The ceramic structures were fabricated using one of the Solid Freeform Fabrication (SFF) methods, particularly Fused Deposition of Ceramics (FDC). The sintered structures were embedded in hard epoxy and the effect of orientation angle on the electrical properties of the composites was evaluated. By increasing the orientation angle of the ceramic phase, the dielectric constant and the piezoelectric strain coefficient of both types of composites decreased. Although the piezoelectric voltage coefficient of the 2-2 composites showed a minor improvement with increasing θ at 45° , the g_{33} value of the 3-3 composites increased considerably with θ and reached 80 mV/N at $\theta = 45^\circ$. Further increase of the orientation angle reduced the g_{33} of such composites.

Keywords: oriented, piezocomposites, depolarizing factor

1. Introduction

Lead based ceramics, specifically PZT (Lead-Zirconate-Titanate), have been widely used in piezoelectric applications due to their excellent piezoelectric and dielectric properties. Lead zirconate titanate ceramics are brittle however, and have high density and acoustic impedance. On the other hand, piezoelectric ceramic-polymer composites offer flexibility, lower density, and lower acoustic impedance. Newnham et al. developed a nomenclature in which ceramic and polymer phases are interconnected with sixteen different patterns [1, 2]. The connectivity pattern provides suitable means to tailor mechanical and electrical properties of composites [3]. Composites with 0-3, 1-3, 2-2, and 3-3 connectivity patterns have been studied in detail for transducer applications such as hydrophone, medical imaging, and non-destructive evaluation [4]. In 2-2 composites, the ceramic and polymer phases are continuous in two dimensions, while in 3-3 composites both phases are tri-dimensionally con-

tinuous. Figure 1(a) shows the schematic of a classical 2-2 composite in which the ceramic walls are aligned along the X_3 -axis of the composite or the poling direction. Figure 1(b) also shows the schematic of a classical 3-3 composite whose ceramic walls are aligned along and perpendicular to the X_3 -axis of the composite.

Recently the effects of poling direction and orientation of the ceramic phase have been studied as an approach to alter the piezoelectric properties of composites with 0-3 and 1-3 connectivity [5, 6]. The theoretical studies with 1-3 composites have shown that the dielectric and piezoelectric properties decrease when the orientation angle of the ceramic rods deviates from the poling direction. These theoretical studies however have not yet been experimentally confirmed.

Many methods have been used to fabricate 2-2 and 3-3 composites such as: dicing from a bulk ceramic, injection molding [7], solvent cast [8] method or hot pressing [9], replamine, BURPS, lost mold, reticulated, relic, and Fused Deposition of Ceramics (FDC) [4]. In



Fig. 1. Schematic of (a) 2-2 and (b) 3-3 connectivity patterns.

this work, the FDC process was utilized to build 2-2 and 3-3 ceramic structures. The Fused Deposition of Ceramics (FDC) is a process in which ceramic loaded thermoplastic filaments are fed into the liquefier of a modified Stratasys™ FDM™ 3D modeler system [8, 9]. The liquefier extrudes a road of the input material through a nozzle, depositing it onto a substrate attached to a platform capable of moving in the z -direction. The liquefier moves in the x - y plane to build the first layer of the part. After depositing the first layer, the platform moves down the thickness of one layer, allowing the deposition of the next layer on top of it. These steps are repeated until the structure is completed. The material used was a filament made of 52.5 vol.% PZT (TRS600, TRS Ceramics, PA) ceramic and 47.5 vol.% thermoplastic binder [10, 11].

2. Experimental Procedure

The green 2-2 and 3-3 structures were made with different orientation angles θ , which varied between 0° and 75° , with 15° increments. Figure 2 shows the cross-sectional views of such green structures. The sample size was $15 \times 15 \times 10 \text{ mm}^3$ for all designs. The binder was removed by slow heating to 550°C , followed by a bisque firing step at 780°C to ease the handling of samples in next steps. The sintering was carried out at 1285°C for one hour in a sealed crucible with a controlled lead oxide atmosphere. After sintering, the average density of the samples was 7.34 g/cm^3 and the longitudinal, transversal and thickness shrinkage were 18%, 16% and 19% respectively. The thickness of the ceramic walls was $\sim 425 \mu\text{m}$ after sintering.

The sintered structures were embedded in Spurr epoxy (Ernest F. Fullam, Inc., Latham, NY) and cured at 60°C for eight hours [12]. Using a Dicing Saw (K&S 885, Willow Grove, Pennsylvania) the 2-2 and 3-3 composites were sliced in 2 mm thickness so that at least

eight samples were obtained for each configuration. The samples were then electroded using silver epoxy (4929N, Silver Composition, DuPont Electronics) and poled via the Corona method [13]. The samples were poled at 60°C for 15 minutes with 28 kV electric potential applied to the tip of the needles. The ceramic volume percent of the composites was determined using mixing rule [14]:

$$\rho_{\text{composite}} = (\rho_{\text{ceramic}} V_{\text{ceramic}}) + (\rho_{\text{polymer}} V_{\text{polymer}}) \quad (1a)$$

$$V_{\text{polymer}} = 1 - V_{\text{ceramic}} \quad (1b)$$

$$V_{\text{ceramic}} = \frac{(\rho_{\text{composite}} - \rho_{\text{polymer}})}{(\rho_{\text{ceramic}} - \rho_{\text{polymer}})} \times 100 \quad (1c)$$

where $\rho_{\text{composite}}$, ρ_{polymer} and ρ_{ceramic} are the densities of composite, Spurr epoxy, and the bulk PZT ceramic, respectively. The densities of bulk PZT ceramic and Spurr epoxy were considered to be 7.34 and 1.01 g/cm^3 , respectively. The capacitance and dissipation factor of the composites were measured at 1 kHz using an RLC Digibridge (model #1689M, GenRad, Inc., Concord, Maine). The dielectric constant was then calculated by [7]:

$$K = \frac{C_p \cdot t}{\epsilon_o \cdot A} \quad (2)$$

where C_p is the capacitance, t is the thickness of the samples, A is the electrode area, and ϵ_o is the permittivity of free space ($8.854 \times 10^{-12} \text{ F/m}$). The piezoelectric charge coefficient, d_{33} , of the composites was measured at 100 Hz by a Berlincourt Piezometer (Channel Products, Inc., Chesterland, Ohio) using two flat probes. The piezoelectric voltage coefficients, g_{33} , of the composites were then calculated using the relation [4]:

$$g_{33} = \frac{d_{33}}{\epsilon_o K} \quad (3)$$

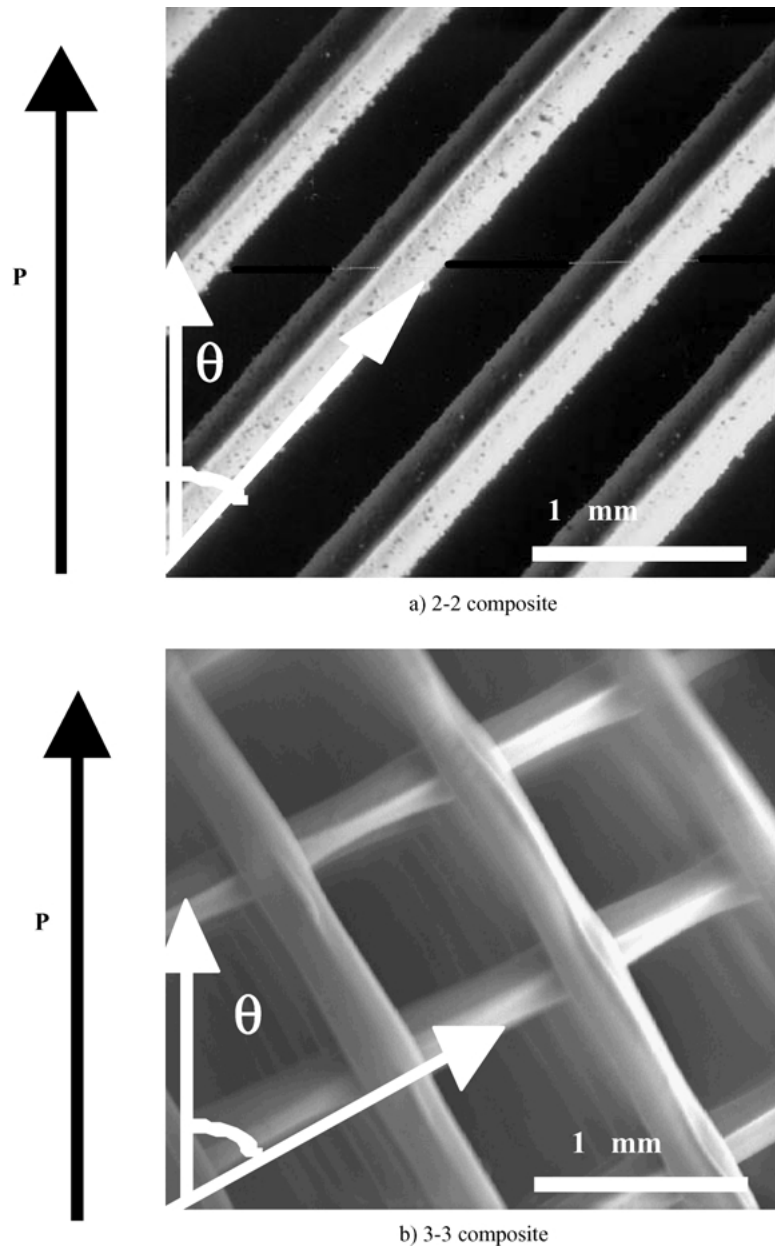


Fig. 2. Cross-sectional view of (a) green 2-2 and (b) green 3-3 structures. The θ (theta) is the orientation angle and P is the poling direction.

3. Results and Discussion

Table 1 presents the electromechanical properties of 2-2 and 3-3 composites with 30 volume percent ceramic at different orientation angles (θ) relative to the poling direction. Figures 3 to 6 show the effect of orientation angle on the piezoelectric charge coefficient,

dielectric constant, depolarizing factor and piezoelectric voltage coefficient of such composites. As shown in Fig. 3, when the ceramic walls deviate from the poling direction and the orientation angle is $<15^\circ$, the 2-2 composites have similar d_{33} value to that of a classical composite ($\theta = 0$). However, the d_{33} decreases abruptly from ~ 380 pC/N to ~ 200 pC/N when $\theta > 15^\circ$. For the

Table 1. Electro-mechanical properties of bulk PZT ceramic and PZT/polymer composites with 2-2 and 3-3 connectivity and different orientation angles.

θ (deg.)	Density (g/cm ³)	Vol. % Ceramic	d_{33} (10 ⁻¹² C/N)	K	g_{33} (10 ⁻³ Vm/N)	$\tan \delta$	N_i (10 ⁻³)
Pressed disk	7.81	100	520 ± 8	4000	15	0.026	–
Bulk FDC	7.34	100	600	3350	25 ± 2.5	0.039	–
<i>2-2 Composites</i>							
0	2.94	30	400 ± 11	1000 ± 10	45 ± 0.8	0.038	0.006
15	3.01	32	390 ± 12	985 ± 35	45 ± 1.6	0.035	0.007
30	2.88	30	300 ± 8	800 ± 26	42 ± 1.6	0.035	0.059
45	2.85	29	230 ± 30	510 ± 20	51 ± 4.8	0.048	0.270
60	2.87	30	90 ± 15	300 ± 15	34 ± 4.2	0.038	0.650
75	2.89	30	50 ± 8	200 ± 11	28 ± 3.5	0.048	1.150
<i>3-3 Composites</i>							
15	3.22	32	425 ± 25	1040 ± 15	46 ± 0.8	0.035	0.004
30	2.95	28	410 ± 26	840 ± 8	55 ± 4.2	0.034	0.110
45	3.11	30	412 ± 22	600 ± 6	78 ± 4.8	0.039	0.212
60	3.15	30	135 ± 8	240 ± 5	64 ± 3.8	0.038	0.895
75	3.14	31	90 ± 5	146 ± 2	70 ± 4.5	0.034	1.845

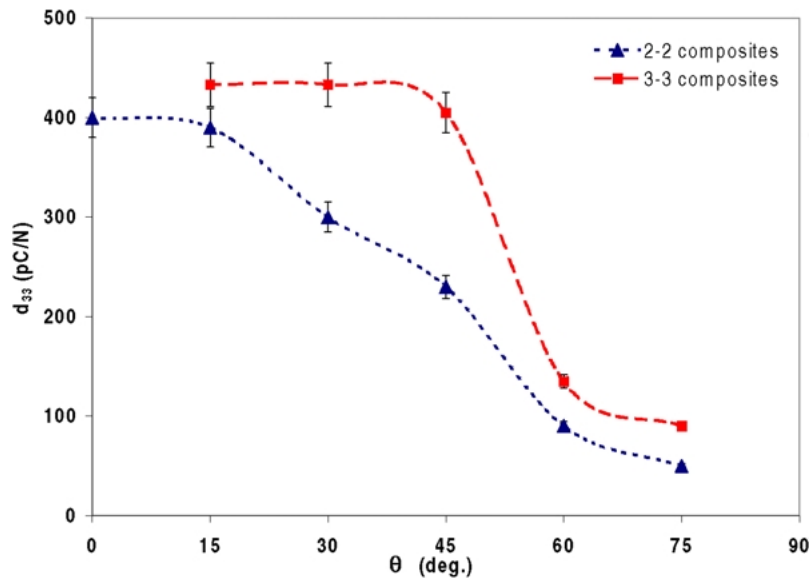


Fig. 3. Piezoelectric charge coefficient d_{33} (pC/N) for 2-2 and 3-3 composites as a function of orientation angle θ (deg.).

3-3 composites with $\theta < 45^\circ$, the deviation from poling direction does not affect the d_{33} values of composites. At $\theta > 45^\circ$, the d_{33} significantly decreases from ~ 450 pC/N to ~ 100 pC/N ($\theta = 75$).

Figure 4 shows that the dielectric constant of the composites decreases as the orientation angle θ of the PZT walls differs from the poling direction. This can be explained by the concept of depolarizing factor developed by Okazaki and Igarashi in

1979 [15]:

$$K_{\text{app}} - 1 = \frac{\left[\left(1 - \frac{P}{100} \right) (K_{\text{st}} - 1) \right]}{[1 + N_i (K_{\text{st}} - 1)]} \quad (4)$$

where P is the polymer volume fraction (≈ 0.30), K_{st} is the standard dielectric constant of the bulk ceramic (≈ 3350), K_{app} is the apparent dielectric constant of the composites with different orientation angles. It is

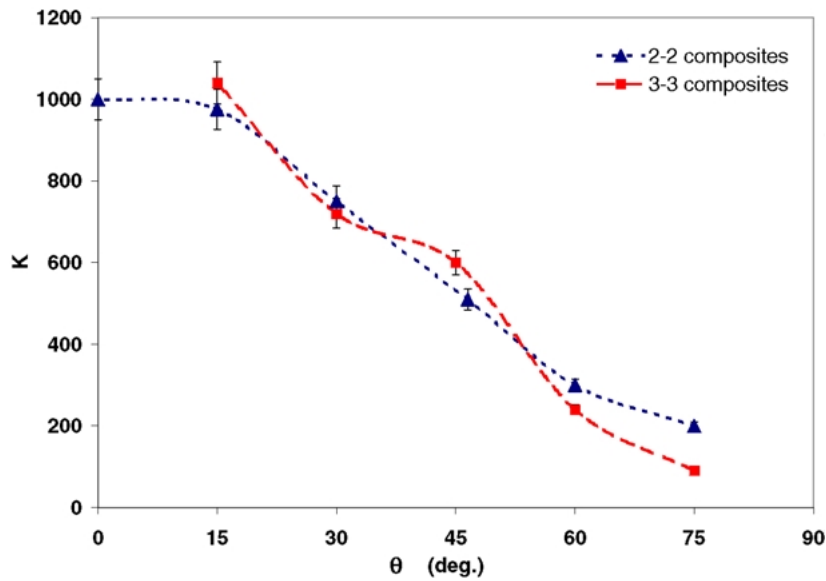


Fig. 4. Dielectric constant K of 2-2 and 3-3 composites as a function of orientation angle θ (deg.).

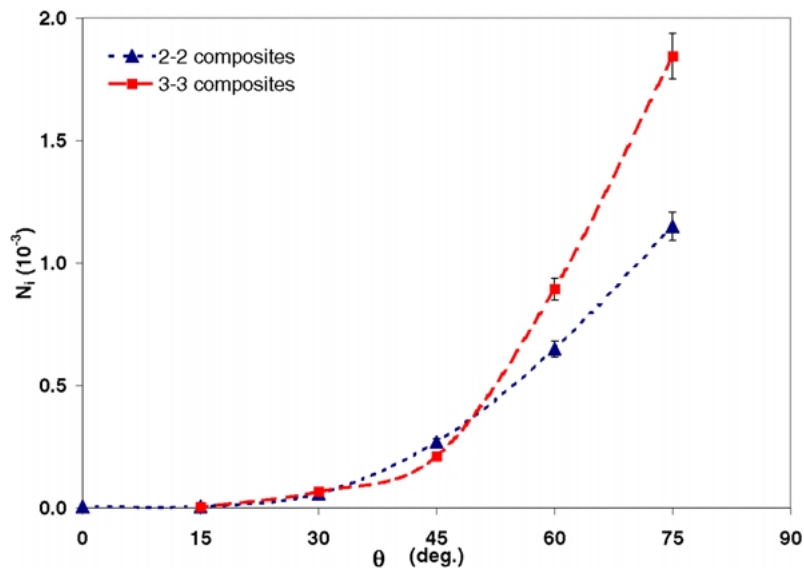


Fig. 5. Depolarizing factor N_i (10^{-3}) for 2-2 and 3-3 composites as a function of orientation angle θ (deg.).

known that for a fully interconnected 3-3 composites, such as honeycomb composites, the depolarizing factor is zero, due to a perfect ceramic continuity between the electrodes along the poling direction. In a classical 2-2 composite ($\theta = 0$), the piezoceramic walls form a continuous path between electrodes along the poling direction. Thus, the depolarizing factor of such composites must be equal to zero. In this work, when θ

equates zero, $N_i = 0.00006$ which is in good agreement with what is expected. The reason for $N_i \neq 0$ is that the PZT ceramic walls reached only $\sim 93\%$ of the theoretical density of PZT-5 H. Thus the presence of closed porosity in ceramic walls gives rise to $N_i \neq 0$. When $\theta > 0$, the ceramic continuity along the poling direction diminishes and instead alternating ceramic-polymer layers form. As θ increases, the number of

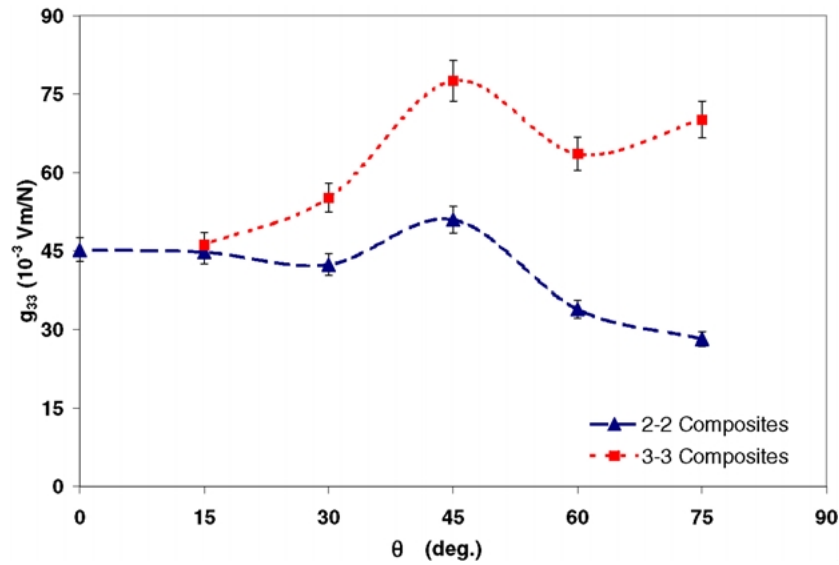


Fig. 6. Piezoelectric voltage coefficient g_{33} (10^{-3} Vm/N) for 2-2 and 3-3 composites as a function of orientation angle θ (deg.).

alternating ceramic-polymer layers increases, which leads to the increase of depolarizing factor. The larger the N_i value, the larger the decrease in the dielectric constant. Figure 5 represents the depolarizing factor of oriented 2-2 and 3-3 composites as a function of the angle θ . A significant increase in the depolarizing factor of the 2-2 composites is observed for $\theta > 30^\circ$ which corresponds to an abrupt decrease of the dielectric constant. However, the increase of depolarizing factor and decrease of dielectric constant for 3-3 composites begins at $\theta > 15^\circ$.

As shown in Fig. 6, the calculated g_{33} coefficient of 2-2 composites shows a minor improvement at $\theta = 45^\circ$ due to the different decrease of K and d_{33} coefficients, meaning the difference in slope of Figs. 4 and 5. Although the g_{33} of the 2-2 composites did not increase notably, the g_{33} coefficient of 3-3 composites significantly increased as a function of θ , reaching a maximum value of $\sim 80 \times 10^{-3}$ mV/N at $\theta = 45^\circ$. Further deviation of ceramic walls from the poling direction (above 45°) had no improvement on the g_{33} coefficient of 3-3 composites.

4. Summary

For the first time, an experimental determination of the effect of orientation angle of piezoelectric ceramic walls with respect to the poling direction in 2-2 and

3-3 composites is reported. The general trend observed was a decrease in the piezoelectric and dielectric properties of composites when the ceramic walls deviated from the poling direction. The d_{33} value of both composites did not vary when the orientation angle was smaller than 15° and 45° for the 2-2 and 3-3 composites respectively. Their piezoelectric charge coefficients however decreased when $\theta > 15^\circ$ and $> 45^\circ$, for 2-2 and 3-3 composites, respectively. The dielectric constant of both composites decreased with increasing orientation angle. This was attributed to the depolarizing factor N_i , which increased with increasing orientation angle.

No major improvement in the g_{33} coefficient of the 2-2 composites was observed. On the other hand, an enhancement was observed for the g_{33} coefficient of 3-3 composites with $\theta = 45^\circ$. Further increase of the orientation angle (above 45°) from the poling direction had no additional beneficial effect on the piezoelectric properties of 3-3 composites.

Acknowledgments

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