# Chapter 77 Piezoelectric Properties of Cement-Based Piezoelectric Composites Containing Fly Ash

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Abstract Piezoelectric properties of 0–3 type cement-based piezoelectric composites with fly ash are investigated, where the piezoelectric inclusion is PZT, and the binder consists of cement and fly ash. Cement was replaced by fly ash from 10 % to 50 vol.% in the binder. Experimental results indicate that all fly ash/cement piezoelectric composites can be successfully polarized. Prior to polarization, relative dielectric constant  $\varepsilon_r$  increases with fly ash, but diminishes with curing time. Piezoelectric properties are stable at the 50th day after the polarization. Curing time is not sensitive to piezoelectric properties, but polarizing voltage is. A 20 vol.% replacement of cement by fly ash in cement-based piezoelectric composite with 50 vol.% PZT reaches a maximum value of 54 pC/N and  $28 \times 10^{-3}$  V-m/N for  $d_{33}$  and  $g_{33}$ , respectively.

Keywords Cement · Piezoelectricity · Fly ash · Curing · Polarization

## 77.1 Introduction

Sensors and actuators installed in civil engineering structure are usually made by piezoelectric ceramics and polymers. Among piezoelectric materials, lead zirconate titanate (PZT) is a ceramic with higher piezoelectric strain factor  $(d_{33})$ that have been used in, such as, ceramic micro-electro-mechanical systems (C-MEMS), ultrasonic generators, ferroelectric thin films and small actuators.

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To overcome the matching problem in concrete structures that conventional sensors and actuators do not contact simultaneously with concrete, 0–3 type cement-based piezoelectric composites have been developed since last decade [\[1–7](#page-8-0)]. Common 0–3 type cement-based piezoelectric composites (PZT/cement composites) consist of cement binder as the matrix and randomly oriented PZT particles as the inclusion. To create piezoelectricity, we need to apply poling voltage to PZT/cement composites. No piezoelectric properties are found without the polarization.

Many factors affect the dielectric and piezoelectric properties of 0–3 type cement piezoelectric composites. Currently, PZT/cement composites containing PZT from 20 to 90 vol.% can be manufactured by pressure forming. The effect of volume fraction and particle size of piezoelectric ceramics was discussed [[8–10\]](#page-8-0). The other factors such as poling time  $[11]$  $[11]$ , poling temperature  $[12]$  $[12]$ , poling field [\[13](#page-8-0)], the thickness and the forming of specimens [[4,](#page-8-0) [14–16\]](#page-9-0) were also investigated. To produce higher piezoelectric strain factor  $(d_{33})$ , adding carbon black into 0–3 type cement-based composites was reported [\[17](#page-9-0)], and adding 80 vol.% nano-PZT powder can obtain  $d_{33} = 53.7$  pC/N [[7\]](#page-8-0).

Dielectric and piezoelectric properties of PZT/cement composites containing pozzolanic materials were rarely reported until a PZT-silica fume cement composite was conducted, where  $5-10$  wt.% silica fume were added [[10\]](#page-8-0). Recently,  $d_{33}$  value up to 70 pC/N for 60 vol.% PZT and 20 wt.% silica-based replacement in cement was manufactured at 38 aging days [\[18](#page-9-0)]. No piezoelectric properties of PZT/cement composites containing fly as were investigated previously.

In this study, we focus on PZT/cement composites containing fly ash, and examine the influence of age effect including curing time and aging time after the polarization. Cement-based piezoelectric composites containing 50 vol.% PZT and partial cements were replaced by fly ash with 10–50 vol.% in the binder.

## 77.2 Materials and Experiments

PZT ceramics (piezoelectric inclusion) are randomly oriented in cement-based binders (matrix) to form a 0–3 type PZT/cement composite. The diameter of PZT particle is 75–150  $\mu$ m, with a specific gravity of 7.9,  $d_{33} = 470$  pC/N, piezoelectric voltage factor (g<sub>33</sub>) of 24  $\times$  10<sup>-3</sup> V-m/N, and relative dielectric factor ( $\varepsilon_r$ ) of 2100. Cement is type I Portland cement with the fineness of 349  $m^2/kg$  and specific gravity of 3.16. Fly ash belongs to Class F produced by Hsinta thermal power plant (Taiwan) with a fineness of  $326 \text{ m}^2/\text{kg}$  and specific gravity of 2.11.

Six kinds of PZT/cement composites are made. The composite denoted by PP is a cement-based piezoelectric composite with 50 % PZT and 50 % cement by volume, and no PZT found in PP is named as PC (100 % cement). PP material containing fly ash is referred as FA groups. There are five replacements of cement by fly ash in PP material from 10 to 50 %, for example, FA10 represents 10 vol.% of cement replaced by fly ash in the binder, and FA50 is a 50 % replacement of fly ash.

PZT powders, cement and fly ash were pre-mixed without adding water. The mixture was placed in a cylindrical steel mold of 15 mm in diameter, and then applied by a compressive stress of 80 MPa for 5 min to form a disk-like shape. Before the polarization, specimens were cured in 90  $^{\circ}$ C and relative humidity of 100 % for 7, 28 and 56 days (curing time), respectively. After curing, specimens were polished to 2 mm in thickness, coated by silver paint as an electrode, and then, baked at 150  $\degree$ C for 30 min in oven. During the polarization, the specimen was subjected to three poling voltages, 0.5, 1.0 and 1.5 kV/mm, respectively, in a 150  $\degree$ C silicone oil bath for 30 min (polarizing time).

After the polarization, specimens were placed in the air for 24 h and measured piezoelectric and dielectric properties based on aging time. Piezoelectric strain factor  $d_{33}$  was directly measured by  $d_{33}$  Piezometer, and other piezoelectric properties were captured by Impedance Phase Analyzer. Each experimental value shown as follows is an average of three specimens, and was measured at  $24 \text{ °C}$  and 50 % humidity condition.

## 77.3 Results and Discussion

#### 77.3.1 Properties Before Polarization

Cement-based composites do not have piezoelectric properties unless the addition of piezoelectric inclusions and a successful polarization  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$  $[1, 4, 11, 16]$ . Prior to the polarization, electric properties including capacitance (C), dielectric loss (D) and relative dielectric factor  $\varepsilon_r$  were measured and calculated.

Table [77.1](#page-3-0) displays the capacitance of PC, PP and FA-group materials. Capacitance gradually decreases as curing time increases. FA-group materials with increasing fly ash always have a higher capacitance, compared with PP material. While the content of fly ash greater than 30 vol. $\%$  in the binder, the capacitance of PZT/cement composites raises tremendously.

Materials with high dielectric loss are difficult to be polarized, and easy to induce current breakdown in the specimen during the polarization. Table [77.2](#page-3-0) indicates that cement-based materials at longer curing time own the lower dielectric loss. PC materials (pure cement) cannot be polarized due to a higher D, and lead to no piezoelectric properties. Compared with PC material, dielectric loss of PP and FA-group materials is lower.

Before the polarization, relative dielectric factor  $\varepsilon_r$  of cement-based composites is shown in Table [77.3](#page-3-0). The development of  $\varepsilon_r$  is similar to the capacitance in Table [77.1,](#page-3-0) so that increasing curing time will reduce  $\varepsilon_r$ . Cement containing PZT (PP material) has the lowest  $\varepsilon_r$ , and continues to develop with increasing fly ash. Obviously, relative dielectric factors of FA40 and FA50 material are dramatically high, compared with the others materials.

PС	PP	FA10	<b>FA20</b>	<b>FA30</b>	FA40	<b>FA50</b>
108	75	84	95	165	644	742
80	70	78	87	158	466	552
56	68	74		121	285	398

<span id="page-3-0"></span>Table 77.1 Capacitance before the polarization (unit: pF)

Table 77.2 Dielectric loss before the polarization

Curing time	PС	PP	FA10	<b>FA20</b>	<b>FA30</b>	FA40	<b>FA50</b>
7 days	0.94	0.21	0.31	0.39	0.49	0.68	0.73
28 days	0.85	0.20	0.27	0.37	0.43	0.62	0.71
56 days	0.76	0.19	0.25	0.34	0.39	0.51	0.69

Table 77.3 Relative dielectric factor before the polarization



## 77.3.2 Piezoelectric Properties

Polarizing voltages applied to PZT/cement composites to create piezoelectric properties as the curing time reached. After the polarization, specimens were measured daily until 60 days. To discuss aging effect (the time after polarization), results of piezoelectric properties are shown in Figs. [77.1,](#page-4-0) [77.2](#page-4-0), [77.3](#page-5-0), [74.4,](#page-5-0) [75.5](#page-6-0), [77.6](#page-6-0) for the material undergone 1.5 kV/mm at 7 and 56 curing days.

Figures [77.1](#page-4-0) and [77.2](#page-4-0) show relative dielectric factor of PP and FA-group materials at 7 and 56 curing days respectively. Relative dielectric factors increase with aging time, and the growth of  $\varepsilon_r$  displays less fluctuant after the polarization of 50 days, where  $\varepsilon_r$  values are between 150 and 200. From Figs. [77.1](#page-4-0) and [77.2](#page-4-0), choosing the day after the polarization of 24 h to determine  $\varepsilon_r$  is not adequate because of rapid variations of the property at early age. After the polarization of 50 days, increasing fly ash to PP material will diminish  $\varepsilon_r$  no matter what curing day is, and this trend is different from that prior to polarization in Table 77.1.

Piezoelectric strain factor  $d_{33}$  and piezoelectric voltage factor  $g_{33}$  are important piezoelectric properties for sensors and actuators. Aging effect for  $d_{33}$  and  $g_{33}$  are shown in Figs. [77.3,](#page-5-0) [77.4,](#page-5-0) [77.5](#page-6-0), [77.6](#page-6-0), where  $d_{33}$  and  $g_{33}$  are on the increase with aging time. Figure  $77.3$  shows  $d_{33}$  at 7 curing days, and  $d_{33}$  values of PP (with 50 % PZT) are 18, 40, 43 and 44 pC/N at aging time of 0, 21, 28 and 60 days respectively. It seems that adding fly ash to PP material does not increase  $d_{33}$ except for FA10 and FA20 material after 40 days.  $d_{33}$  values of FA20 material are

<span id="page-4-0"></span>

23, 42, 45 and 54 pC/N for aging time of 0, 21, 28 and 60 days respectively. In Fig. [77.4](#page-5-0), the trend of  $d_{33}$  at 56 curing days is similar to Fig. [77.3](#page-5-0).

Figure  $77.5$  shows experimental results for  $g_{33}$  at 7 curing days, and indicates that  $g_{33}$  reduces tremendously at early aging time.  $g_{33}$  values for FA10 and FA20 at the 28th day of aging time are 30.6 and 37.4 mV-m/N respectively, those even greater than that for PZT ceramic ( $g_{33} = 24$  mV-m/N). The replacement (fly ash) less 30 vol.% is a better choice to increase  $g_{33}$ . In Fig. [77.6,](#page-6-0) the trend of  $g_{33}$  with the aging day is also similar to Fig. [77.5](#page-6-0).

Experimental results display that all FA-group materials can be successfully polarized. Now, we select the experimental data at the 60th day after the polarization to show the effect of curing time and fly ash contents. In Fig. [77.7](#page-6-0), curing time shows less effective to enhance  $\varepsilon_r$ , and increasing poling voltage will reduce  $\varepsilon_{\rm r}$ . A 20 % replacement by fly ash is the most effective to improve the dielectric constant.



The results for  $d_{33}$  and  $g_{33}$  at 60 days are shown in Figs. [77.8](#page-7-0) and [77.9](#page-7-0) respectively.  $d_{33}$  and  $g_{33}$  have a less fluctuation for different curing times at the constant poling voltage, but increase with poling voltages. Both figures indicate that a 20 % replacement by fly ash is the best choice to promote piezoelectric properties.  $d_{33}$  values for PZT/cement piezoelectric composites with fly ash from 0 to 50 % at 56 curing days and 1.5 kV/mm are 46, 49, 54, 39, 28 and 24 pC/N respectively, and  $g_{33}$  are 24.9, 25.9, 28.0, 22.1, 17.5 and 15.6 mV-m/N in turn. Hence,  $d_{33}$  and  $g_{33}$  of FA20 material reaches a maximum value, where  $d_{33} = 54$  pC/N and  $g_{33} = 28.0$  mV-m/N.

<span id="page-5-0"></span>Fig. 77.3 Aging effect of  $d_{33}$ at 7 curing days

<span id="page-6-0"></span>



<span id="page-7-0"></span>

## 77.4 Conclusions

Cement-based piezoelectric composites without adding water were pressed by a 80 MPa compression and cured for 7, 28 and 56 days respectively, after that, specimen were polarized by three poling voltages. Experimental data were measured daily till 60 days after the polarization. Experimental results are concludes as follows.

- (1) Prior to polarization, capacitance, dielectric loss, and relative dielectric factor of FA-group materials increase as increasing fly ash, but decrease with curing time. However, adding fly ash to PP material will diminish  $\varepsilon_r$  after the polarization.
- (2) All FA-group materials containing fly ash up to 50 vol.% replacement can be successfully polarized.
- <span id="page-8-0"></span>(3) Relative dielectric factor,  $d_{33}$  and  $g_{33}$  of PP and FA-group materials gradually increase with aging time, but have less effective to the effect of curing time. Meanwhile, increasing poling voltage will reduce  $\varepsilon_r$ , but increase  $d_{33}$  and  $g_{33}$ .
- (4) To promote  $d_{33}$ , the content of fly ash had better not exceed 20 vol.% replacement of cement.
- (5) Some  $g_{33}$  values of FA/cement composites, for example FA10 and FA20, are even greater than that of PZT ceramic.
- (6) A 20 vol.% replacement of cement by fly ash is the best choice to improve the dielectric constant, piezoelectric strain factor and piezoelectric voltage factor of PZT/cement composites.
- (7) Due to rapid increase of piezoelectric properties  $(\varepsilon_r, d_{33} \text{ and } g_{33})$  at early aging time, a suitable timing to represent piezoelectric properties of PZT/cement is to choose a relatively stable value after 50 days of the polarization.

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