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Effect of aged binder on piezoelectric properties of cement-based piezoelectric composites

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Abstract Age-dependent piezoelectric properties of cement piezoelectric composites containing cement-based binder and 50 vol. % PZT piezoelectric inclusions are conducted. The effect of binder with 10 to 50 % cement replaced by slag and fly ash is investigated. Specimens are polarized by 1.5 kV/mm for 30 min when the curing time reaches 7, 28 and 56 days, respectively. Experimental values are measured daily till 120 days after the polarization. Prior to polarization, dielectric loss needs to be less than 0.73 to guarantee the feasibility of polarization. Piezoelectric properties including d_{33}, g_{33} and ε_r are age-dependent unless the age is higher than 60 days after the polarization. The electromechanical coupling coefficient κ_t is independent of the ages. The curing time shows less efficient to piezoelectric properties while hydration reaction is completed. 20 vol. % cement replaced by slag or fly ash provides optimum d_{33} and $g_{33.}$ Compared with slag replacement, fly ash replacement can diminish ε_r, but increase κ_t. In addition, a modified equation to calculate the dielectric constant of PZT/cement composites is also proposed.

1 Introduction

Smart materials, such as shape memory alloys, magnetostrictive materials, piezoelectric materials or some functional materials, have been developed and applied to many industrial fields. Among them, piezoelectric materials with high dielectric constant are usually fabricated to be sensors and actuators. Conventional sensors and actuators made by piezoelectric ceramics, polymers or composites can sense or respond to deformations in many applications, such as electronic instruments, precise locator, optical and medical apparatus. To infrastructures, for instance, tunnel, high-rise building, bridge and important structures, or facilities near a hillside, mountain, and river bank potentially undergone earthquake, floods, high speed impacts, explosion and machine vibration had better installed sensors and actuators for monitoring and alerting to prevent from calamities.

Generally, sensors and actuators used in concrete structures are made by piezoelectric ceramics, in which the differences of acoustic impedance and volume stability between piezoelectric ceramics and concrete are unavoidable. Acoustic impedance of piezoelectric ceramics, for example lead zirconate titanate (PZT), is 21.2×10^{-6} kg-m^{-2} s^{-1}, and that of concrete is about 9.0×10^{-6} kg-m^{-2} s^{-1} [1]. This difference lowers the precision of a PZT sensor when used in concrete structures. Thereby, 0–3 type cement-based piezoelectric composites were developed to overcome the compatibility for concrete structures in which conventional sensors and actuators do not respond synchronously with concrete since the last decade [1–7]. To date, 0–3 type cement-based piezoelectric composites (PZT/cement composites) consist of Portland cement as matrix and randomly

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oriented PZT particles as functional inclusion, where the cement-based matrix is age-dependent. To create piezoelectric properties, a voltage field applying to PZT/cement composites is required. No piezoelectric properties are found without successful polarization.

Dielectric and piezoelectric properties of 0–3 type cement piezoelectric composites depend on many factors like forming method, poling conditions, admixture, the size and the content of PZT (or piezoelectric materials). Although the piezoelectric strain constant (d_{33}) for PZT/cement composites made by blending with water is higher than that fabricated without water by pressure, most PZT/cement composites are produced by pressure forming at present due to less variations [8]. Specimens with PZT from 20 to 90 vol. % were successfully manufactured and polarized by pressure from 32 MPa to 128 MPa [9]. The effect of volume fraction and particle size of piezoelectric ceramics on PZT/cement piezoelectric composites was investigated in [5,10,11]. Chaipanich [5] found that d_{33} increases with increasing diameter of PZT. Li and Gonga [12] also had a similar conclusion and in addition indicated that the dielectric constant ε_{33} reduces with larger diameter of PZT. Li et al. [10] and Chaipanich et al. [13] pointed out that higher content of PZT is beneficial to d_{33} and ε_{33} of cement piezoelectric composites.

Piezoelectric strain constant d_{33} and electromechanical coupling coefficient κ_t were also found to increase with increasing poling time up to 45 min, but will reduce for poling time beyond 45 min [14]. Polarization with poling time between 30 and 45 min provides optimum piezoelectric properties. Dong et al. [15] polarized PZT/cement composites under poling temperatures of 20 °C, 90 °C, 130 °C and 160 °C, respectively, to examine κ_t, and found that κ_t rises for specimens subjected to longer poling time and higher poling temperature. Huang et al. [16] and Dong et al. [15] applied 2.0–5.0 kV/mm and 1.0–6.5 kV/mm, respectively, to the specimen and found that higher poling field induces higher d_{33} and κ_t.

Except for the technique mentioned above by considering particle size and the content of piezoelectric inclusions, fabrication process [8,13], polarization conditions and curing time, some special cement or piezoelectric inclusions were presented to improve the piezoelectric properties of cement-based piezoelectric composites. Cheng et al. [17] provided a cement piezoelectric composite by using sulphoaluminate cement and lead magnesium niobate (PMN) piezoelectric ceramic, and Hunpratub et al. [18] manufactured a new piezoelectric ceramic, BZT-BCT, to replace PZT in cement piezoelectric composite. Both cement piezoelectric composites were found to increase d_{33} and ε_{33}. Besides, d_{33} of cement-based piezoelectric composites with 1.0 vol. % carbon black has the optimum value proposed by Gong et al. [19]. Huang et al. [20] used P(LN)ZT, sulphoaluminate cement and carbon black to prepare cement-based piezoelectric composites and concluded that d_{33} and piezoelectric voltage constant g_{33} reach the maximum value when carbon black of 0.3 wt % is added, and, except for ε_{33} and dielectric loss D, continuously increase with carbon black content. Meanwhile, Li et al. [7] tested the composite with 80 vol. % nano-PZT powder and obtained $d_{33} = 53.7$ pC/N. Furthermore, carbon nanotube (CNT) was also chosen to increase d_{33} and g_{33}, and the content of 0.3 vol. % CNT was the most effective [21].

For the sake of saving the cost and increasing the strength and durability of concrete, pozzolanic materials such as silica fume, blast furnace slag and fly ash are usually chosen as the replacement of partial cement. For PZT/cement composites with pozzolanic materials, Chaipanich [22] in 2007 first used 5 and 10 wt % silica fume to replace partial cement. Experimental results showed that adding silica fume can increase ε_{33}, but have less improvement to d_{33} measured at the polarization of 24 h. In 2012, a d_{33} value up to 70 pC/N for the 0–3 PZT/cement composites with 60 vol. % PZT and 20 wt % silica-based replacement was measured at 38 aging days, and reached a constant value of 99 pC/N after 90 days [23]. Recently, Pan et al. [24] investigated PZT/cement composites containing 20 vol. % replacement of cement by fly ash, slag and silica fume, respectively, up to 21 aging days and found that except for κ_t, piezoelectric properties of d_{33}, g_{33} and ε_{33} were still developed with age. After compared with fly ash and blast furnace slag, polarizing PZT/cement composites with silica fume is difficult though adding silica fume can improve the piezoelectric properties.

Here, we focus on piezoelectric properties of PZT/cement composites containing fly ash and blast furnace slag, and examine the material age effect including curing time and aging time (the age after the polarization). Cement-based piezoelectric composites with 50 vol. % PZT inclusion and 50 vol. % cement-based binder were investigated, in which partial cements of 10 % to 50 vol. % were replaced by fly ash or blast furnace slag in the binder.

2 Materials and experiments

PZT particle is of a diameter of 75–150 μm, a specific gravity of 7.9, piezoelectric strain constant $d_{33} = 470$ pC/N, piezoelectric voltage constant $g_{33} = 24 \times 10^{-3}$ V-m/N, and relative dielectric constant $\varepsilon_r = 2{,}100$,

Table 1 Properties of PZT powder

Parameter	Properties
Piezoelectric strain constant d_{33} (10^{-12} C/N)	470
Piezoelectric voltage constant g_{33} (10^{-3} V-m/N)	24
Planar electromechanical coupling factor κ_p (%)	70
Thickness electromechanical coupling factor κ_t (%)	72
Mechanical quality factor Q_m (%)	65
Elastic modulus E_{33} (N/m^2)	5.2×10^{10}
Density ρ (10^3 kg/m^3)	7.9
Dielectric loss D (%)	1.5
Relative dielectric constant ε_r ($\varepsilon_{33}^T/\varepsilon_0$)	2,100

Table 2 Mixture proportions of PZT/cement-based piezoelectric composite

Composite	PZT (vol. %)	Cement (vol. %)	Slag (vol. %)	Fly ash (vol. %)
PP	50	50		
SL10	50	45	5	
SL20	50	40	10	
SL30	50	35	15	
SL40	50	30	20	
SL50	50	25	25	
FA10	50	45		5
FA20	50	40		10
FA30	50	35		15
FA40	50	30		20
FA50	50	25		25

shown in Table 1. 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 m^2/kg and specific gravity of 2.11. Blast furnace slag was produced by CHC Resources Corporation (Taiwan) conforming to ASTM C989 with a fineness of 572 m^2/kg and specific gravity of 2.88.

Three groups of PZT/cement composite, PP, SL and FA, were made. PP composite is a cement piezoelectric composite with 50 % PZT and 50 % cement by volume, where acoustic impedance (ρ_v) of PP is 10×10^{-6} kg-m^{-2} s^{-1} close to concrete with $\rho_v = 9.0 \times 10^{-6}$ kg-m^{-2} s^{-1}. SL and FA composites are PP composites containing partial slag and fly ash, respectively. There are five replacements, 10, 20, 30, 40 and 50 vol. %, of cement in PP composite, shown in Table 2. For instance, SL10 represents 10 vol. % of cement replaced by slag in PP composite, or the volume fraction of slag is 5 % in SL piezoelectric composites.

To prepare specimens, the constituents of PZT/cement composite were pre-mixed by a solar-planetary mill for 5 min without adding water. The composite as a whole is uniform. Then, the mixture was cast in a cylindrical steel mold of 15 mm diameter with a compressive stress of 80 MPa to obtain the disk specimen. Specimens were cured in 90 °C water for 7, 28 and 56 days (three curing times), respectively, before the polarization. While the curing time is reached, specimens were polished to 2 mm thickness and coated with silver paint as an electrode. At this stage (prior to polarization), we measured capacitance (C) and dielectric loss (D) with an impedance phase analyzer at 1 kHz. Relative dielectric constant ε_r was calculated from $Ct/\varepsilon_0 A$ [9], where t is the thickness of the specimen (here is 2 mm), ε_0 is a vacuum dielectric constant (8.854 pF/m), and A is the electrode area (15 mm).

Afterward, the polarization procedure was conducted by applying 1.5 kV/mm voltage in a 150 °C silicone oil bath for 30 min. If the specimen is successfully polarized, we start to count on aging time till 120 days. Piezoelectric strain constant d_{33} was directly measured by d_{33} piezometer, and the other piezoelectric properties were captured by an impedance phase analyzer daily. Each experimental value shown here is an average of three specimens and was measured at 24 °C and 50 % relative humidity.

3 Results and discussion

3.1 Properties before polarization

Cement-based composites are not piezoelectric materials due to high dielectric loss, but cement containing PZT (PP) undergone a successful polarization does [1,4,8,14]. In other words, cement-based composites do not have piezoelectric properties without adding piezoelectric inclusions and a successful polarization.

Table 3 Electric properties of PC before polarization

Curing time	7 days	28 days	56 days
D	0.94	0.85	0.76
ε_r	138	102	72
C (pF)	108	80	56

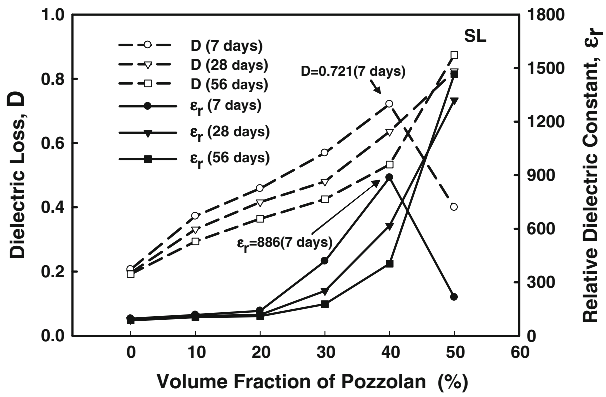

Fig. 1 Dielectric loss and relative dielectric constant of SL composites before polarization

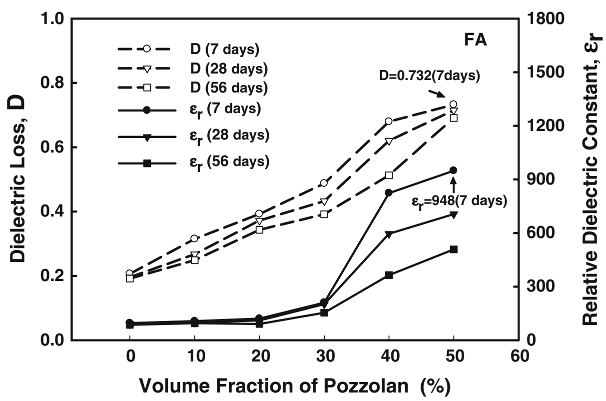

Fig. 2 Dielectric loss and relative dielectric constant of FA composites before polarization

Prior to the polarization, electric properties including dielectric loss D and relative dielectric constant ε_r were measured at three curing times (7, 28 and 56 days). In Table 3, dielectric loss for PC (100 % cement) at 7, 28 and 56 days is 0.94, 0.85 and 0.76, respectively, and ε_r is 138, 102 and 72, in turn. The decrease in D and ε_r is believed to be due to higher cement hydration and would benefit from such curing region which diminished the pores in cement paste. Cement-based materials with longer curing time have the lower dielectric loss and ε_r.

Materials with high dielectric loss are not easy to be polarized and often induce current breakdown of the specimen during the polarization. In Figs. 1 and 2, D and ε_r decrease with increasing curing time except for SL50, where SL and FA composites without slag or fly ash are PP composites. Dielectric loss for all PZT/cement composites except for SL50 at 28 and 56 curing days is less than that for PC shown in Table 3.

For SL composites except for SL50 in Fig. 1, adding slag into the PP composite can increase D and ε_r, and the maximum D and ε_r are 0.72 and 886, respectively. This is because slag particles are pozzolanic in reaction like silica fume in [22] and can densify the structure of the cement matrix. Increasing curing time will reduce ε_r. The curing time effect becomes prominent for ε_r if slag replacement is larger than 20 %. Similar to SL composites, adding fly ash also increases D and ε_r, and the maximum D and ε_r is 0.73 and 948, respectively,

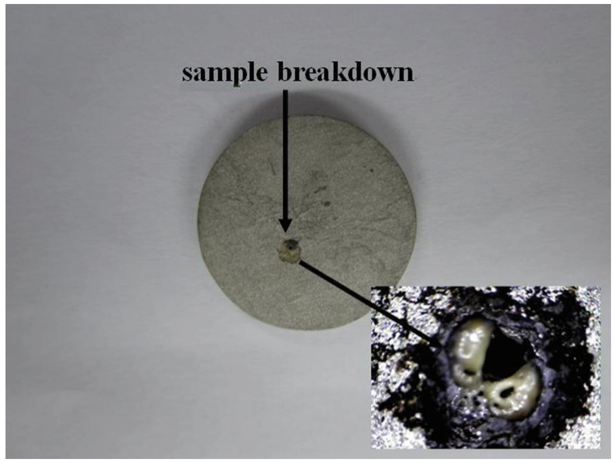

Fig. 3 Current breakdown of the specimen due to failure of polarization

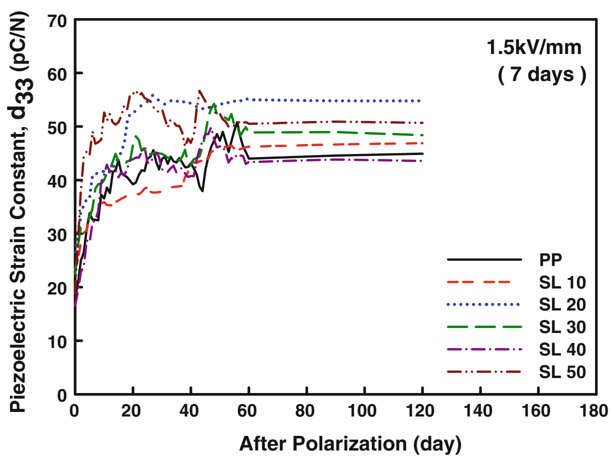

Fig. 4 Piezoelectric strain constant of SL composites with 7 curing days

shown in Fig. 2. PP material has the lowest ε_r, but the tendency will be reversed with increasing fly ash. While the content of fly ash is more than 30 vol. % in the binder, ε_r raises tremendously.

3.2 Piezoelectric properties after polarization

To gain piezoelectric properties, PZT/cement composites were applied by a poling field of 1.5 kV/mm for 30 min when the specific curing time was reached. Experimental results indicate that PZT/cement composites were successfully polarized except for SL50 at 28 and 56 curing days. By comparing with the results of dielectric loss in Figs. 1 and 2, we conclude that in order to polarize easily, dielectric loss of cement-based piezoelectric composites had better not be larger than 0.73 before polarization or a threshold of dielectric loss less than 0.76 for PC in Table 3. The polarization fails if current breakdown of the specimen is found, shown in Fig. 3. When the specimen is successfully polarized, piezoelectric properties of PZT/cement composites were measured daily until 120 days.

3.2.1 Aging effect

To investigate the aging effect, piezoelectric properties with 7 curing days are shown in Figs. 4, 5, 6, 7, 8, 9, 10, 11. Figures 4 and 5 show d_{33} of SL and FA composites, respectively, where d_{33} values for a PP composite (no slag and fly ash) at aging times of 1, 21, 28, 56 and 120 days are about 21, 40, 43, 51 and 45 pC/N, respectively. The d_{33} value for PP composite is 21 pC/N at 1 day that lies in the values of previous reports with

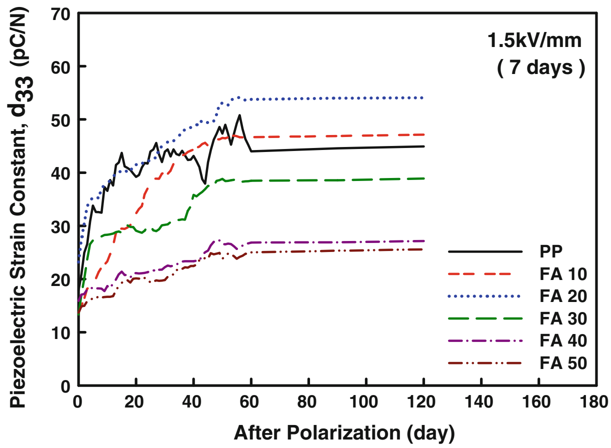

Fig. 5 Piezoelectric strain constant of FA composites with 7 curing days

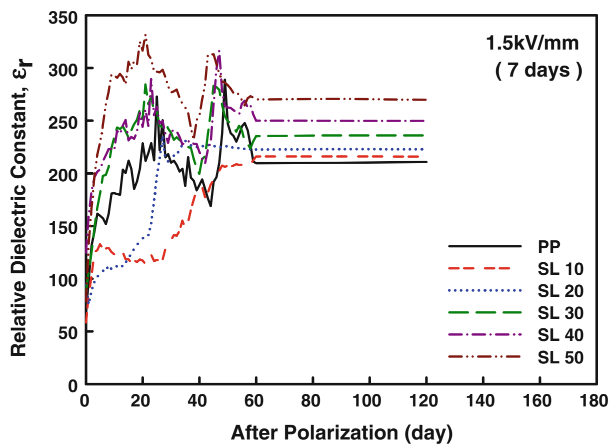

Fig. 6 Relative dielectric constant of SL composites with 7 curing days

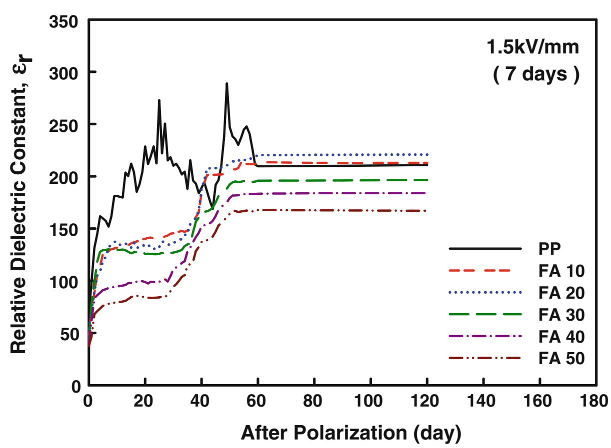

Fig. 7 Relative dielectric constant of FA composites with 7 curing days

$d_{33} = 7 - 30$ pC/N [10,13,16,17,22]. It seems that d_{33} values display less fluctuation after the polarization for 50–60 days. Previous results [10,17,23,24] indicated that d_{33} having a steady value is always observed from 10 to 50 days after the polarization, depending on PZT content and size, forming technique, poling time, curing time and applying voltages. According to cement hydration, there are still a lot of pores existing in cement-based composites at an early stage of hydration reaction. These pores affect the binding of PZT and

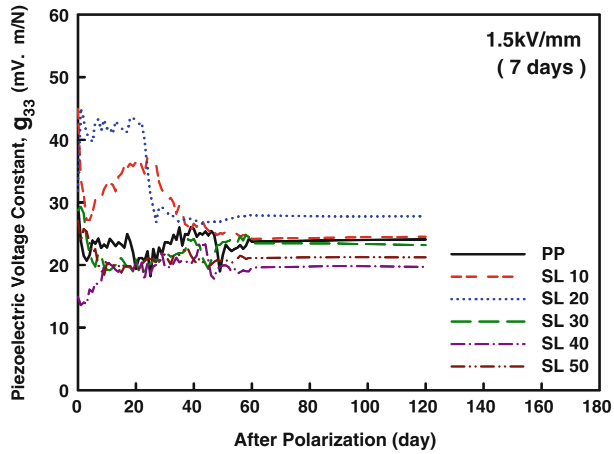

Fig. 8 Piezoelectric voltage constant of SL composites with 7 curing days

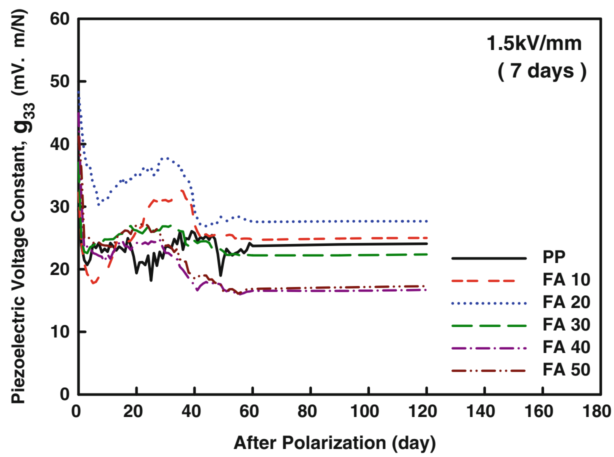

Fig. 9 Piezoelectric voltage constant of FA composites with 7 curing days

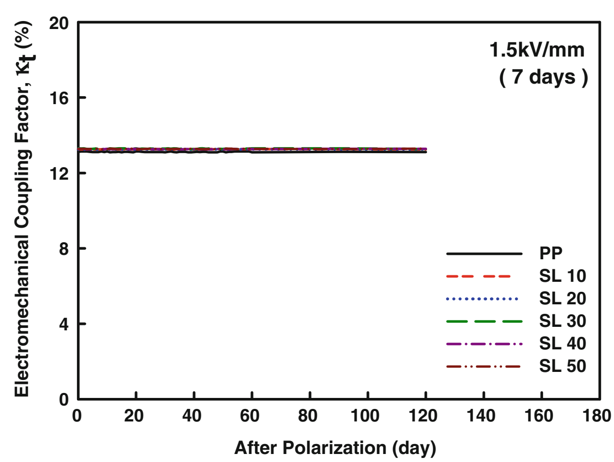

Fig. 10 Thickness electromechanical coupling factor κ_t of SL composites with 7 curing days

the matrix and reduce the stress transmission inside the material induced by applied loads which decreases d_{33}. As the material age continues to develop, hydration and pozzolanic reaction provide more efficient filling to large capillary space [25], thus improving d_{33} of PZT/cement composites.

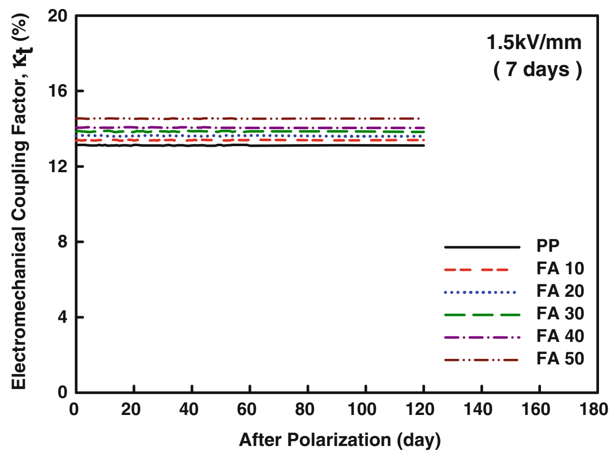

Fig. 11 Thickness electromechanical coupling factor κ_t of FA composites with 7 curing days

Table 4 Relative dielectric constants for cement-based composites with 7 curing days

Polarization	PC	PP	SL10	SL20	SL30	SL40	SL50	FA10	FA20	FA30	FA40	FA50
Before	138	96	117	140	419	886	216	107	121	211	824	948
After	–	71	79	107	111	159	174	72	89	65	56	55

Except for SL50, adding slag into a PP composite in Fig. 4 first increases d_{33} and reaches the maximum at SL20, after that decreases d_{33}. The trend of d_{33} for all FA composites in Fig. 5 is similar to that for SL composites. Compared with PP composite, adding slag almost increases d_{33}, and adding fly ash does not increase d_{33} except for FA20 and FA10. This is because the particle size of slag is smaller than that of fly ash, and the capacity to fill pores with slag between PZT and cement is better.

Figures 6 and 7 demonstrate the relative dielectric constant of SL and FA composites with 7 curing days after the polarization. From previous results with $\varepsilon_r = 75$–200 [10,13,22], the values of $\varepsilon_r = 71$–211 for a PP composite in Figs. 6 and 7 are in an acceptable range. The trend of the aging effect for ε_r is similar to d_{33} in Figs. 4 and 5. Relative dielectric constants for SL and FA composites increase with aging time, and the growth of ε_r becomes steady after 60 days, where ε_r values for SL and FA composites are 200–280 and 150–200, respectively. To obtain better ε_r, adding slag is more efficient than fly ash.

From the values of ε_r after 60 days, the ε_r increases with increasing slag shown in Fig. 6, and the trend of ε_r is similar to that prior to polarization in Fig. 1. While cement replaced by fly ash increases in Fig. 7, the ε_r at 60 days after polarization first increases and then decreases as the content is over 20 %. This result seems to be different from that prior to polarization in Fig. 2. To explain this phenomenon, relative dielectric constants for cement-based composites with 7 curing days are shown in Table 4, where ε_r was measured before and after polarization as the curing time was reached. Obviously, for PZT/cement composites, ε_r after polarization is smaller than that before polarization. This is because electric charge on 0–3 type PZT/cement composites is randomly distributed prior to polarization, and electric dipole occurs due to the polarization which induces the decrease of capacitance inside the material [8]. Besides, the ε_r of FA composites after polarization is located at the point of 0 days in Fig. 7, with 72, 89, 65, 56 and 55 from FA10 to FA50, respectively. The trend of these ε_r is similar to that at 60 days first increasing and, then, reducing after FA20. This trend coincides with material knowledge in civil engineering, and the maximum usage for slag and fly ash replacement used in concrete is 40–50 % and 20 % of cement, respectively.

The piezoelectric voltage constant g_{33} can be calculated from $d_{33}/\varepsilon_r \times \varepsilon_0$ [17] and depicted in Figs. 8 and 9 for SL and FA composites, where g_{33} for a PP composite is 24.9×10^{-3} V-m/N. Results indicate that g_{33} drops tremendously at early aging time, and the values become steady after the polarization of 50–60 days. The g_{33} for SL10, SL20, FA10 and FA20 is even higher than that for PZT piezoelectric ceramic ($g_{33} = 24 \times 10^{-3}$ V-m/N). The replacement of cement by slag and fly ash less than 30 vol. % is a better choice to increase g_{33}. It is noted that pozzolanic materials (slag or fly ash) added into cement needs alkali (supplied by cement hydration) to create the so-called pozzolanic reaction. Cement hydration and pozzolanic reaction provide hydration gels to combine cement with pozzolanic materials as a whole of the binder matrix. Partial cement replaced by

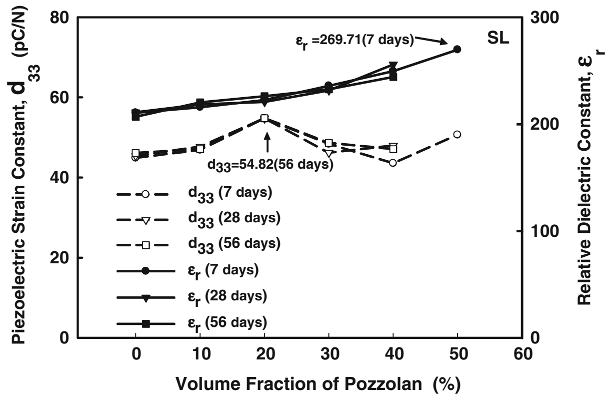

Fig. 12 Curing effect for d_{33} and ε_r of SL composites

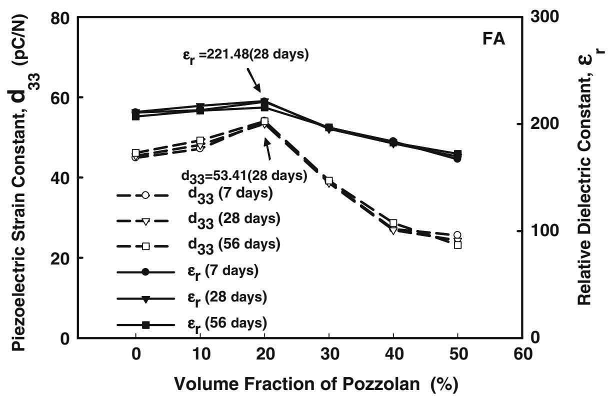

Fig. 13 Curing effect for d_{33} and ε_r of FA composites

proper proportions of slag or fly ash in PZT/cement composites can densify the microstructure of the matrix, where the volume fractions of PZT inclusion and the matrix are always constant here. From the observations of Figs. 4 to 9, choosing the day after the polarization for 24 h or 7 days to determine d_{33}, ε_r and g_{33} is not adequate for PZT/cement piezoelectric composites because of rapid change of the properties at an early age.

The thickness electromechanical coupling coefficient κ_t is calculated by the frequency at the minimum and maximum impedance [17]. The results of κ_t for SL and FA composites are displayed in Figs. 10 and 11. The $\kappa_t = 13.11\,\%$ for PP composite is within those reported previously [14,19] with $\kappa_t = 10-18\,\%$. The fluctuations of κ_t are pretty small with increasing material ages, in other words, aging time does not affect κ_t for PZT/cement composites. Compared with PP composite, fly ash is more efficient to increase κ_t, but with no influence by adding slag into cement.

3.2.2 Curing effect

One selects piezoelectric properties at 120 days after the polarization to discuss the effect of curing time because the experimental value approaches to constant at the moment. Three curing times (7, 28 and 56 days) are investigated. Piezoelectric properties are found except for SL50 with 28 and 56 curing days, and results at 120 days are plotted in Fig. 12, 13, 14, 15. Although piezoelectric properties at three curing times are different, the differences are slight. Obviously, curing time shows small influence on d_{33}, ε_r, g_{33} and κ_t.

In fact, the strength (microstructure) of PZT/cement composites still develops due to hydration and pozzolanic reaction if material age is less than 60 days. The piezoelectric composite polarized to obtain piezoelectric properties still depends on curing time (results are not shown here). Longer curing time having lower dielectric loss, shown in Figs. 1 and 2, is easy to polarize PZT/cement composites. However, all piezoelectric properties become stable after 60 days because most chemical reactions in the cement-based composite are completed, shown in Figs. 12, 13, 14, 15. Therefore, in order to polarize PZT/cement composites, the curing time of 7 days is better than that of 56 days because piezoelectric properties finally are close to each other.

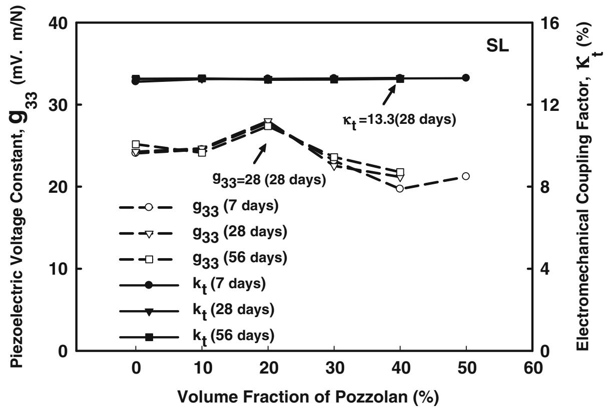

Fig. 14 Curing effect for g_{33} and κ_t of SL composites

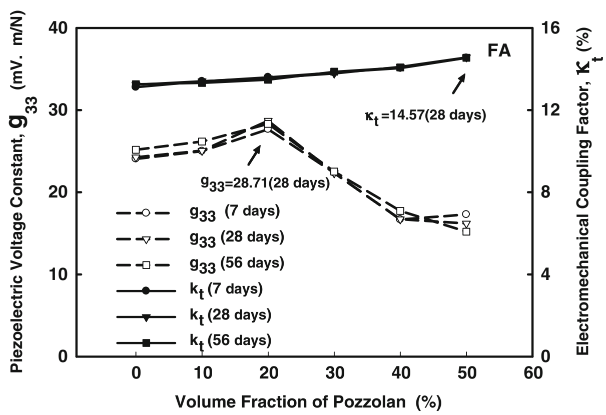

Fig. 15 Curing effect for g_{33} and κ_t of FA composites

Table 5 Piezoelectric properties at 120 days for PZT/cement composite with 7 curing days

Composite	d_{33} (pC/N)	ε_r	g_{33} (10^{-3}V-m/N)	κ_t (%)
PP	45	211	24.1	13.11
SL10	47	216	24.5	13.24
SL20	55	223	27.8	13.25
SL30	48	236	23.2	13.27
SL40	44	250	19.7	13.28
SL50	51	270	21.2	13.29
FA10	47	213	25.0	13.40
FA20	54	221	27.7	13.60
FA30	39	196	22.4	13.83
FA40	27	184	16.7	14.04
FA50	26	167	17.3	14.54

For convenience, piezoelectric properties at 120 days for PZT/cement composite with 7 curing days are recaptured in Table 5. A 20 % replacement of cement by slag and fly ash is the optimum quantity to improve d_{33} and g_{33}. The maximum value of d_{33} and g_{33} for SL composites is in SL20 with $d_{33} = 55$ pC/N and $g_{33} = 27.8 \times 10^{-3}$ V-m/N and that for FA20 is $d_{33} = 54$ pC/N and $g_{33} = 27.7 \times 10^{-3}$ V-m/N. Compared with PP, there are 20 % increment for d_{33} and 15 % for g_{33}, respectively. In Table 5, adding slag into PP only obtains 1 % increment of κ_t. Nevertheless, the 10 to 50 % replacement of cement by fly ash can enhance κ_t from 13.11 to 14.54 %.

3.2.3 Theoretical calculations for dielectric permittivity

To evaluate dielectric permittivity of a two-phase piezoelectric composite, two theoretical equations have been proposed. Yamada et al. [26] used electrical potentials to derive the relative dielectric constant of a binary system based on a continuous medium. Dielectric permittivity ε_r for the composite system is given by

$$\varepsilon_r = \varepsilon_0 \left\{ 1 + \frac{c_1 n(\varepsilon_1 - \varepsilon_0)}{n\varepsilon_0 + (\varepsilon_1 - \varepsilon_0)(1 - c_1)} \right\} \tag{1}$$

where ε_0 and ε_1 are the dielectric permittivity for the matrix and piezoelectric inclusion, respectively; n is the parameter dependent on the shape of the ellipsoidal inclusion, and c_1 is the volume fraction of the inclusion. Theoretical values well agreed with experimental results when the parameter n was 8.5 for PZT/polymer composites and aspect ratio of inclusion $\alpha = 2.8$. Cheng et al. [17] also used Eq. (1) to calculate the dielectric permittivity for high-content PMN/sulphoaluminate cement composites and had a good agreement between theoretical and experimental results. Both comparisons depend on the volume fraction of the inclusions.

If piezoelectric inclusions are well dispersed in the matrix and the polarization of the inclusion is saturated, the theoretical equation of the cubes model [27] in a two-phase system for relative dielectric constant ε_r is the following:

$$\varepsilon_r = \varepsilon_0 \left\{ \frac{\varepsilon_1}{c_1^{-1/3}(\varepsilon_0 - \varepsilon_1) + c_1^{-2/3}\varepsilon_1} + (1 - c_1^{2/3}) \right\}. \tag{2}$$

Experimental and theoretical results for ε_r with different c_1 were compared by Li et al. [10], and the values of the cubes model are lower than the experimental values.

For 0–3 type PZT/cement composites, many small defects and pores are easy to observe between PZT and cement-based matrix though the PZT particles are uniformly dispersed. Here, specimens were polarized by applying 1.5 kV/mm in a temperature of 150 °C for 30 min. While the specimen was successfully polarized, the phase angle was also measured from the impedance–frequency spectrum with −69° approximately. That means the polarization of PZT inclusion was unsaturated. Thereby, in order to calculate the relative dielectric constant, we modify the equation of the cubes model in Eq. (2) by an unsaturated factor A as

$$\varepsilon_r = \mathrm{A} \cdot \varepsilon_0 \left\{ \frac{\varepsilon_1}{c_1^{-1/3}(\varepsilon_0 - \varepsilon_1) + c_1^{-2/3}\varepsilon_1} + (1 - c_1^{2/3}) \right\} \tag{3}$$

with

$$\mathrm{A} = \begin{cases} \frac{157.45+R}{194.71+4.25R} & \text{for SL composites} \\ \frac{3.10+R}{3.81+1.67R} & \text{for FA composites} \end{cases} \tag{4}$$

where R is R % cement replaced by slag or fly ash. Here, $c_1 = 0.5$ always because 50 vol. % PZT was used. As specimens with 7 curing days were polarized, $\varepsilon_1 = 1{,}705$, and ε_0 is shown in Table 6.

Experimental and numerical results for the relative dielectric constant are shown in Fig. 16, where the solid lines represent experimental data and dot lines refer to theoretical calculations. The ε_r results calculated from Yamada's equation, Eq. (1), are higher than that of experimental data. However, the prediction of ε_r calculated from Eqs. (3) and (4) had a good agreement with experimental results. The modified equation for ε_r in Eq. (3) depends on the replacement of pozzolanic materials.

Table 6 Relative dielectric constants of the matrix after polarization with 7 curing days

Replacement	10 %	20 %	30 %	40 %	50 %
Slag	115	129	155	196	230
Fly ash	121	135	118	105	96

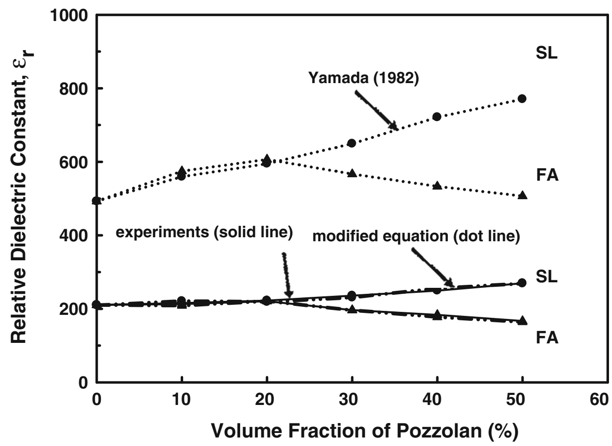

Fig. 16 Comparisons of experimental and theoretical results

4 Conclusions

Cement-based piezoelectric composites were drily pressed with 80 MPa and cured at 7, 28 and 56 days, respectively. Then, the polarization with 1.5 kV/mm voltage was applied to the composite to create piezoelectric properties. Before the polarization, the value of dielectric loss for PZT/cement composites with 50 vol. % PZT had better be less than 0.73 to ensure the completion of polarization. Piezoelectric properties chosen at early age are not suitable for assigning as representative values because of rapid change of the properties at early age. Piezoelectric properties at the age after the polarization of 60 days are recommended. Curing time is not an important factor to piezoelectric properties. A 20 % replacement of cement by slag and fly ash is the optimum quantity to enhance d_{33} and g_{33}. A modified formula is proposed to calculate ε_r for PZT/cement composites containing slag and fly ash.

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