

Available online at www.sciencedirect.com



Cement & Concrete Composites 27 (2005) 27-32



www.elsevier.com/locate/cemconcomp

Influence of polarization on properties of 0–3 cement-based PZT composites

Zongjin Li a,*, Biqin Dong a, Dong Zhang b

a Department of Civil Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China
 b State Key Lab of Concrete Materials Research, Tongji University Shanghai, 200092, PR China

Received 2 April 2003; accepted 5 January 2004

Abstract

In this paper, studies on a new 0–3 type cement-based PZT (lead zirconate titanate) composite are presented. Using a normal mixing and compacting method, up to 50 vol.% PZT ceramic powder can be easily incorporated into the composites. The behaviors of the cement-based PZT composites under different polarizing conditions have been investigated on the piezoelectric properties both theoretically and experimentally. It shows that cement-based PZT composites have their own unique characteristics. There is a good potential for the application of 0–3 type cement based piezoelectric composites in civil engineering.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Cement; Polarization; Piezoelectric properties; Composites

1. Introduction

With the modern development of civil engineering, the health monitoring of structures is being introduced [1–3]. Real-time structural health monitoring systems can provide instantaneous information on a condition of a specified structure. This will result in a significant increase of safety margin and reductions in maintenance cost [3]. Different types of sensors have been designed and used according to different applications. It is noted that the sensors suitable for application in other engineering fields, such as mechanical engineering, may not be applicable in civil engineering due to the differences in the properties between sensor and the host. For example, the acoustic impedance, temperature coefficient and shrinkage and creep characteristics of concrete, which is the most popular material in civil engineering, are quite different from those of the metal and alloy which are frequently used in mechanical engineering. The sensors used in mechanical engineering cannot be simply transplanted into the civil engineering applications. Thus a new kind of sensor should be developed to meet the requirements of civil engineering applications.

E-mail address: zongjin@ust.hk (Z. Li).

Among the techniques used in sensors and actuators, piezoelectricity has been proved to be one of the most efficient technology for most applications in smart structures [4-7]. Piezoelectric materials have attracted great attention in research activities towards the applications of sensors and actuators [8-14]. Piezoelectric materials can be classified into three categories: piezoelectric ceramics, piezoelectric polymers, and piezoelectric composites. The piezoelectric composites are especially noticeable in different fields. On the one hand, they are becoming increasingly important as the materials for the study of charge transport and energy storage in multi-component systems. On another hand, there has been a rapid development in applications of various devices. The most well known application of such composites include electromechanical transducer [15-20].

Lead zirconate titanate (PZT) has good pyroelectric and piezoelectric properties and is used in a variety of applications [21,22]. However, their incompatibility with the construction materials limits their use in the civil engineering. To develop a new kind of smart material suitable for building and infrastructures, cement-based piezoelectric composites incorporating lead zirconate titanate (PZT) in cement paste matrix have been fabricated and studied at HKUST [23]. Since this is the first stage of the study for such a composite, the polarizing

^{*}Corresponding author. Tel.: +852-2358-8751; fax: +852-2358-1534.

Table 1
Properties of PZT powder, hardened Portland cement paste, and normal concrete

	PZT ceramics	Cement paste	Concrete	
Piezoelectric strain factor d_{33} (10 ⁻¹² C/N)	513	\	\	
Piezoelectric voltage factor g_{33} (10^{-3} V m/N)	15.9	\	\	
Dielectric constant ε_r (at 1 kHz)	3643	56	\	
Electromechanical coupling coefficient K_P (%)	67	\	\	
Mechanical quality $Q_{\rm m}$	43	\	\	
Elastic compliance s_{33} (10 ⁻¹² m ² /N)	16.7	72	30	
Density ρ (10 ³ kg/m ³)	7.5	2.0	2.4	
Acoustic velocity V (10 ³ m/s)	2.83	2.64	3.73	
Acoustic impedance ρV (10 ⁶ kg/m ² s)	21.2	5.3	9.0	

behaviors and piezoelectric properties of the composites are focused.

The polarizing behavior and piezoelectric properties are the characteristics of piezoelectric materials [24]. In this study, the factors that affect the polarizing behaviors of cement-based piezoelectric composites are studied in details. The factors include polarizing voltage, duration and PZT content. Their effects on the piezoelectric properties are evaluated both theoretically and experimentally.

2. Experiment

In this study, lead zirconate titanate (PZT) ceramic Powder (Shanghai Keda Electronic Ceramics Co. Ltd.) and white Portland cement (H.S.L. Enterprises Co. Ltd.) were used to prepare the 0–3 type cement-based piezoelectric composites. The properties of The PZT ceramic are listed in Table 1. The particle size distribution of PZT ceramic and white Portland cement were measured by a laser particle size analyzer (LS 230, Coulter Corporation, USA). Fig. 1 shows that the mean diameter of PZT ceramic is 153.6 μ m with median of 83.52 μ m, mean the diameter of white Portland cement is 15.32 μ m and median of 12.55 μ m.

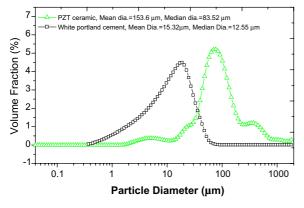


Fig. 1. Particle size distribution of PZT powder and white Portland cement.

PZT ceramic powder and white Portland cement are mixed together to make the 0-3 type piezoelectric composites. In order to improving the fluidity of the fresh mixture, a superplasticizer (W19, W. R. Grace) was used. Using a normal mixing (mixing duration is about 2 min) and vibrating (using small shaking table) method (vibrating duration is about 1 min), up to 50% volume content of PZT ceramic powder could be incorporated into the composites. The mixing proportions are listed in Table 2. To achieve a uniform mixture, cement and PZT particles were mixed thoroughly first, then water and superplasticizers were added into the mixture. The mixing process was continued until the mixture became uniform. Then the mixture was compacted into the glass (or plastic) model. After casting, the specimens were put in the curing room with a temperature of 65 °C and relative humidity of 98% for 24 h. After curing, the specimens could be polarized immediately. Before polarization, the specimens were cut into square slices of $8 \times 8 \times 1.5 \text{ mm}^3$ (or cube of $8 \times 8 \times 8 \text{ mm}^3$, seeing Fig. 2). Then the surfaces of the slices were polished and coated with silver paint (AGAR Scientific Ltd.). In order to ensure the reliability of experiment results, three specimens are tested for every kind of composites and take the average value of test results as its property index.

A key technique for fabrication of piezoelectric materials is polarizing procedure. Polarizing was carried out in a silicon oil bath with a temperature of 160 °C.

Table 2
The mixing proportions of cement-based PZT composites

	C18	C30	C50 ^a	
Ceramic (g)	100	100	100	
Cement (g)	76.76	41.33	17.71	
Water (g)	38.38	20.67	8.85	
ADVA ^b (g)	0.64	0.34	0.30	

C18, C30 and C50 are used to identify the specimens of cement-based piezoelectric composites. The numbers (18, 30 and 50) are the indication of volume fraction of PZT powder in whole system.

^a For C50 specimens, the ratio (w%) of ADVA/Water = 1%; other two kinds of specimens, the ratio (w%) of ADVA/Water = 0.5%.

 $^{^{}b}$ A type of Superplasticizer (water solution, the solid content is 30 w%).

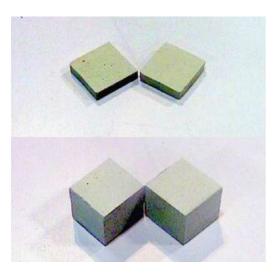


Fig. 2. The specimens of 0-3 type cement-based PZT composites.

After polarization the specimens were immersed in cold silicon oil to for fast cooling in order to maintain the status of polarization. Then the polarized specimens were wrapped with aluminum foil to eliminate remnant charge generated during polarizing process.

Piezoelectric strain factor d_{33} was measured with a piezo d_{33} meter (model ZJ-3B, fabricated by Institute of Acoustics of Academia Sinca). The impedance spectra were measured with a Hewlett Packard impedance/gain-phase analyzer (model 4194A) at 1 kHz. The entire tests were carried out at 22 °C temperature and 50% relative humidity.

3. Results and analysis

3.1. Polarizing behavior of the composites

The 0–3 type cement-based PZT composites were polarized in a silicon oil bath at the temperature of 160 °C. Different polarizing parameters were selected to study.

3.1.1. The aging influence on polarizing behavior

Fig. 3 shows the dependence of piezoelectric factor d_{33} on aging for ceramic/cement composites and ceramic/polymer composites. It can be seen that d_{33} value of cement-based PZT composites improved with the curing time before reaching saturation. On the other hand ceramic/polymer composite presented opposite trend. Its d_{33} value decreased with the aging procedure. And the final d_{33} value of ceramic/cement composites is much higher than that of ceramic/polymer composites [24]. This interesting phenomenon shows that the ceramic/cement composites may have a coupling effect between ceramic powder and cement particle.

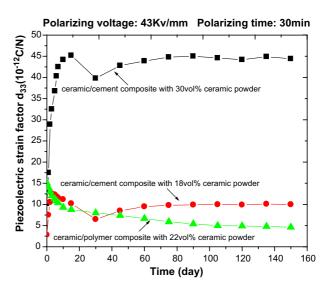


Fig. 3. Aging influence on piezoelectric factor d_{33} for cement-based piezoelectric composites and ceramic/polymer composites.

3.1.2. The influence of polarizing voltage on polarizing behavior

Fig. 4 shows the polarizing voltage dependence of piezoelectric strain factor d_{33} for 0–3 type cement-based composites (C50) with 50% volume content PZT ceramic powder. It can be seen that with the voltage increasing, d_{33} rises greatly. Low voltage cannot polarize the composites effectively. For example, when the voltage is about 3.3 kV/cm, d_{33} value is quite low. The peaks appeared in the figure are the results caused by remnant charge in the composites during the polarizing procedure. It is clear that the larger the polarizing voltage, the higher the peaks in the figure. After removing the remnant charge, d_{33} values are reduced. However, with

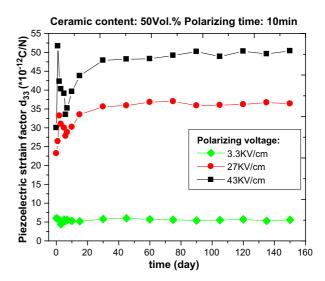


Fig. 4. The effect of polarizing voltage on d_{33} for 0–3 type cement-based PZT composites.

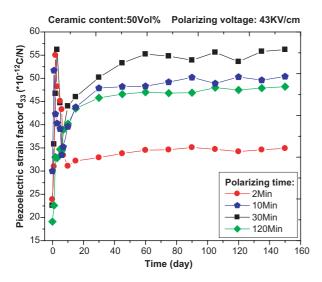


Fig. 5. The effect of polarizing duration on d_{33} for 0–3 type cement-based PZT composites.

aging, the d_{33} values go up again. For the whole process, the specimen polarized with higher voltage shows superior d_{33} values to that with lower voltage.

3.1.3. The influence of polarizing duration on polarizing behavior

Changing the polarizing duration also affects the piezoelectric properties of the composites obviously. Fig. 5 gives the results of time dependence of d_{33} for 0–3 type cement-based PZT composites. The curves demonstrate a similar trend with the results in the Fig. 3. It can be seen from the figure that for samples polarized 2, 10 and 30 min, the longer the polarizing duration, the higher the d_{33} values. However for samples polarized for

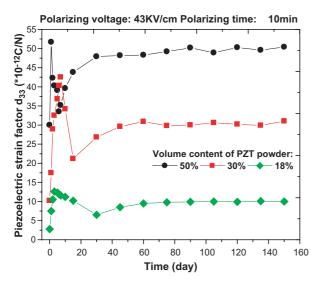


Fig. 6. The effect of PZT content on d_{33} for 0–3 type cement-based PZT composites.

120 min, their d_{33} values are lower than those polarized for 10 min. This phenomenon may be attributed to a partial breakdown of the saturated piezoelectric materials.

3.1.4. The influence of PZT content on polarizing behavior

Fig. 6 shows the polarizing behavior of 0-3 type cement-based piezoelectric composites with different content PZT ceramic powder. It can be found in the figure that the higher the content of PZT ceramic, the larger the d_{33} value. It can be easily understood that as a functional phase in the composites, higher PZT ceramic content is beneficial to the piezoelectric performance of 0-3 type cement-based PZT composites.

4. Piezoelectric properties of the composites

By utilizing the impedence analyzer, the capacitance of the cement-based piezoelectric composites can be determined. After obtaining the capacitance, relative dielectric constant can be calculated according to the plate condenser Eq. (1):

$$C = \frac{\varepsilon_{\rm r} \cdot \varepsilon \cdot S}{d} \tag{1}$$

where S is the area of the specimen and d is thickness of the specimen. ε is the vacuum dielectric constant $(\varepsilon = 8.855 \times 10^{-12} \text{ F/m})$. The relative constant values calculated by Eq. (1) are listed in the Table 3. Basically, ε_r increases with PZT contents increase. In the Fig. 7, the dielectric constants for samples polarized for 30 min are plotted against PZT content in the composites. In the figure, the theoretical predictions are also provided based different models. In the calculation, it is assumed that the polarization of PZT particle is saturated. It is clear that the experimental results are close to the theoretical value of the cubes models, which means that the PZT particles in the composites are well dispersed. This conclusion is confirmed by the result of SEM image for the composites. From the backscatter scanning electronic microscopy (SEM) image (Fig. 8), uniform distribution of PZT particles can be observed.

In Fig. 9, the test results of piezoelectric strain factor d_{33} of the composites polarized for 30 min are plotted against PZT content in company with the theoretical curves of different models. The experimental results

Table 3
Capacitance and relative dielectric constant value of the composites

Specimen codes	C18	C30	C50
Size of specimen	$8 \times 8 \times 1.5$ mm ³	$8 \times 8 \times 1.5$ mm ³	$8 \times 8 \times 1.5$ mm ³
Capacitance (pF)	38.4	63.8	112.5

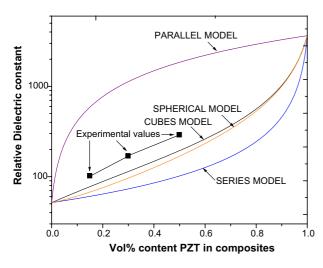


Fig. 7. Comparison between experimental and theoretical values for dielectric constants of composites with different vol.% content PZT particle. Theoretical values are based on parallel, series, cubes and spherical models.

confirm that the polarizing behaviors of the 0–3 type cement-based PZT composites can be well described by the cubes model. The theoretical equations of cubes model for the relative dielectric constant (ε_r) and piezoelectric strain factor (d_{33}) in two-phase systems are as following [12,24]:

Theoretical equation of cubes model for the dielectric constant:

$$\varepsilon_{33} = \frac{{}^{1}\varepsilon_{33} \cdot {}^{2}\varepsilon_{33}}{\left({}^{2}\varepsilon_{33} - {}^{1}\varepsilon_{33}\right) \cdot {}^{1}\nu^{-\frac{1}{3}} + {}^{1}\varepsilon_{33} \cdot {}^{1}\nu^{-\frac{2}{3}}} + {}^{2}\varepsilon_{33} \cdot \left(1 - {}^{1}\nu^{\frac{2}{3}}\right)$$
(2)

Theoretical equation of cubes model for the piezoelectric strain factor:

$$d_{33} = {}^{1}d_{33} \cdot \frac{{}^{1}v^{\frac{1}{3}} + \left(1 - {}^{1}v^{\frac{1}{3}}\right) \cdot \frac{{}^{1}\varepsilon_{33}}{2\varepsilon_{33}}} \cdot \frac{1}{1 - {}^{1}v^{\frac{1}{3}} + {}^{1}v}$$
(3)

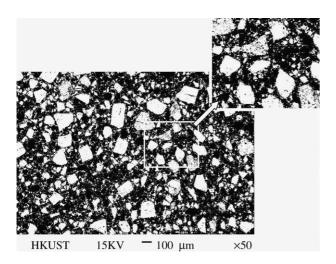


Fig. 8. Backscatter SEM image of 0–3 type cement-based PZT composites.

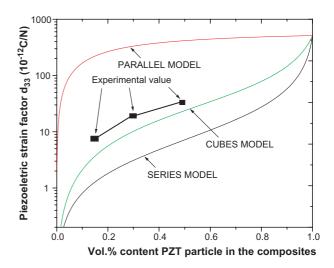


Fig. 9. Comparison between experimental and theoretical values for piezoelectric strain factor d_{33} of composites with different vol.% content PZT. Theoretical values are based on parallel, series and cubes model.

Table 4
Comparison the relative dielectric constant and piezoelectric strain factor with PZT/polymer and PZT/cement

Material	\mathcal{E}_{r}	d_{33}	
Ceramic PZT	3000	500	
PZT/PVDF	120	20	
PZT/rubber	55	35	
PZT/POM	95	17	
PZT/cement	300	55	

where

 ε_{33} : the relative dielectric constant of composites,

 $^{1}\varepsilon_{33}$: the relative dielectric constant of PZT ceramic,

 ${}^{2}\varepsilon_{33}$: the relative dielectric constant of cement paste,

¹v: the volume ratio of PZT particle in the composites,

 d_{33} : the piezoelectric strain factor of the composites, d_{33} : the piezoelectric strain factor of PZT ceramic.

From Eq. (3), it can be obtained easily that the larger d_{33} value of the PZT/cement composite compared to the PZT/polymer composite can be simply attributed to the larger dielectric permittivity of cement. Comparing the relative dielectric constant and piezoelectric strain factor of the PZT/polymer and PZT/cement composites (Table 4), the piezoelectric properties of PZT/cement composite seems to be much different with to those of PZT/polymer composites.

5. Conclusion

In this study, the polarizing behaviors and piezoelectric properties of the cement-based composites are studied. The following conclusions can be drawn from this study:

- (1) 0–3 type cement-based PZT composites can be fabricated using normal mixing and compacting method. It is an easier procedure as compared to those methods for producing PZT/polymer composites.
- (2) The polarizing behavior of cement-based piezoelectric composites performs different from the ceramic/polymer piezoelectric composites. With the aging, d_{33} value of cement-based piezoelectric composites increases while d_{33} values of cement/polymer composites show a decrease trend according to literature.
- (3) The polarizing conditions largely influence the piezoelectric behavior of cement-based piezoelectric composites. The piezoelectric properties are better when a higher voltage and longer duration are applied. Provided that they are under the threshold of breakdown.
- (4) Higher content of PZT ceramic is beneficial to the piezoelectric performance of 0–3 type cement-based PZT composites.
- (5) The relative dielectric constant ε_r and piezoelectric strain factor d_{33} obtained from experiment are close to the predictions of the cubes model, which manifests that the PZT particles in the composites are uniformly dispersed. This conclusion is confirmed by SEM image.
- (6) Comparing the relative dielectric constant and piezoelectric strain factor of the PZT/polymer and PZT/cement composites, the piezoelectric properties of PZT/cement composite seems to be much different with to those of PZT/polymer composites. Adding the excellent chemical and physical stability of cement and the simple polarizing conditions, cement-based PZT composites have great potential for application, especially in civil engineering.

Acknowledgements

The financial support from Hong Kong Research Grant Council under grant HKUST 6212/02E is greatly acknowledged.

References

- [1] Chang F-K, editor. Structural health monitoring 2000. Lancester, Pennsylvania: Technomic Publishing Co. Inc; 1999.
- [2] Tzou H-S, Guran A, editors. Structronics systems: smart structures, devices and systems (Parts I & II). Singapore: World Scientific; 1998.

- [3] Aizawa S, Kakizawa T, Higasino M. Case studies of smart materials for civil structures. Smart Mater Struct 1998;7(5):617– 26
- [4] Hilczer B, Mailecki J. Electrets and piezopolymers. Warsaw: PWN; 1992 [in polish].
- [5] Banks HT, Smith RC, Wang Y. Smart material structures: modeling, estimation, and control. New York: John Wiley & Sons, Inc.; 1996.
- [6] George EP, Gotthardt R, Otsuka K, Trolier-McKinstry S, Wun-Fogle M, editors. Materials for smart systems II Symposium Proceedings of Materials Research Society, Vol. 459. Pittsburgh, Pennsylvania: Materials Research Society; 1997.
- [7] Tao B. Smart/intelligent materials and structures. Beijing: Defense Industry Press; 1997 [in Chinese].
- [8] Wetherhold RC, Panthalingal N. Piezoelectric PZT/expoxy composites for sensing and actuating torsional motion. Smart Structures and Materials 1993, SPIE. p. 266–74.
- [9] Xu Y. Ferroelectric materials and their applications. Amsterdam: North-Holland; 1991.
- [10] Furukawa T. Piezoelectricity and pyroelectricity in polymers. IEEE Trans Electrical Insul 1989;24(3):375–94.
- [11] Okazaki K. Developments in fabrication of piezoelectric ceramics. In: Taylor GW, Gagnepain JJ, Meeker TR, Nakamura T, Shuvalov LA, editors. Piezoelectricity. Switzerland: Gordon and Breach Science Publishers; 1985. p. 131–50.
- [12] Banno H. Recent developments of piezoelectric composites in Japan. In: Saito S, editor. Advanced ceramics. Oxford University Press; 1988. p. 8–26.
- [13] Safari A, Sa-gong G, Giniewicz J, Newnham RE. Composites piezoelectric sensors. In: Rosen CZ, Hiremath BV, Newnham R, editors. Piezoelectricity. College Park, MD: American Institute of Physics; 1992. p. 195–204.
- [14] Latour M, Jolivet S, Rahmoune M, Lagarrigue O, Roure A. Piezopolymer transducers in the active control of vibrations. In: Proceedings of 8th International Symposium on Electrets, 1994. p. 985–90
- [15] Wang TT, Herbert JM, Glass AM, editors. The applications of Ferroelectric Polymers. Glasgow and London: Blacke; 1988.
- [16] Newnham RE. Composites electroceramics. Ferroelectrics 1986;68:1.
- [17] Newnham RE, Bowen LJ, Klicker KA, Cross LE. Composite piezoelectric transducer. Mater Eng 1980;2:93.
- [18] Howarth TR, Rottenmyer KM. Transduction applications. In: Nalwa HS, editor. Ferroelectric polymers.
- [19] Wang S, Han J, Du S. Development of research on fabrication and properties of piezoelectric ceramic/polymer composites. Funct Mater 1999;30(2):113–7 [in Chinese].
- [20] Dias CJ, Das-Gupta DK. Inorganic ceramic/polymer ferroelectric composites electrets. IEEE Trans Dielectrics Electrical Insul 1996;3(5):706–34.
- [21] Zheng Z, Qu Y, Ma W, Hou F. Electric properties and applications of ceramic-polymer composites. Acta Mater Compos Sinica 1998;15(4):14–9 [in Chinese].
- [22] Furukawa T, Ishida K, Fukada E. Piezoelectric properties in thee composites systems of polymer and PZT ceramics. J Appl Phys 1979;50(7):4904–12.
- [23] Li Z, Zhang D, Wu K. Cement-based 0–3 piezoelectric composites. J Am Ceram Soc 2002;85(2):305–13, Publisher: American Ceramic Soc, USA.
- [24] Mazur K. Polymer–ferroelectric ceramic composites. In: Nalwa HS, Dekker M, editors. Ferroelectric polymers: chemistry, physics, and applications. New York: Inc.; 1995. p. 539– 610.