Pergamon

Cement and Concrete Research 32 (2002) 335–339

CEMENT AND CONCRETE RESEARCH

Piezoelectric cement-based materials with large coupling and voltage coefficients

Sihai Wen, D.D.L. Chung*

Composite Materials Research Laboratory, Department of Mechanical and Aerospace Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260-4400, USA

Received 18 April 2001; accepted 31 August 2001

Abstract

Cement paste containing short steel fibers (8 μm diameter, 0.18 vol.%) and polyvinyl alcohol (0.16 vol.%) exhibits longitudinal piezoelectric coupling coefficient $d = 2.5 \times 10^{-11}$ m/V and piezoelectric voltage coefficient $g = 1.1 \times 10^{-3}$ m^2/C (10 kHz), compared to values of $d = 3.0 \times 10^{-13}$ m/V and $g = 1.1 \times 10^{-3}$ m^2/C for cement paste without admixture, and values of $d = 1.4 \times 10^{-11}$ m/V and $g = 1.5 \times 10^{-3}$ m^2/C for lead zirconotitanate (PZT).

Keywords: Electrical properties; Strain effect; Cement paste; Fiber reinforcement; Piezoelectric

1. Introduction

Piezoelectricity, known as direct piezoelectricity, refers to the change of the electric polarization with stress; this change results in a change in voltage across the material in the direction of the polarization. Conventional piezoelectric materials are the perovskite ceramics (e.g., titanates, zirconates and zirconotitanates). However, this work uses cement pastes as piezoelectric materials. Cement pastes are attractive due to their low materials and processing costs, in addition to their mechanical ruggedness and processability compared to the conventional materials mentioned above. Furthermore, cement paste relates to concrete, which is widely used for structures. The use of a structural material for piezoelectricity eliminates or reduces the need for embedded or attached devices, which are expensive and limited in durability, in addition to causing mechanical property degradation of the structure in the case of embedded devices.

Piezoelectricity is valuable for strain sensing, which is relevant to structural vibration control, traffic monitoring and weighing in motion. In addition to its usefulness in sensing, piezoelectricity is useful for energy conversion. Piezoelectricity allows the conversion of mechanical energy to electrical energy. The energy conversion can be used for the generation of electrical power. Even if the efficiency of the energy conversion is not high, the large volume of concrete in a concrete structure may make the effect significant enough for technological use.

Piezoresistivity (to be distinguished from piezoelectricity) refers to the change of the electrical resistivity with strain. It is useful for strain sensing and has been observed in cement-based materials [1–12]. However, piezoresistivity is not the subject of this paper.

Piezoelectricity relates to the dielectric behavior. The static dielectric constant (ε) is a material property that relates to the electric dipole moment per unit volume. It is the product of the permittivity of free space (ε_o) and the relative dielectric constant (κ). The dipole moment per unit volume, also called the polarization, is proportional to $\kappa - 1$, which is called the electric susceptibility.

Due to the presence of ionic bonding and moisture in cement, electric dipoles are present and the dielectric constant has been measured for the purpose of fundamental understanding of cement-based materials. Such fundamental studies have addressed the effects of moisture [13–18], chlorides [19], curing age [20–29], aggregate type [19], air entrainment [30] and admixtures such as silica fume [31,32], latex [32] and short fibers [32]. In particular, it has been reported that κ at 10 kHz to 1 MHz is decreased by

* Corresponding author. Tel.: +1-716-645-3875x2243; fax: +1-716-645-3875.

E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

0008-8846/02/$ – see front matter
PII: S0008-8846(01)00682-2

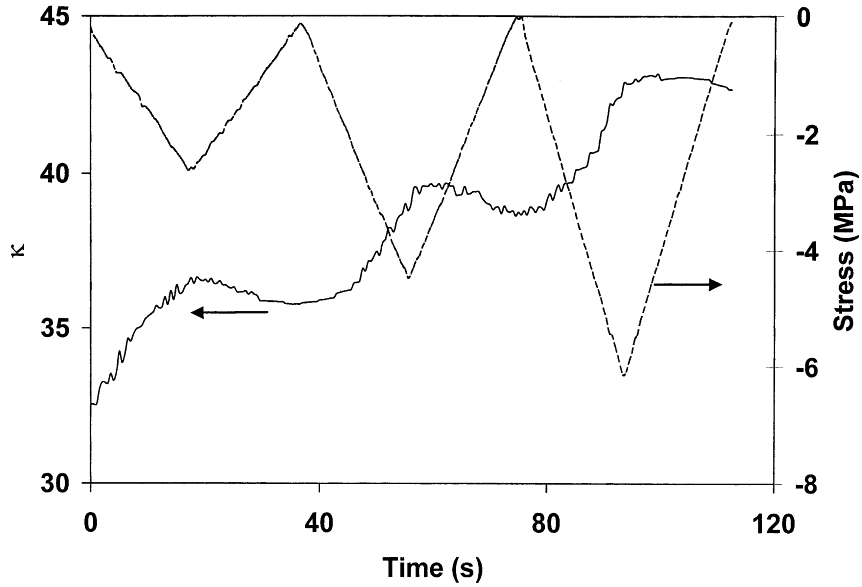

Fig. 1. Variation of the relative dielectric constant κ (solid curve, 10 kHz) with time, and of the stress (dashed curve) with time during repeated uniaxial compression of cement paste (i) at increasing stress amplitudes.

silica fume addition, increased by latex addition, decreased by stainless steel fiber (60 μm diameter) addition, and increased by carbon fiber (15 μm diameter) addition [32].

The direct piezoelectric effect was observed in cement pastes by voltage measurement [33] and by observing the effect of stress on the electric polarization [32]. It is attributed mainly to the movement of ions in response to stress.

2. Experimental methods

No aggregate (fine or coarse) was used. The cement used was portland cement (Type I) from Lafarge (Southfield, MI).

The steel fibers (Beka-Shield) were made of No. 304 austenitic stainless steel, as obtained from Bekaert Fiber Technologies (Marietta, GA). The fiber diameter was 8 μm. The fiber length was 6 mm. The fibers included 10 wt.% (47 vol.%) of a polyvinyl alcohol (PVA) binder, which was hydrophilic and dissolved in water during cement mixing, thus allowing fiber dispersion.

Two types of cement pastes were prepared, namely (i) plain cement paste, which consists of just cement and water, and (ii) steel-fiber cement paste, which consists of cement, water, steel fibers in the amount of 0.9% by mass of cement, corresponding to 0.18 vol.%, and PVA in the amount of 0.10% by mass of cement, corresponding to 0.16 vol.%.

A rotary mixer with a flat beater was used for mixing. Cement, water (water/cement ratio = 0.35) and fiber were mixed for 5 min. After pouring into oiled molds, an external electrical vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 1 day and cured in air at room temperature (relative humidity = 100%) for 28 days.

Specimens were in the form of cylindrical discs of diameter 12.3 mm and thickness 2.0 mm. Due to the small thickness, the fibers in each specimen were bound to have a degree of preferred orientation. A specimen, after mechanical polishing on both sides by using alumina particles of size 0.25 μm, was sandwiched by two copper discs (similarly polished) of diameter 12.3 mm at a pressure of 1.68 kPa, unless noted otherwise. The copper discs served as electrical contacts. Silver paint was applied between the specimen and each copper disk.

The impedance was measured along the thickness of the specimen using the two-probe method and an RLC meter (QuadTech 7600) at frequencies ranging from 10 kHz to 1 MHz. The magnitude of voltage applied across the thickness (2 mm) of a specimen was 1.000 V. Hence, the magnitude of the applied electric field was 500 V/m. The resistance and reactance were obtained from the impedance by assuming that they were in series connection. The capacitance was obtained from the reactance. The dielectric constant was obtained from the capacitance. Six specimens of each type were tested.

To show that the dielectric constant measurement using the method described above was accurate, measurement was made on a Kapton (a polymer) film. The known dielectric constant of Kapton is 3.9 at 1 kHz. Measurement in this work at 1 kHz gave a value of 3.9 also.

For testing the piezoelectric behavior, during the impedance measurement, compressive stress was applied to the sandwich, so that the stress was parallel to the direction of impedance measurement. The stress (repeated loading at increasing stress amplitudes within the elastic regime) was provided by a hydraulic mechanical testing system (MTS Model 810). The minimum compressive stress was 1.68 kPa. Six specimens of each type were tested.

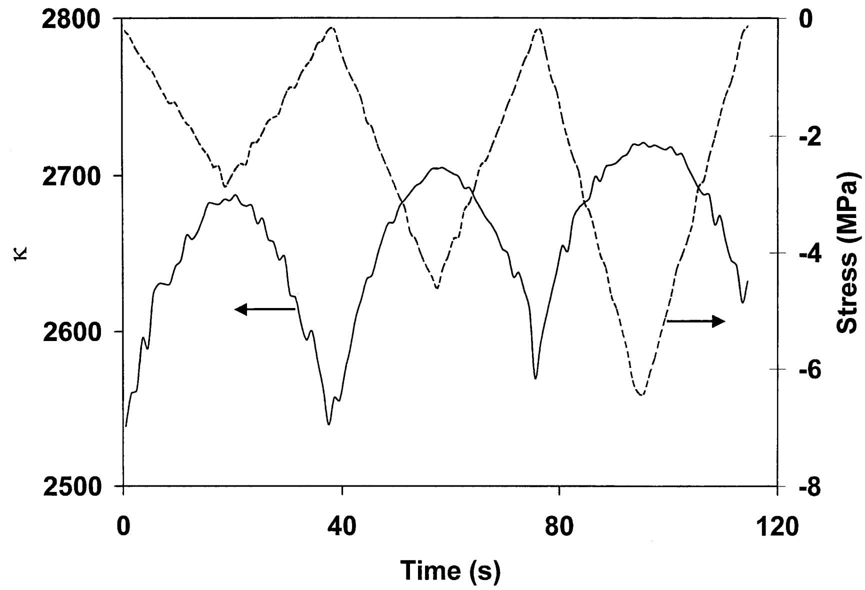

Fig. 2. Variation of the relative dielectric constant κ (solid curve, 10 kHz) with time, and of the stress (dashed curve) with time during repeated uniaxial compression of cement paste (ii) at increasing stress amplitudes.

The longitudinal piezoelectric coupling coefficient d was obtained from Eq. (1):

$$d = \varepsilon_o \mathrm{E} \left| \frac{\partial \kappa}{\partial \sigma} \right| \quad (1)$$

where κ is the relative dielectric constant, σ is the stress, E is the electric field amplitude (500 V/m) and ε_o is the permittivity of free space. Thus, d is proportional to the change in κ per unit change in stress.

The piezoelectric voltage coefficient g was obtained from the equation

$$g = \frac{d}{(\kappa - 1)\varepsilon_o} \quad (2)$$

The voltage change ∂V resulting from a stress change $\partial\sigma$ was calculated by using the equation

$$\partial V = lg\partial\sigma, \quad (3)$$

where l is the length of the specimen in the direction of polarization. The value of ∂V can be enhanced by increasing g, which can be increased by increasing d or decreasing κ, as shown by Eqs. (2) and (3).

3. Results and discussion

Figs. 1 and 2 show the relative dielectric constant (κ) and the applied stress (negative for compression) during repeated compressed loading of cement pastes (i) and (ii), respectively. For both pastes, κ increases (i.e., the reactance decreases) upon loading and the piezoelectric effect is quite reversible. The greater the stress amplitude, the more κ increases. The longitudinal piezoelectric coupling coefficient d, as averaged over the first half of the first stress cycle for each specimen, is shown in Table 1 for each of the two cement pastes.

For both pastes, the piezoelectric coupling coefficient d varies with stress. In general, the magnitude of d tends to decrease nonlinearly with increasing stress magnitude, such that the decrease occurs mainly at stress magnitudes below 1 MPa. The decrease in the magnitude of d with increasing stress magnitude is essentially reversible.

Table 1
Measured longitudinal piezoelectric coupling coefficient d, measured relative dielectric constant κ, calculated piezoelectric voltage coefficient g and calculated voltage change resulting from a stress change of 1 kPa for a specimen thickness of 1 cm in the direction of polarization

Material	d (m/V)[a]	κ[b]	g (10^{-3} m^2/C)[b]	Voltage change (mV)[b]
Cement paste (plain)[c]	3.0×10^{-13}	33	1.1	11
Cement paste with steel fibers and PVA[d]	2.5×10^{-11}	2500	1.1	11
PZT	1.4×10^{-11}	1000	1.5	15

[a] Averaged over the first half of the first stress cycle.
[b] At 10 kHz.
[c] Cement paste (i).
[d] Cement paste (ii).

A strong piezoelectric effect was attained by using steel fibers (8 μm diameter). It corresponds to $d = 2.5 \times 10^{-11}$ m/V and $g = 1.1 \times 10^{-3}$ m^2/C. These values are comparable to those of the conventional ceramic piezoelectric material lead zirconotitanate, i.e., $PbZrO_3-PbTiO_3$ solid solution, or, in short, PZT, as similarly measured in this work and shown in Table 1. The piezoelectric characteristics of cement paste (ii) and PZT are similar in spite of the differences in mechanism and in material texture. In the cement case, the mechanism relates to the movement of the mobile ions under stress. In the case of conventional ceramic piezoelectric materials, the mechanism relates to the small change in spacing between ions of opposite charge under stress.

Table 1 shows the comparative piezoelectric performance of various cement pastes and PZT. Cement paste (ii) of this work gives the highest values of d and κ, while PZT gives the highest g. The overall performance in terms of both d and g is comparable between cement paste (ii) and PZT.

The coefficient d is much smaller for cement paste (i) than cement paste (ii), though g is the same for both due to the difference in κ. The difference in d is probably due to the contribution by the interphase between steel fiber and the cement paste [34].

The change in voltage obtained in the direct piezoelectric effect stems from the change in electric field. For the same electric field change, the voltage change is larger when the specimen length in the field direction is larger, as shown by Eq. (3). Due to the low cost and structural usage of cement, practical dimensions tend to be larger for cement than PZT. As a consequence, the voltage change obtained by using cement can be large compared to typical voltage changes obtained by using PZT.

4. Conclusion

Cement paste containing short steel fibers (8 μm diameter, 0.18 vol.%) and PVA (0.16 vol.%) exhibits longitudinal piezoelectric coupling coefficient $d = 2.5 \times 10^{-11}$ m/V and piezoelectric voltage coefficient $g = 1.1 \times 10^{-3}$ m^2/C at 10 kHz, compared to $d = 1.4 \times 10^{-11}$ m/V and $g = 1.5 \times 10^{-3}$ m^2/C for PZT. The voltage change resulting from the cement paste is 73% of that resulting from PZT. In contrast, cement paste without any admixture exhibits $d = 3.0 \times 10^{-13}$ m/V and $g = 1.1 \times 10^{-3}$ m^2/C.

References

[1] D.D.L. Chung, Self-monitoring structural materials, Mater. Sci. Eng. Rev. R22 (2) (1998) 57–78.
[2] X. Wang, X. Fu, D.D.L. Chung, Strain sensing using carbon fiber, J. Mater. Res. 14 (3) (1999) 790–802.
[3] S. Wen, S. Wang, D.D.L. Chung, Piezoresistivity in continuous carbon fiber polymer–matrix and cement–matrix composites, J. Mater. Sci. 35 (14) (2000) 3669–3675.
[4] X. Fu, W. Lu, D.D.L. Chung, Ozone treatment of carbon fiber for reinforcing cement, Carbon 36 (9) (1998) 1337–1345.
[5] X. Fu, D.D.L. Chung, Effect of curing age on the self-monitoring behavior of carbon fiber reinforced mortar, Cem. Concr. Res. 27 (9) (1997) 1313–1318.
[6] X. Fu, E. Ma, D.D.L. Chung, W.A. Anderson, Self-monitoring in carbon fiber reinforced mortar by reactance measurement, Cem. Concr. Res. 27 (6) (1997) 845–852.
[7] P.-W. Chen, D.D.L. Chung, Carbon fiber reinforced concrete as an intrinsically smart concrete for damage assessment during static and dynamic loading, ACI Mater. J. 93 (4) (1996) 341–350.
[8] P.-W. Chen, D.D.L. Chung, Concrete as a new strain/stress sensor, Composites, Part B 27B (1996) 11–23.
[9] P.-W. Chen, D.D.L. Chung, Carbon fiber reinforced concrete as a smart material capable of non-destructive flaw detection, Smart Mater. Struct. 2 (1993) 22–30.
[10] Q. Mao, B. Zhao, D. Sheng, Z. Li, Resistance changement of compression sensible cement specimens under different stresses, J. Wuhan Univ. Technol., Mater Sci. Ed. 11 (3) (1996) 41–45.
[11] M. Sun, Q. Mao, Z. Li, Size effect and loading rate dependence of the pressure-sensitivity of carbon fiber reinforced concrete (CFRC), J. Wuhan Univ. Technol., Mater. Sci. Ed. 13 (3) (1998) 58–61.
[12] Z.-Q. Shi, D.D.L. Chung, Carbon fiber reinforced concrete for traffic monitoring and weighing in motion, Cem. Concr. Res. 29 (3) (1999) 435–439.
[13] A. Hu, Y. Fang, J.F. Young, Y.-J. Oh, Humidity dependence of apparent dielectric constant for DSP cement materials at high frequencies, J. Am. Ceram. Soc. 82 (7) (1999) 1741–1747.
[14] P. Gu, J.J. Beaudoin, Dielectric behaviour of hardened cement paste systems, J. Mater. Sci. 15 (2) (1996) 182–184.
[15] R. Zoughi, S.D. Gray, P.S. Nowak, Microwave nondestructive estimation of cement paste compressive strength, ACI Mater. J. 92 (1) (1995) 64–70.
[16] V. Janoo, C. Korhonen, M. Hovan, Measurement of water content in portland cement concrete, J. Transp. Eng. 125 (3) (1999) 245–249.
[17] M. Keddam, H. Takenouti, X.R. Novoa, C. Andrade, C. Alonso, Impedance measurement on cement paste, Cem. Concr. Res. 27 (8) (1997) 1191–1201.
[18] C. Alonso, C. Andrade, M. Keddam, X.R. Novoa, H. Takenouti, Study of the dielectric characteristics of cement paste, Mater. Sci. Forum 289–292 (pt 1) (1998) 15–28.
[19] I.L. Al-Qadi, R.J. Haddad, S.M. Riad, Detection of chlorides in concrete using low radio frequencies, J. Mater. Civ. Eng. 9 (1) (1997) 29–34.
[20] A. van Beek, M.A. Hilhorst, Dielectric measurements to characterize the microstructural changes of young concrete, Heron 44 (1) (1999) 3–17.
[21] Y. El Hafiane, A. Smith, P. Abelard, J.P. Bonnet, P. Blanchart, Dielectric characterization at high frequency (1 MHz–1.8 GHz) of a portland cement at the early stages of hydration, Ceram.-Silik. 43 (2) (1999) 48–51.
[22] S.J. Ford, J.-H. Hwang, J.D. Shane, R.A. Olson, G.M. Moss, H.M. Jennings, T.O. Mason, Dielectric amplification in cement pastes, Adv. Cem. Based Mater. 5 (2) (1997) 41–48.
[23] N. Miura, N. Shinyashiki, S. Yagihara, M. Shiotsubo, Microwave dielectric study of water structure in the hydration process of cement paste, J. Am. Ceram. Soc. 81 (1) (1998) 213–216.
[24] X.Z. Ding, X. Zhang, C.K. Ong, B.T.G. Tan, J. Yang, Study of dielectric and electrical properties of mortar in early hydration period at microwave frequencies, J. Mater. Sci. 31 (20) (1996) 5339–5345.
[25] X. Zhang, X.Z. Ding, C.K. Ong, B.T.G. Tan, J. Yang, Dielectric and electrical properties of ordinary portland cement and slag cement in the early hydration period, J. Mater. Sci. 31 (5) (1996) 1345–1352.
[26] S.S. Yoon, H.C. Kim, R.M. Hill, Dielectric response of hydrating porous cement paste, J. Phys. D: Appl. Phys. 29 (3) (1996) 869–875.
[27] I.L. Al-Qadi, O.A. Hazim, W. Su, S.M. Riad, Dielectric properties of

portland cement concrete at low radio frequencies, J. Mater. Civ. Eng. 7 (3) (1995) 192–198.
[28] X. Zhang, X.Z. Ding, T.H. Lim, C.K. Ong, B.T.G. Tan, J. Yang, Microwave study of hydration of slag cement blends in early period, Cem. Concr. Res. 25 (5) (1995) 1086–1094.
[29] R.A. Olson, G.M. Moss, B.J. Christensen, J.D. Shane, R.T. Coverdale, E.J. Garboczi, H.M. Jennings, T.O. Mason, Microstructure–electrical property relationships in cement-based materials, Proceedings 1994 MRS Fall Meeting, Microstructure of Cement-Based Systems/Bonding and Interfaces in Cementitious Materials, vol. 370, Materials Research Society, Warrendale, PA, 1995, pp. 255–264.
[30] R.H. Haddad, I.L. Al-Qadi, Measuring dielectric properties of concrete over low RF, Proceedings 1996 4th Materials Engineering Conference, vol. 2, Materials for the New Millennium, ASCE, New York, NY, 1996, pp. 1139–1149.
[31] P. Gu, J.J. Beaudoin, Dielectric behaviour of hardened cementitious materials, Adv. Cem. Res. 9 (33) (1997) 1–8.
[32] S. Wen, D.D.L. Chung, Effect of stress on the electric polarization in cement, Cem. Concr. Res. 31 (2) (2001) 291–295.
[33] M. Sun, Q. Liu, Z. Li, Y. Hu, A study of piezoelectric properties of carbon fiber reinforced concrete and plain cement paste during dynamic loading, Cem. Concr. Res. 30 (10) (2000) 1593–1595.
[34] D.D.L. Chung, Fibrous composite interfaces studied by electrical resistance measurement, Adv. Eng. Mater. 2 (12) (2000) 788–796.