

# PIEZOELECTRIC CEMENT CONTAINING SHORT CARBON FIBERS

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## 1. Introduction

The direct piezoelectric effect is useful for strain sensing, which is needed for structural vibration control, traffic monitoring and smart structures in general. The effect is also useful for conversion from mechanical energy to electrical energy, as in converting the stress exerted by a vehicle running on a highway to electricity. This effect is well-known for ceramic materials that exhibit the distorted Perovskite structure. These ceramic materials are expensive and are not rugged mechanically, so they are not usually used as structural materials. Devices made from these ceramic materials are commonly embedded in a structure or attached to a structure. Such structures tend to suffer from high cost and poor durability. The use of the structural material itself (e.g., concrete) to provide the piezoelectric effect is desirable, as the concrete is low-cost and durable.

The direct piezoelectric effect has been reported in cement paste with and without short carbon fibers, such that the effect is stronger in the absence of fibers [1]. The fiber content (0.5% by weight of cement) [1] was below the percolation threshold [2]. In this paper, we confirm this result, but furthermore show that the piezoelectric effect is greatly enhanced by the use of short carbon fibers beyond the percolation threshold. Thus, we have attained a piezoelectric effect that is much stronger than that of plain cement paste (without fiber).

The impedance is a complex quantity, the real part of which is the resistance and the imaginary part of which is the reactance. The reactance relates to the capacitance, which in turn relates to the relative dielectric constant  $\kappa$ . Resistance pertains to the conduction behavior, whereas reactance pertains to the dielectric behavior. The change of the resistivity with strain pertains to piezoresistivity [3], whereas the change of the dielectric constant with strain pertains to direct piezoelectricity, which is associated with polarization [4]. This paper is focused on the effect of repeated compressive loading

on the relative dielectric constant ( $\kappa$ ) of cement pastes with and without fibers.

## 2. Experimental methods

### 2.1 Materials

No aggregate (fine or coarse) was used. The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI). The fibers used were in the amount of either 0.5% or 1.0% by mass of cement.

Either silica fume or latex was used as an admixture when carbon fibers were used. Silica fume (Elkem Materials, Inc., Pittsburgh, PA, EMS 965) was used in the amount of 15% by mass of cement. The methylcellulose, used along with silica fume in the amount of 0.4% by mass of cement, was Dow Chemical Corp., Midland, MI, Methocel A15-LV. The defoamer (Colloids, Inc., Marietta, GA, 1010) used along with methylcellulose was in the amount of 0.13 vol.%.

The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer (Dow Chemical Co., Midland, MI, 460NA) with the polymer making up about 48% for the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The latex was used along with an antifoaming agent (Dow Corning Corp., Midland, MI, No. 2410, 0.5% by mass of latex).

The carbon fibers were isotropic pitch based, unsized, and of length  $\sim 5$  mm, diameter 15  $\mu\text{m}$  and density 1.6  $\text{g}/\text{cm}^3$ , as obtained from Ashland Petroleum Co. (Ashland, Kentucky). The fiber resistivity was  $3.0 \times 10^{-3} \Omega\cdot\text{cm}$ . Ozone treatment of the fibers was performed to improve the fiber-matrix bond. The steel fibers were made of stainless steel No. 434, as obtained from International Steel Wool Corp. (Springfield, OH). The fiber of diameter 60  $\mu\text{m}$  were cut into pieces of length 5 mm prior to use in the amount of 0.5% by mass of cement. The fiber resistivity was  $6 \times 10^{-5} \Omega\cdot\text{cm}$ .

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the methylcellulose mixture (if applicable), the latex mixture (if applicable), cement, water, silica fume (if applicable) and fibers were mixed in the mixer 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.

Seven types of cement paste were prepared, namely (i) plain cement paste (consisting of just cement and water), (ii) silica-fume cement paste (consisting of cement, water and silica fume), (iii) latex cement paste (consisting of cement, water, latex and antifoam), (iv) carbon-fiber (0.5 vol. %) silica-fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer and carbon fibers in the amount of 0.5% by mass of cement, corresponding to 0.5 vol. %), (v) carbon-fiber latex cement paste (consisting of cement, water, latex, antifoam and carbon fibers in the amount of 0.5% by mass of cement, corresponding to 0.4 vol. %), (vi) carbon-fiber (1.0 vol. %) silica fume cement paste (consisting of cement, water, silica fume, methylcellulose, defoamer and carbon fibers in the amount of 1.0% by mass of cement, corresponding to 1.0 vol. %), and (vii) steel-fiber cement paste (consisting of cement, water and steel fibers in the amount of 0.5% by mass of cement, corresponding to 0.1 vol. %). The water/cement ratio was 0.35 for pastes (i), (ii), (iv), (vi) and (vii), and was 0.23 for pastes (iii) and (v).

Table 1 shows the relative dielectric constant of seven types of cement paste, each at three frequencies [5]. The electrical properties of pastes (i), (iv), (v), (vi) and (vii) are shown in Table 2.

Table 1 Relative dielectric constant of cement pastes [5]

Paste No.	Fiber type	Fiber content		Admixture
		% by mass of cement	vol. %	
(i)	/	0	0	/
(ii)	/	0	0	SF
(iii)	/	0	0	L
(iv)	Carbon	0.5	0.48	SF
(v)	Carbon	0.5	0.41	L
(vi)	Carbon	1.0	0.95	SF
(vii)	Steel	0.5	0.10	/

Paste No.	Relative dielectric constant		
	10 kHz	100 kHz	1 MHz
(i)	28.6 ± 3.4	24.8 ± 3.6	23.7 ± 2.8
(ii)	20.8 ± 3.4	19.6 ± 3.2	16.5 ± 0.8
(iii)	34.9 ± 4.5	31.5 ± 2.9	24.3 ± 2.9
(iv)	53.7 ± 7.0	38.3 ± 4.8	28.1 ± 2.9
(v)	63.2 ± 5.2	40.4 ± 5.9	33.2 ± 6.8
(vi)	48.7 ± 4.8	29.6 ± 5.0	25.0 ± 5.0
(vii)	19.6 ± 4.8	19.0 ± 1.0	13.7 ± 2.4

SF: silica fume  
L: latex

Table 2 DC resistivity and absolute thermoelectric power of carbon fiber cement pastes [5]

Paste No.	Fiber type	Fiber content		Admixture
		% by mass of cement	vol. %	
(i)	/	0	0	/
(iv)	Carbon	0.5	0.48	SF
(v)	Carbon	0.5	0.41	L
(vi)	Carbon	1.0	0.95	SF
(vii)	Steel	0.5	0.10	/

Paste No.	Resistivity ( $\Omega \cdot \text{cm}$ ) <sup>†</sup>	Absolute thermoelectric power* ( $\mu\text{V}/^\circ\text{C}$ )
(i)	$(4.7 \pm 0.4) \times 10^5$	$1.96 \pm 0.05$
(iv)	$(1.5 \pm 0.1) \times 10^4$	$0.89 \pm 0.09$
(v)	$(9.7 \pm 0.6) \times 10^4$	$1.14 \pm 0.05$
(vi)	$(8.3 \pm 0.5) \times 10^2$	$-0.48 \pm 0.11$
(vii)	$(7.8 \pm 0.5) \times 10^4$	$53.3 \pm 4.8$

\*  $1.98 \pm 0.03 \mu\text{V}/^\circ\text{C}$  for silica-fume cement paste without fiber, and  $2.04 \pm 0.02 \mu\text{V}/^\circ\text{C}$  for latex cement paste without fiber [8].

† Measured within 1 s from the start of resistivity measurement in order to avoid polarization effect [4].

SF: silica fume  
L: latex

## 2.2 Testing

Specimens were in the form of cylindrical discs of diameter (12.3 mm) and thickness 2.0 mm. A specimen, after mechanical polishing on both sides by using alumina particles of size 0.25  $\mu\text{m}$ , was sandwiched by two copper discs (similarly polished) of diameter 12.7 mm at a pressure of 1.68 kPa. The copper discs served as electrical contacts.

The impedance was measured along the thickness of the specimen using the two-probe method and an RLC meter (QuadTech 7600) at a fixed frequency (10 kHz). 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 quality of the electrical contacts was good, the relative dielectric constant was also measured when silver paint had been applied between each copper disc and the specimen for the case of cement paste (i). The relative dielectric constant was only slightly higher when silver paint was present [5]. Hence, the small amount of air gap at the interface between copper and specimen in the absence of silver paint contributed little to the measured dielectric constant.

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.

The longitudinal piezoelectric coupling coefficient  $d$  was obtained from the equation

$$d = \epsilon_0 E \left| \frac{\partial \kappa}{\partial \sigma} \right| \quad (1)$$

where  $\kappa$  is the relative dielectric constant,  $\sigma$  is the stress,  $E$  is the electric field amplitude (500 V/m) and  $\epsilon_0$  is the permittivity of free space. Thus,  $d$  is

proportional to the change in  $\kappa$  per unit change in stress.

## 3. Results and discussion

Figure 1 shows the relative dielectric constant ( $\kappa$ ) and the applied stress (negative for compression) during repeated compressive loading of cement paste (vi). For all the pastes,  $\kappa$  increases (i.e., the reactance decreases) upon loading and the piezoelectric effect is quite reversible. The greater the stress amplitude, the more  $\kappa$  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 3 for each of the cement pastes studied.

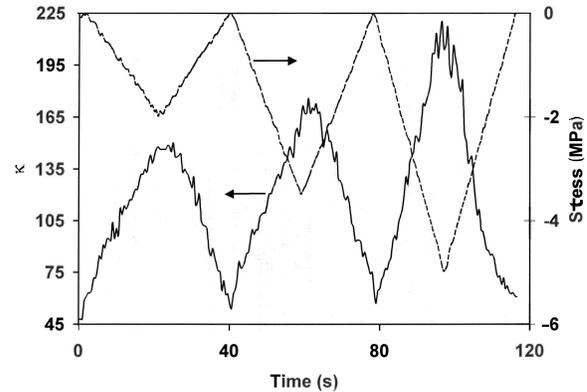


Fig. 1 Variation of the relative dielectric constant  $\kappa$  (solid curve) with time, and of the stress (dashed curve) with time during repeated uniaxial compression of cement paste (vi) at increasing stress amplitudes.

Table 3 Longitudinal piezoelectric coupling coefficient  $d$  in the first half of the first stress cycle.

Paste No.	Fiber type	Fiber content % by mass of cement	vol. %	Admixture	Piezoelectric coupling coefficient ( $10^{-15}$ m/V)
(i)	/	0	0	/	$0.659 \pm 0.031$
(ii)	/	0	0	SF	$0.168 \pm 0.015$
(iii)	/	0	0	L	$0.517 \pm 0.042$
(iv)	Carbon	0.5	0.48	SF	$0.477 \pm 0.034$
(v)	Carbon	0.5	0.41	L	$0.116 \pm 0.009$
(vi)	Carbon	1.0	0.95	SF	$3.618 \pm 0.396$
(vii)	Steel	0.5	0.10	/	$0.189 \pm 0.062$

For any of the seven 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.

Fig. 2 shows the variation of  $d$  upon stress variation for paste (vi), which is the paste which exhibits the strongest piezoelectric effect. For this paste, the decrease in the magnitude of  $d$  with increasing stress magnitude is quite reversible, especially in the first stress cycle; the partial irreversibility is more significant as the stress amplitude increases.

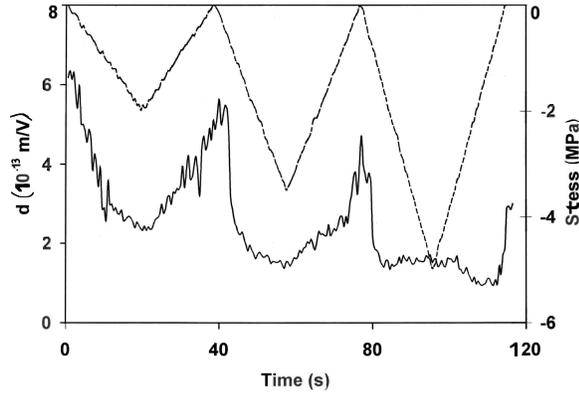


Fig. 2 Variation of the longitudinal piezoelectric coupling coefficient  $d$  (solid curve) with time, and of the stress (dashed curve) with time during repeated uniaxial compression of cement paste (vi) at increasing stress amplitudes.

The piezoelectric effect for paste (i) (with no admixture at all) is attributed to the movement of mobile ions in response to the loading, as the ions are mainly responsible to the  $\kappa$  value of  $29 \pm 3$  (Table 1) prior to stress cycling (1.68 kPa prior to stress cycling) [5].

The piezoelectric effect for paste (ii) (with silica fume) is also attributed to the ions in the cement. Both the  $\kappa$  value prior to stress cycling ( $21 \pm 3$ , Table 1) and the magnitude of the piezoelectric coupling coefficient  $d$  (Table 3) are lower for paste (ii) than paste (i), due to the volume occupied by the silica fume in place of cement and the relatively small contribution of silica fume to  $\kappa$  or to the piezoelectric effect.

The piezoelectric effect for paste (iii) (with latex) is attributed mainly to the movement of ions in the cement and partly to the movement of functional groups at the interface between cement and latex, as both contribute to the relatively high  $\kappa$  value of  $35 \pm 4$  (Table 1) prior to stress cycling. Latex addition contributes much to increasing  $\kappa$  prior to stress cycling, but fails to enhance the piezoelectric coupling coefficient (Table 3). This means that the movement of the functional groups upon loading is

too limited to significantly enhance the piezoelectric effect, though the presence of the functional groups increases  $\kappa$  prior to stress cycling. The enhancement of the piezoelectric effect by the functional groups, if any, is probably overshadowed by the reduction of the piezoelectric effect by the decrease in volume occupied by cement due to the presence of latex.

The piezoelectric effect for paste (iv) (with carbon fibers in the amount of 0.5% by mass of cement, and silica fume) is attributed mainly to the ions in the cement, and partly to the functional groups at the fiber-matrix interface, as both contribute to the very high  $\kappa$  value of  $54 \pm 7$  (Table 1) prior to stress cycling. The carbon fibers contribute much to increasing  $\kappa$  prior to stress cycling, but fail to enhance the piezoelectric coupling coefficient (Table 3). This means that the movement of the functional groups upon loading is too limited to significantly enhance the piezoelectric effect, though the presence of the functional groups increases  $\kappa$  prior to stress cycling. The enhancement of the piezoelectric effect by the functional groups, if any, is probably overshadowed by the reduction of the piezoelectric effect by the decrease in volume occupied by cement due to the presence of the fibers.

The piezoelectric effect for paste (v) (with carbon fibers and latex) is attributed to the movement of the ions in the cement. Carbon fiber addition contributes much to increasing  $\kappa$  prior to stress cycling, but diminishes the piezoelectric coupling coefficient (Table 3). This means that the presence of latex at the fiber-matrix interface causes the functional groups at the fiber surface to move with more difficulty upon loading, thereby failing to contribute to the piezoelectric effect. However, the presence of the functional groups increases  $\kappa$  prior to stress cycling. Moreover, the fibers cause the piezoelectric effect to diminish, due to the decrease in volume occupied by cement.

The piezoelectric effect for paste (vi) (with carbon fibers in the amount of 1.0% by mass of cement, and silica fume) in Fig. 1 is attributed mainly to the ions in the cement and partly to the functional groups on the fiber surface. An increase in the fiber content from 0.5% by mass of cement (below the percolation threshold, Table 2) to 1.0% by mass of cement (above the percolation threshold, Table 2) decreases  $\kappa$  prior to stress cycling (Table 1) and greatly enhances the piezoelectric coupling coefficient  $d$  (Table 3). Percolation causes charges to move more readily upon loading, thereby enhancing

the piezoelectric effect. On the other hand, percolation causes the dipole moment per unit volume to decrease, thereby decreasing  $\kappa$  prior to stress cycling. That the magnitude of  $d$  decreases with increasing stress magnitude (Fig. 2) is because the ion movement occurs readily at a low stress amplitude ( $<1$  MPa) and an increase in stress amplitude only has incremental effect on the extent of further ion movement.

The piezoelectric effect for paste (vii) (with steel fibers) is attributed to the ions in the cement. The steel fiber addition diminishes both  $\kappa$  prior to stress cycling (Table 1) and the piezoelectric coupling coefficient (Table 3). Both effects of steel fiber addition are due to the decrease in volume occupied by cement.

The strongest piezoelectric effect attained in this work corresponds to a longitudinal piezoelectric coupling coefficient  $d$  of  $4 \times 10^{-13}$  m/V. The value of  $d$  is lower for the cement pastes than the conventional ceramic piezoelectric materials ( $d$  is  $1.4 \times 10^{-11}$  m/V for PZT, as measured in this work by using a specimen of size  $25 \times 25 \times 2$  mm), due to 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.

An increase in  $\kappa$  corresponds to a decrease in the reactance. The reactance was observed in this work (28 days of curing) to decrease upon compressive loading. In contrast, Ref. 6 (7 days of curing) reported that the reactance of carbon fiber mortar increased upon compressive loading. The difference in trend is attributed to the difference in curing age. This explanation is consistent with the report that the resistance increases upon compression at 7 days of curing but decreases upon compression at 28 days of curing [7].

#### 4. Conclusion

The direct piezoelectric effect was observed in cement pastes by measurement of the relative dielectric constant  $\kappa$  in the stress direction during repeated compressive loading in the elastic regime. The piezoelectric effect is mainly due to the movement of ions in the cement. The effect is particularly large when the cement paste contains short carbon fibers at a volume fraction (1.0%) above the percolation threshold. In this case, the

longitudinal piezoelectric coupling coefficient is  $4 \times 10^{-13}$  m/V. The use of admixtures (silica fume, latex, or carbon or steel fibers below the percolation threshold) diminishes the piezoelectric effect, due to the volume occupied by the admixtures in place of cement.

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