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Cement and Concrete Research 33 (2003) 1675–1679

CEMENT AND CONCRETE RESEARCH

Pyroelectric behavior of cement-based materials

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Received 24 April 2001; accepted 14 April 2003

Abstract

The pyroelectric effect, which is useful for temperature sensing, was observed in cement-based materials. The use of short steel fibers (8 μm diameter), together with polyvinyl alcohol (PVA), as admixtures greatly enhances the effect, thereby attaining pyroelectric coefficient 6×10^{-8} C/m^2 K (10 kHz). However, due to the high value (2500) of the relative dielectric constant, the pyroelectric voltage is lower than those of plain cement paste or carbon fiber (15 μm diameter) cement paste. Carbon fiber cement paste and plain cement paste are comparable in the pyroelectric voltage, though the pyroelectric coefficient is higher for carbon fiber cement paste than plain cement paste. The pyroelectric effect in cement-based materials is attributed to the increase in mobility of the ions as the temperature increases.

Keywords: Electrical properties; Cement paste; Pyroelectric

1. Introduction

Pyroelectric behavior refers to the change in electric polarization in a material due to a change in temperature. The change in polarization gives rise to a change in voltage across the material in the direction of the polarization. In this way, thermal energy is converted to electrical energy. The pyroelectric effect is used for temperature sensing, particularly for infrared detection, which is used, for example, in intruder alarms, as the infrared radiation from a warm human or animal body raises the temperature of the pyroelectric detector, which generates a voltage that actuates an alarm [1]. In addition, the effect is useful for fire detection.

The most well-known pyroelectric materials are the perovskite ceramics (e.g., $BaTiO_3$ and PZT) and some polymers (e.g., PVDF). Due to the low cost and mechanical ruggedness of concrete compared to these materials and the wide usage of concrete in structures, it is attractive to use concrete itself as a pyroelectric material. In this way, concrete becomes a smart material.

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 [2–7], chlorides [8], curing age [9–18], aggregate type [8], air entrainment [19], and admixtures (components added to the cement mix) such as silica fume [20,21], latex [21], and fibers [21]. In particular, it has been reported that κ at 10 kHz–1 MHz is decreased by 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 [21].

The value of κ changes with strain or stress; the phenomenon is the direct piezoelectric effect [22,23]. However, the effect of temperature on κ has not been previously investigated. The direct piezoelectric effect in cement is mainly due to the movement of ions in response to strain or stress [22,23]. The movement of ions is expected to diminish with decreasing temperature, thereby causing κ to decrease with decreasing temperature, and hence, the pyroelectric effect. This paper is aimed at observing the pyroelectric effect in cement-based materials and determining the pyroelectric coefficient, which is defined as the change in polarization per unit change in temperature.

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doi:10.1016/S0008-8846(03)00147-9

2. Experimental methods

2.1. Materials

No aggregate (fine or coarse) was used. The cement used was Portland cement (Type I) from Lafarge (Southfield, MI). The water/cement ratio was 0.35.

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.

The carbon fibers were isotropic pitch based, unsized, and of length ~5 mm, diameter 15 μm, and density 1.6 g/cm^3, as obtained from Ashland Petroleum (Ashland, KY). The fiber resistivity was 3.0×10^{-3} Ω cm. Ozone treatment of the fibers [24] was performed to improve the fiber-matrix bond.

Silica fume was used as an admixture when carbon fibers were used. Silica fume (Elkem Materials, 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 from Dow Chemical, Midland, MI, Methocel A15-LV. The defoamer (Colloids, Marietta, GA, 1010) used along with methylcellulose was in the amount of 0.13 vol.%.

Three types of cement paste were prepared, namely, (i) plain cement paste, which consists of cement and water, (ii) steel-fiber cement paste, which consists of cement, water, steel fibers in the amount of 0.90% by mass of cement, corresponding to 0.18 vol.%, and PVA in the amount of 0.1% by mass of cement, corresponding to 0.16 vol.%, and (iii) carbon fiber silica-fume cement paste, which consists of cement, water, silica fume, methylcellulose, and carbon fibers in the amount of 1.0% by mass of cement, corresponding to 1.0 vol.%.

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

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 μm, was sandwiched by two copper discs (similarly polished) of diameter 12.3 mm at a pressure of 1.68 kPa. The copper discs served as electrical contacts. Due to the small thickness, preferred orientation of the fibers in the plane of the specimen disc was bound to occur.

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. Variation of the voltage from 5 mV to 2 V did not give any significant or systematic variation of the impedance. 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 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 [21]. The relative dielectric constant was only slightly higher when silver paint was present. 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.

To show that the dielectric constant measurement using the method described above was accurate, measurement was made on a Kapton (a commercial 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.

The measurement of κ was conducted above at and below room temperature. Temperatures below room temperature (down to -4 °C) were attained by putting the specimen in a freezer with temperature control. Temperatures above room temperature (up to 35 °C) were attained by using a furnace that provided resistance heating.

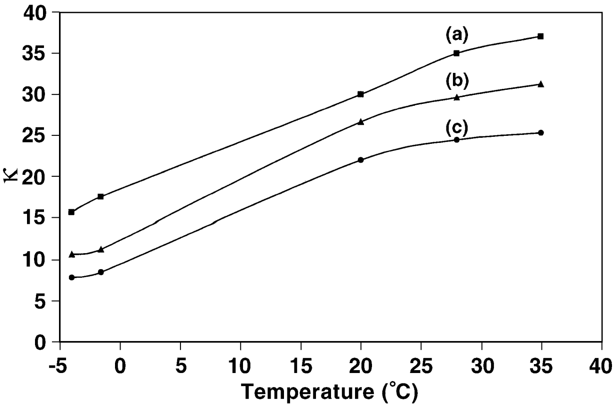

Fig. 1. Variation of relative dielectric constant κ of plain cement paste with temperature at (a) 10 and (b) 100 kHz and (c) 1 MHz.

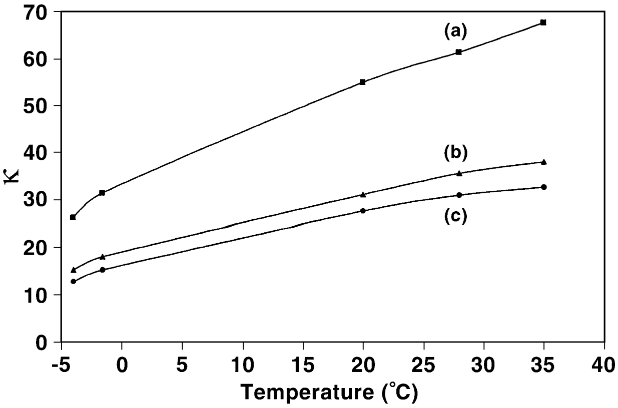

Fig. 2. Variation of the relative dielectric constant κ of carbon fiber cement paste with temperature at (a) 10 and (b) 100 kHz and (c) 1 MHz.

The pyroelectric coefficient p is given by

$$p = \frac{\partial P}{\partial T} \tag{1}$$

where P is the polarization, and T is the temperature.

The voltage change ∂V resulting from a temperature change ∂T in a pyroelectric material can be calculated by using Eq. (1) and the following equations:

$$\partial E = \frac{\partial P}{\varepsilon_o(\kappa - 1)} \tag{2}$$

and

$$\partial V = \ell \partial E \tag{3}$$

where ε_o is the permittivity of free space (8.85×10^{-12} C/V m) and ∂E is the change in electric field. Eq. (2) assumes that κ is independent of the electric field for the relevant range of electric field. The value of ∂V can be enhanced by increasing p or decreasing κ as shown by Eqs. (1) and (2), respectively.

The electric field E consists of the inherent electric field (due to the inherent polarization that occurs in the absence of an applied electric field) and the applied electric field. The inherent electric field is substantial in case of the perovskite ceramics, but is negligible in case of cement. Polarization in the perovskite ceramics is due to the short-range movement of the ions of opposite charge within a unit cell, whereas polarization in cement is believed to be due to the longer range movement of ions, with contribution from the slight movement of functional groups. Thus, the electric field E is essentially the applied electric field, which was 500 V/m.

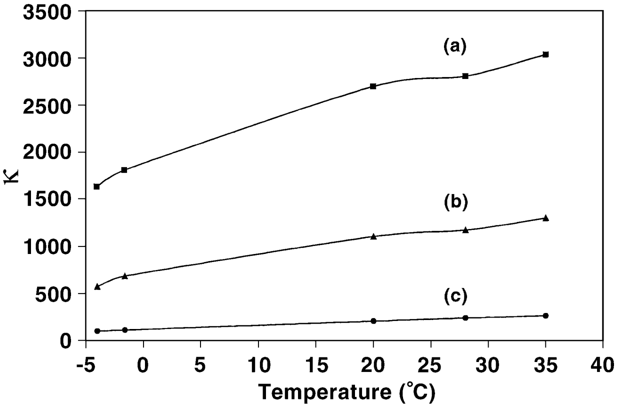

Fig. 3. Variation of the relative dielectric constant κ of steel fiber cement paste with temperature at (a) 10 and (b) 100 kHz and (c) 1 MHz.

Table 1
Pyroelectric coefficient p at 20–28°C and various frequencies

Cement paste	p (10^{-9} C/m^2 K)		
	10 kHz	100 kHz	1 MHz
(i) Cement paste (plain)	0.28	0.16	0.14
(ii) Cement paste with steel fibers and PVA	61	39	19
(iii) Cement paste with carbon fibers	3.5	2.4	1.8

3. Results and discussion

Figs. 1–3 give the variation of κ with temperature for three frequencies (10 and 100 kHz and 1 MHz) for plain cement paste, carbon fiber cement paste, and steel fiber cement paste, respectively. For each paste, at any temperature, κ decreases with increasing frequency, as expected; at any frequency, the lower the temperature, the lower is κ. The κ value at any combination of frequency and temperature is much higher for the steel fiber cement paste than carbon fiber cement paste or plain cement paste, probably due to the ions provided by PVA in the former and the functional groups on the steel fiber surface in the former.

Table 1 gives the values of pyroelectric coefficient p for different frequencies. The pyroelectric coefficient decreases with increasing frequency as expected. The change in polarization is believed to involve ion movement, which is affected by the temperature and the frequency. The coefficient p increases in the following order: plain cement paste, carbon fiber cement paste, and steel fiber cement paste.

The pyroelectric coefficient of steel fiber cement paste is below those of barium titanate and polyvinylidene fluoride by three orders of magnitude. Nevertheless, for $\kappa = 2500$ (the value for steel fiber cement paste at room temperature and 10 kHz) and for $p = 6.1 \times 10^{-8}$ C/m^2 K (the value for

Table 2
Pyroelectric coefficient p (10^{-9} C/m^2 K) of plain cement paste for different temperature ranges

Temperature range (°C)	10 kHz	100 kHz	1 MHz
− 4 to − 1.6	3.5	1.1	1.2
− 1.6 to 20	2.6	3.2	2.8
20 to 28	2.8	1.6	1.4
28 to 35	1.3	1.0	0.5

Table 3
Pyroelectric coefficient p (10^{-8} C/m^2 K) of steel fiber cement paste for different temperature ranges

Temperature range (°C)	10 kHz	100 kHz	1 MHz
− 4 to − 1.6	32.2	20.3	1.7
− 1.6 to 20	18.4	8.6	1.9
20 to 28	6.1	3.9	1.9
28 to 35	14.6	8.2	1.6

steel fiber cement paste at room temperature), a change in temperature of 10^{-3} K gives a change in electric field of 3×10^{-3} V/m. For a cement paste of thickness 1 cm, this change in electric field results in a voltage change of 30 μV (a measurable quantity). A similar calculation for the case of carbon fiber cement paste gives a voltage change of 70 μV. A similar calculation for the case of plain cement paste also gives a voltage change of 70 μV. The voltage is higher for plain cement paste and carbon fiber cement paste than steel fiber cement paste in spite of the lower values of p for plain cement paste and carbon fiber cement paste, because κ is much higher for steel fiber cement paste than plain cement paste or carbon fiber cement paste. The voltage is the same for plain cement paste and carbon fiber cement paste in spite of the lower value of p for plain cement paste, because κ is higher for carbon fiber cement paste than plain cement paste.

Tables 2 and 3 give the values of p for different temperature ranges for plain cement paste and steel fiber cement paste, respectively. The pyroelectric coefficient decreases with increasing frequency as expected. It decreases with increasing temperature, but there are some exceptions.

The observed increase in κ with increasing temperature (Figs. 1–3) is attributed to the increase in mobility of the ions as the temperature increases. Temperatures above room temperature may cause some moisture loss, which would mean a decrease in the amount of mobile ions. In spite of this, κ increases with increasing temperature above room temperature. Hence, moisture loss, if any, could not mask the pyroelectric effect.

4. Conclusion

The pyroelectric effect was observed in cement-based materials at temperatures from − 4 to 35 °C and at frequencies from 10 kHz to 1 MHz. It is attributed to the increase in mobility of the ions as the temperature increases. Cement paste containing short steel fibers (8 μm diameter) and PVA exhibits relatively high values of the pyroelectric coefficient. Plain cement paste and carbon fiber cement paste have much lower values of the pyroelectric coefficient compared to steel fiber cement paste, but their much lower values of the relative dielectric constant result in pyroelectric voltage that is higher than that of steel fiber cement paste. The pyroelectric coefficient is higher for carbon fiber cement paste than plain cement paste, but carbon fiber cement paste and plain cement paste are comparable in the pyroelectric voltage. Although the values of the pyroelectric coefficient of cement-based materials are lower than those of barium titanate and polyvinylidene fluoride by three or four orders of magnitude, the effect in cement-based materials is sufficient for detecting very small temperature changes (even 10^{-3} K).

Acknowledgements

This work was supported by the National Science Foundation of the United States.

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