



Effect of admixtures on the dielectric constant of cement paste

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Abstract

The relative dielectric constant of cement paste at 10 kHz–1 MHz is decreased by silica fume addition (from 29 to 21 at 10 kHz) and by steel fiber addition (from 29 to 20 at 10 kHz), due to the volume occupied by these admixtures in place of cement. It is increased by latex addition (from 29 to 35 at 10 kHz) and by carbon fiber addition (from 21 to 54 for silica fume cement at 10 kHz) due to the interface between cement and these admixtures. Increasing the carbon fiber content beyond the percolation threshold decreases the relative dielectric constant (from 54 to 49 at 10 kHz). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

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_0) 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 [1–6], chlorides [7], curing age [8–17], aggregate type [7], silica fume [18], and air entrainment [19]. The effect of fibers and latex on the dielectric constant has not been previously investigated. This paper is focused on the effect of admixtures, including fibers, latex, and silica fume. Carbon fibers are of particular interest in relation to the dielectric effect, due to the ability of carbon fibers to render to cement the ability to sense its own strain by reactance measurement [20]. Reactance is inversely related to the dielectric con-

stant. The effect behind this sensing ability is actually the direct piezoelectric effect [21]. Strain sensing is valuable for smart structures, particularly in relation to structural vibration control.

Dielectric constant measurement using a capacitor probe provides a technique of nondestructive detection of subsurface deterioration [22] and a technique of nondestructive estimation of the compressive strength [3]. Moreover, the dielectric constant is information needed for the use of microwaves (e.g., radars) to inspect concrete structures [23].

Dielectric constant measurement involves subjecting the material under investigation to an AC electric field. One configuration involves the coaxial cable method (i.e., the transmission line method), in which the electromagnetic wave is allowed to propagate and hit the specimen under study [23–25]. The wave can be reflected, absorbed, and/or transmitted by the specimen. Another configuration involves that of a parallel-plate capacitor [19] in which the AC electric field is applied across the two electrodes of the capacitor while the specimen is sandwiched by the electrodes. The first method is relevant to the use of microwaves to inspect concrete structures. The second method is relevant to the use of a capacitor probe for nondestructive inspection. The second method is used in this work, mainly due to its ability to provide quantitative determination of the dielectric constant.

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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 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, 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.%.

The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer (Dow Chemical, 460NA) with the polymer making up about 48% of 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, Midland, MI, No. 2410, 0.5% by mass of latex).

The carbon fibers were isotropic pitch based, unsized, and of length ~ 5 mm, diameter $15 \mu\text{m}$, and density 1.6 g/cm^3 , as obtained from Ashland Petroleum (Ashland, KY). The fiber resistivity was $3.0 \times 10^{-3} \Omega \text{ cm}$. Ozone treatment of the fibers [26] 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 $6 \times 10^{-5} \Omega \text{ cm}$.

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). The electrical properties of pastes (i), (iv), (v), (vi), and (vii) are shown in Table 1.

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, 100 kHz, and 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

Table 1
DC resistivity and absolute thermoelectric power of carbon fiber cement pastes

Paste no.	Fiber type	Fiber content		Admixture	Resistivity ($\Omega \text{ cm}$) ^a	Absolute thermoelectric power ^b ($\mu\text{V}/^\circ\text{C}$)
		% by mass of cement	vol.%			
(i)	–	0	0	–	$(4.7 \pm 0.4) \times 10^5$	1.96 ± 0.05
(iv)	Carbon	0.5	0.48	SF	$(1.5 \pm 0.1) \times 10^4$	0.89 ± 0.09
(v)	Carbon	0.5	0.41	L	$(9.7 \pm 0.6) \times 10^4$	1.14 ± 0.05
(vi)	Carbon	1.0	0.95	SF	$(8.3 \pm 0.5) \times 10^2$	-0.48 ± 0.11
(vii)	Steel	0.5	0.10	–	$(7.8 \pm 0.5) \times 10^4$	53.3 ± 4.8

SF: silica fume. L: latex.

^a Measured within 1 s from the start of resistivity measurement in order to avoid polarization effect [28].

^b $1.98 \pm 0.03 \mu\text{V}/^\circ\text{C}$ 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 [27].

Table 2
Effect of silver paint at the electrical contact on the measured relative dielectric constant of cement paste (i)

	10 kHz	100 kHz	1 MHz
Without silver paint	28.6±3.4	24.8±3.6	23.7±2.8
With silver paint	30.6±3.3	26.1±4.0	24.8±2.7

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, as shown in Table 2. 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 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.

This work used specimens in the form of thin discs. The use of thick discs or cubes gave dielectric constant values that are unreasonably large, due to the distortion of the electric field lines near the edge of the specimen.

3. Results

Table 3 shows the relative dielectric constant of seven types of cement paste, each at three frequencies. For any type of cement paste, the relative dielectric constant decreases with increasing frequency, as expected. At any of the frequencies, the addition of silica fume decreases the relative dielectric constant, and the addition of latex increases the relative dielectric constant. The further addition of carbon fibers to a paste containing either silica fume

or latex increases the relative dielectric constant. However, an increase in fiber content from 0.5% to 1.0% by mass of cement decreases the relative dielectric constant slightly. All three pastes containing fibers exhibit significantly higher values of the relative dielectric constant than all three pastes which contain no fiber.

4. Discussion

Ref. [18] reported that, at frequencies from 1 MHz to 1.5 GHz, silica fume appears to have a small effect on the dielectric constant of cement paste. However, at a low frequency (10 kHz–1 MHz), we found that silica fume decreases the dielectric constant of cement paste. Since the dielectric constant decreases with increasing frequency, the effect of silica fume is harder to observe when the frequency is higher. Our observation regarding the effect of silica fume cannot be due to the air voids, as silica fume is known to decrease the air void content, and air voids tend to decrease the dielectric constant. In other words, a decrease in air void content is expected to increase the dielectric constant. We attribute the decrease of the dielectric constant by the silica fume addition to the low dielectric constant of silica fume (SiO_2) compared to cement; the moisture and ions in cement cause the dielectric constant to be relatively high.

Latex addition increases the dielectric constant of cement paste. This effect is partly attributed to the decrease in air void content (a well-known effect of latex addition). However, the air void content cannot explain the large (up to 27%) increase in the dielectric constant. Latex itself is relatively low in the dielectric constant, since it is a polymer. The observed effect is attributed to the large amount of interface between latex and cement, and the electric dipoles at the interface.

Carbon fiber addition increases the dielectric constant of cement paste. This effect is attributed to the functional groups on the fiber surface (which had been ozone treated) and the resulting dipoles at the fiber-matrix interface. The dielectric constant decreases when the fiber volume fraction is increased from 0.48 to 0.95 vol.%, because of percolation.

Table 3
Relative dielectric constant of cement pastes

Paste no.	Fiber type	Fiber content		Admixture	Relative dielectric constant		
		% by mass of cement	vol.%		10 kHz	100 kHz	1 MHz
(i)	–	0	0	–	28.6±3.4	24.8±3.6	23.7±2.8
(ii)	–	0	0	SF	20.8±3.4	19.6±3.2	16.5±0.8
(iii)	–	0	0	L	34.9±4.5	31.5±2.9	24.3±2.9
(iv)	Carbon	0.5	0.48	SF	53.7±7.0	38.3±4.8	28.1±2.9
(v)	Carbon	0.5	0.41	L	63.2±5.2	40.4±5.9	33.2±6.8
(vi)	Carbon	1.0	0.95	SF	48.7±4.8	29.6±5.0	25.0±5.0
(vii)	Steel	0.5	0.10	–	19.6±4.8	19.0±1.0	13.7±2.4

SF: silica fume. L: latex.

As shown by the resistivity data in Table 1, the percolation threshold is between 0.48 and 0.95 vol.% fibers.

For cement paste containing short steel fibers in the amount of 0.5% by mass of cement (0.10 vol.%, which is much below the percolation threshold) in the absence of silica fume or latex, the relative dielectric constant is lower than that of the paste without any admixture (first entry in Table 3), and is comparable to that of the paste with silica fume (second entry in Table 3). Hence, steel fiber addition diminishes the relative dielectric constant, in sharp contrast to the effect of carbon fiber addition. The effect of steel fiber addition is attributed mainly to the volume occupied by the fibers in place of cement, although it is also due to the air void content increase (a well-known effect of fiber addition). The contribution of the fiber-matrix interface to the dipole moment is apparently small, due to the oxide on the fiber surface. Hence, the effects on the dielectric constant can be very different for different types of fiber.

Of the seven types of paste listed in Table 3, the use of carbon fibers plus latex gives the highest value of the relative dielectric constant, whereas the use of either steel fibers or silica fume gives the lowest value of the relative dielectric constant. A low value is desirable for application as substrates in electronic packaging. A high value is desirable for application as a capacitor for electrical energy storage.

The values of the relative dielectric constant in Table 3 are low compared to the value of 80 previously reported for cement paste without admixture [5,10]. The difference is related to the higher water content in the specimens of previous work [5].

5. Conclusion

The relative dielectric constant of cement paste at 10 kHz–1 MHz is decreased by silica fume addition and by steel fiber addition, but is increased by latex addition and by carbon fiber addition. The effects are explained in terms of the interfaces and the dielectric behavior of the admixtures themselves. Increasing the carbon fiber content beyond the percolation threshold decreases the relative dielectric constant.

Acknowledgments

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