

Partial replacement of carbon fiber by carbon black in multifunctional cement–matrix composites

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Abstract

Cement reinforced with discontinuous carbon fiber is known for its piezoresistivity-based strain sensing ability, its electrical conductivity and the consequent multifunctionality. The high cost of carbon fiber is disadvantageous. Both carbon fiber and carbon black (used with silica fume in the amount of 15% by mass of cement) increase the DC conductivity and the EMI shielding effectiveness of cement, but carbon fiber is more effective than carbon black. Partial (50%) replacement of carbon fiber by carbon black lowers the cost, in addition to increasing the workability, while the electrical conductivity and the electromagnetic interference shielding effectiveness are maintained. However, the partial replacement reduces the strain sensing effectiveness. Total replacement of carbon fiber by carbon black diminishes both the conductivity and the shielding effectiveness, further reduces the strain sensing effectiveness, decreases the compressive modulus and increases the compressive strain at failure, while the compressive strength is maintained. The increased workability due to the partial replacement enables a higher total conductive admixture content to be attained. The maximum total conductive admixture content is 3.5% by mass of cement. In contrast to fiber replacement, the addition of carbon fiber to cement with carbon black decreases the compressive strength, strain at failure and density.

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1. Introduction

Multifunctional cement–matrix composites are useful as structural materials that provide functional properties, which allow applications such as electrical grounding, electrical contacts for cathodic protection, deicing, electromagnetic interference (EMI) shielding, antistatic flooring and strain sensing [1,2]. Multifunctionality is attractive for cost reduction, durability enhancement, large functional volume, design simplification and absence of mechanical property loss (which tends to occur if embedded devices are used in place of a multifunctional structural material).

The functions mentioned above hinge on the electrical conductivity, as rendered by the use of electrically conduc-

tive admixtures. In grounding and in electrical contacts for cathodic protection, the cement–matrix composite is used as an electrical conductor [3]. In deicing, the composite is used as a resistance heating element [4–6]. In EMI shielding, the composite is used to block electromagnetic radiation, particularly radio wave and microwave, for the purpose of protecting electronics, providing cell-phone-proof buildings and deterring electromagnetic forms of spying [7–10]. In strain sensing, the composite is used as a strain sensor, thereby allowing weighing, traffic monitoring, room occupancy monitoring (for building facility management and building evacuation monitoring), intruder detection and structural vibration control [11–26]. In damage sensing, the composite is used as a damage sensor, thereby allowing structural health monitoring [27–30]. All these potential applications are enabled by the use of electrically conductive admixtures, which result in decrease in the electrical resistivity (as needed for electrical grounding and deicing), increase in the EMI shielding effectiveness

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(mainly through reflection of the radiation), and enhancement of the strain sensing ability (through reversible change of the electrical resistivity with strain – a phenomenon known as piezoresistivity).

Electrically conductive fibers (e.g., carbon and steel fibers) that are discontinuous are effective as admixtures for providing electrically conductive cement–matrix composites [1,31]. Electrically conductive particles (e.g., graphite powder) are less effective [1], due to their low aspect ratio. However, particles tend to be much less expensive than fibers and low cost is important for the practicality of a concrete technology. Thus, the combined use of fibers and particles is of economical interest. Furthermore, the particles between adjacent fibers may enhance the electrical connectivity of the composite, thereby resulting in a synergistic effect. In other words, particles that are used in conjunction with fibers may have more effect on the electrical conductivity of the composite than particles that are used in the absence of fibers. Therefore, for both economical and scientific reasons, it is important to investigate the combined use of fibers and particles for providing electrically conductive cement–matrix composites. Prior work in the combined use of conductive fibers and conductive particles in cement–matrix composites include the combined use of carbon fiber and carbon black for electrical conduction [32] and the combined use of steel fiber (diameter larger than that of carbon fiber by a few orders of magnitude) and steel shaving (more like an aggregate than an admixture, due to its large particle size of 0.15–4.75 mm) [5].

Carbon fibers have been shown to be the most effective admixture for rendering the strain sensing ability [11–26]. Steel fibers are much less effective for strain sensing [14], though they can be more effective for electrical grounding and deicing [4]. Grounding and deicing require very low resistivity, whereas piezoresistivity does not. The strain sensing ability of carbon fiber reinforced cement stems from the slight pull-out of crack-bridging fibers during tension affecting the electrical contact between fiber and cement matrix. Carbon fibers (15 μm diameter) are more effective than steel fibers (8 μm diameter), probably due to the fiber–fiber contact rather than the fiber–matrix contact governing the piezoresistivity in steel fiber cement [14].

For the purpose of avoiding galvanic couples, the particles and fibers that are used together as admixtures are preferably the same in composition. Therefore, this work focuses on the combined use of carbon fibers and carbon black. Carbon black has been used as an admixture in cement for enhancing the electrical conductivity [32–34], decreasing the liquid permeability [35], blocking gases [36] and increasing the fluidity [37]. However, the effects of carbon black on the strain sensing ability and the EMI shielding effectiveness have not been previously reported. Furthermore, the relative effectiveness of carbon black and carbon fiber for enhancing the electrical conductivity has not been previously investigated, as the prior work

[32] investigated carbon black and carbon fiber that were at very different mass contents.

Carbon black is an attractive admixture, due to its electrical conductivity, low cost and its being in the form of porous agglomerates of nanoparticles. This structure causes carbon black to be highly compressible (or squishable) [38,39]. Due to its compressibility (or squishability), carbon black can spread upon being squeezed. The spreadability helps the electrical connectivity. In contrast, carbon fiber or nanofiber does not exhibit this spreadability. The spreadability of carbon black is shown by the reported observation that the electrical resistivity of a compact of carbon black and manganese dioxide particles is lower than that of a compact of carbon nanofiber and manganese dioxide particles, though the resistivity of a compact of carbon black alone is higher than that of a compact of carbon nanofiber alone [40]. The spreadability of the carbon black between the manganese dioxide particles, in contrast to the non-spreadability of carbon nanofiber, is responsible for the relatively low resistivity of the compact of carbon black and manganese dioxide. This low resistivity occurs in spite of the low aspect ratio of carbon black compared to carbon nanofiber [40]. Another advantage of carbon black is its nanostructure, which allows carbon black to fill the microscopic space between adjacent fibers, in case that carbon black is used in combination with fibers. Both of these advantages of carbon black are utilized in this work, which involves the combined use of carbon black and carbon fiber in cement–matrix composites.

As silica fume (particles of size about 0.1 μm) has been shown to be effective for helping the dispersion of carbon fiber in cement [41], it is used along with carbon black and/or carbon fiber in this work. In contrast, fine particulates such as silica fume are not used in prior work on cement paste containing carbon black [32,42].

Carbon fiber as an admixture in the amount of 0.5% by mass of cement provides a strain-sensing cement paste with a gage factor (fractional change in resistance per unit strain) of 330 [11]. On the other hand, carbon black as an admixture in the amount of 15% by mass of cement results in a cement paste with a gage factor of 60 [42]. Thus, carbon fiber is much more effective than carbon black for providing the ability to sense strain. However, the effect of combined use of carbon fiber and carbon black on the strain sensing effectiveness has not been previously addressed.

This work is mainly aimed at investigating the partial and total replacement of carbon fiber by carbon black for providing multifunctional cement–matrix composites of reduced cost. In addition, this work compares the effectiveness of carbon fiber and carbon black for providing multifunctionality. The properties addressed are the electrical resistivity, the EMI shielding effectiveness, the strain sensing effectiveness and the compressive properties. The compressive properties are basic to structural use of cement-based materials.

An AC sensing method is electrical time domain reflectometry, which uses a continuous electrical conductor (such as a continuous carbon fiber [43] or, more commonly, a coaxial cable [44]) as a transmission line element. Continuous fibers and cables are disadvantageous compared to discontinuous fibers in that they cannot be incorporated in a concrete mix and that they are relatively expensive.

2. Experimental methods

2.1. Materials

The carbon black was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was in the form of porous agglomerates of carbon particles of average size 30 nm, a nitrogen specific surface area of 254 m²/g, a volatile content of 1.07%, a maximum ash content of 0.2% and a density of 1.7–1.9 g/cm³. It was used in the amount of 0.5% by mass of cement.

The carbon fiber was isotropic pitch based and unsized, as obtained from Ashland Petroleum Co. (Ashland, KY). The fiber diameter was 15 µm. The nominal fiber length was 5 mm. Fibers in the amount of 0.5% by mass of cement (corresponding to 0.5 vol.%) were used. The percolation threshold is between 0.5 and 1.0 vol.% [31]. Prior to using the fibers in the cement, they were dried at 110 °C in air for 1 h and then surface treated with ozone by exposure to O₃ gas (0.6 vol.%, in O₂) at 160 °C for 10 min. The ozone treatment was for improving the wettability of fibers by water [45]. The ozone treatment is associated with the formation of oxygen-containing functional groups on the surface of the fibers. Although the surface functional groups result in increased contact electrical resistivity between the fiber and the cement matrix, the improved bonding between fiber and matrix and the enhanced degree of fiber dispersion resulting from the treatment make the treatment valuable, as reported in detail previously [45].

The carbon black content used ranged from 0.5% to 2.0% by mass of cement. The carbon fiber content used ranged from 0.5% to 3.5% by mass of cement. These ranges are similar to those in prior work that also used carbon black and carbon fiber together in cement [32].

The cement used was portland cement (Type I) from Lafarge Corp. (Southfield, MI). No aggregate (whether fine or coarse) was used. The water/cement ratio was 0.35. A water reducing agent (WR) was used in the amount of 1.0% by mass of cement. The WR was TAMOL SN (Rohm and Haas, Philadelphia, PA) which contained 93–96% sodium salt of a condensed naphthalene sulfonic acid. The silica fume (Elkem Materials Inc., Pittsburgh, PA, microsilica, EMS 965) was used in all the specimens of this work in the amount of 15% by mass of cement. In case that carbon fiber was used (whether together with carbon black or not), silica fume was used along with (i) methylcellulose (Dow Chemical Corp., Midland, MI, Methocel A15-LV) in the amount of 0.4% by mass of cement and (ii) a defoamer (Colloids Inc., Marietta, GA, 1010) in the amount of 0.13 vol.% (% of specimen volume). Methylcellulose and the defoamer were not used in case that carbon black was used in the absence of carbon fiber.

A rotary mixer with a flat beater was used for mixing. Methylcellulose was dissolved in water and then the defoamer and carbon fiber (if applicable) were added and stirred by hand for about 2 min. Then, this methylcellulose mixture, cement, water, silica fume, carbon black (if applicable) and water reducing agent were mixed for 5 min. After pouring the mix into oiled molds, an external electric vibrator was used to facilitate compaction and decrease the amount of air bubbles. The specimens were demolded after 1 day and then allowed to cure at room temperature in air (relative humidity = 100%) for 28 days.

2.2. Electrical resistivity measurement

The DC volume resistivity was measured using the Keithley 2001 multimeter and the four-probe method. In this method, four electrical contacts were applied by silver paint around the whole perimeter at four planes per-

pendicular to the length of the specimen (160 × 40 × 40 mm). The four planes were symmetrical around the mid-point along the length of the specimen, such that the outer contacts (for passing current) were 140 mm apart and the inner contacts (for measuring the voltage in relation to resistivity determination) were 80 mm apart. This method of resistivity measurement was used in previous work on cement-based materials [31].

2.3. EMI shielding effectiveness measurement

The attenuations upon reflection and transmission were measured using the coaxial cable method (the transmission line method (Fig. 1)). The set-up consisted of an Elgal (Israel) SET 19 A shielding effectiveness tester with its input and output connected to a Hewlett-Packard (HP) 8510A vector network analyzer, which provided both power and phase information. This analyzer consisted of a sweep oscillator, a test set which included two ports, a control panel, an information display and radio frequency cables. Each port of the test set included dual directional couplers and a complex ratio measuring device. An HP APC-7 calibration kit was used to calibrate the system. The frequency was either 1.0 or 1.5 GHz. The samples placed in the center plane of the tester (with the input and output of the tester on the two sides of the sample) was in the form of an annular ring of outer diameter 97 mm and inner diameter 28 mm. The sample thickness was measured for each specimen, and all values were around 4.2 mm. Silver paint was applied at both inner and outer edges of each specimen and at the vicinity of the edges in order to make electrical contact with the inner and outer conductors of the tester [46].

2.4. Strain sensing evaluation and compressive testing

For compressive testing according to ASTM C109-80, specimens were prepared using a 2 × 2 × 2 in (51 × 51 × 51 mm) mold. The strain was measured by using a strain gage attached to the middle of one of four side surfaces of a specimen. The strain gage was centered on the side surface and was parallel to the stress axis. Compressive testing under load control was performed using a hydraulic mechanical testing system (MTS Model 810). Testing was conducted under static loading up to failure, with six specimens of each composition tested. In addition, testing was conducted under repeated loading at progressively increasing stress amplitudes, such that four cycles were conducted at each stress amplitude (5, 10, 15, 20 and 25 MPa), for the purpose of investigating the degree of reversibility of the resistance change and of the strain change for each strain amplitude. Moreover, cyclic loading at a fixed stress amplitude (50 MPa, unless noted otherwise) was conducted for the purpose of investigating the effect of cyclic loading on the degree of reversibility of the resistance change and of the strain change.

For each composition, three specimens were subjected to progressively increasing stress amplitudes, whereas three other specimens were subjected to cyclic loading at a fixed stress amplitude.

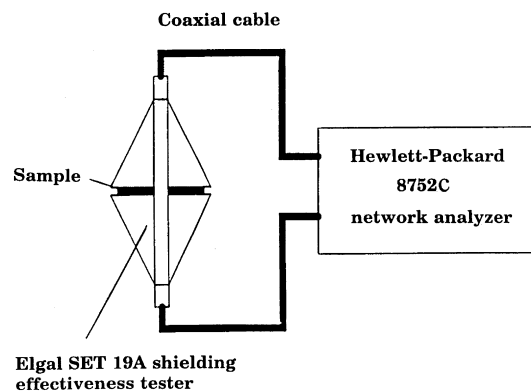


Fig. 1. Set-up for measuring the electromagnetic interference shielding effectiveness.

During compressive testing, DC electrical resistance measurement was made in the stress axis, using the four-probe method, in which silver paint in conjunction with copper wires served as electrical contacts. Four contacts were made perimetrically around the specimen at four planes that were all perpendicular to the stress axis and that were symmetric with respect to the mid-point along the height of the specimen. The outer two contacts (40 mm apart) were for passing current. The inner two contacts (30 mm apart) were for measuring the voltage. A Keithley 2001 multimeter was used for DC resistance measurement.

2.5. Workability testing

The workability (i.e., the consistency) of the cement paste mixes was tested by measuring the slump in accordance with the ASTM C143–90a method. Three specimens were tested for each composition.

3. Results and discussion

3.1. Resistivity and EMI shielding effectiveness

The electrical resistivity of cement paste without conductive admixture is $6 \times 10^5 \Omega \text{ cm}$ [1]. Table 1 shows that both carbon fiber and carbon black are effective in decreasing the resistivity. However, as shown in Table 1, carbon fiber is more effective than carbon black at the same mass content (whether 0.5% or 1.0% by mass of cement) in lowering the resistivity and in enhancing the shielding effectiveness. This is consistent with prior report that carbon fiber at 2% by mass of cement gives lower resistivity than carbon black at 4% by mass of cement [32].

Upon increasing the fiber content, the resistivity decreases particularly abruptly at a carbon fiber content between 0.5% and 1.0% by mass of cement (Table 1). This suggests that the percolation threshold (conductive admixture volume fraction above which the adjacent admixture units, whether fibers or particles, touch one another, thereby forming a continuous electrically conductive path) is at a carbon fiber content between 0.5% and 1.0% by mass of cement, as previously reported [31].

Upon increasing the carbon black content, the resistivity decreases particularly abruptly at a carbon black content between 0.5% and 1.0% by mass of cement, although the decrease is less significant than that in the case of carbon fiber (Table 1). Thus, the percolation threshold for carbon black is probably also between 0.5% and 1.0% by mass of cement. In contrast, prior work [42] reported a carbon black percolation threshold between 10% and 15% by mass of cement. The large discrepancy is attributed to the presence of silica fume in this work and the absence of silica fume in prior work [42]. Silica fume is believed to help the dispersion of the carbon black, since it helps the dispersion of carbon fiber in cement [41]. A lower degree of dispersion of a conductive admixture is expected to hinder the attainment of percolation, thereby increasing the percolation threshold.

The resistivity is higher for carbon black as the sole conductive admixture than for carbon fiber as the sole conductive admixture at the same mass content, whether the content is 0.5% or 1.0% by mass of cement. Even with car-

Table 1
EMI shielding effectiveness (same as the attenuation upon transmission) and DC electrical resistivity of cement pastes with silica fume and various contents of carbon fiber (CF) and/or carbon black (CB)

Admixture content (by mass of cement)	Resistivity ($\Omega \text{ cm}$)	EMI performance		Attenuation upon transmission (dB)		Attenuation upon reflection (dB)	
		Thickness (mm)		1.0 GHz		1.5 GHz	
				1.0 GHz	1.5 GHz	1.0 GHz	1.5 GHz
0.5% CF	$(1.24 \pm 0.14) \times 10^4$	4.20 ± 0.40		8.56 ± 0.90	9.12 ± 1.0	4.06 ± 0.44	4.25 ± 0.51
0.5% CB	$(1.94 \pm 0.26) \times 10^4$	/		/	/	/	/
0.5% CF + 0.5% CB	$(6.04 \pm 0.73) \times 10^2$	4.12 ± 0.36		12.0 ± 1.0	12.5 ± 1.3	3.20 ± 0.36	3.31 ± 0.37
1.0% CF	$(7.91 \pm 0.95) \times 10^2$	4.27 ± 0.38		13.2 ± 1.1	13.7 ± 1.2	3.48 ± 0.40	3.79 ± 0.41
1.0% CB	$(3.13 \pm 0.48) \times 10^3$	4.19 ± 0.42		9.10 ± 0.95	9.24 ± 1.2	3.81 ± 0.42	3.83 ± 0.38
1.5% CF + 0.5% CB	$(4.25 \pm 0.50) \times 10^2$	4.17 ± 0.39		15.4 ± 1.4	15.9 ± 1.7	3.06 ± 0.31	3.08 ± 0.33
1.5% CF + 1.0% CB	$(4.10 \pm 0.36) \times 10^2$	4.21 ± 0.37		17.6 ± 1.9	18.2 ± 1.8	3.01 ± 0.33	2.96 ± 0.26
1.5% CF + 1.5% CB	$(3.84 \pm 0.32) \times 10^2$	4.15 ± 0.43		18.8 ± 1.7	19.3 ± 2.1	2.87 ± 0.35	2.85 ± 0.29
1.5% CF + 2.0% CB	$(3.55 \pm 0.29) \times 10^2$	4.18 ± 0.41		21.3 ± 1.8	21.8 ± 2.2	2.64 ± 0.30	2.57 ± 0.25
2.0% CB	$(1.74 \pm 0.27) \times 10^3$	4.24 ± 0.45		12.3 ± 1.1	12.7 ± 1.4	3.73 ± 0.38	3.72 ± 0.28

For cement without conductive admixture, the DC resistivity and shielding effectiveness (1 GHz) are $6 \times 10^5 \Omega \text{ cm}$ and 4 dB respectively [1].

bon black in the amount of 2.0% by mass of cement, the resistivity remains high at $2 \times 10^3 \Omega \text{ cm}$ (Table 1).

The shielding effectiveness (i.e., attenuation upon transmission) at 1.0 GHz is 4 dB in the absence of conductive admixture [1], 13 dB for carbon fiber (1.0% by mass of cement), and 9 dB for carbon black (1.0% by mass of cement). This means that both carbon fiber and carbon black enhance the shielding effectiveness, though carbon fiber is more effective than carbon black. Even with carbon black in the amount of 2.0% by mass of cement, the shielding effectiveness is just 12 dB (Table 1), which is slightly below the value for carbon fiber in the amount of 1.0% by mass of cement.

The use of carbon fiber (0.5% by mass of cement) and carbon black (0.5% by mass of cement) gives essentially the same resistivity and the same shielding effectiveness as the use of carbon fiber (1.0% by mass of cement) as the sole conductive admixture. This means that partial (50%) replacement of carbon fiber by carbon black essentially does not affect the resistivity or the shielding effectiveness. This result is consistent with prior report that the use of carbon black (1.0% by mass of cement) and carbon fiber (0.75% by mass of cement) gives lower resistivity than the use of carbon fiber (2.0% by mass of cement) without carbon black [32].

At a fixed carbon fiber content of 1.5% by mass of the cement, the resistivity decreases monotonically with increasing carbon black content from 0.5% to 2.0% by mass of cement, while the shielding effectiveness increases monotonically. This reflects the increase in total conductive admixture content from 2.0% to 3.5% by mass of cement.

3.2. Workability

Table 2 shows that the workability is increased by partial replacement of carbon fiber by carbon black, whether the total conductive admixture content is 1.0% or 3.5% by mass of cement. In the absence of carbon black, a total conductive admixture content of 3.5% (Tables 1 and 2) cannot be reached without substantially sacrificing the workability. Thus, workability enhancement and the consequent attainment of a high total conductive admixture content provide additional advantages for the combined use of carbon fiber and carbon black.

Table 2
Workability of cement pastes with silica fume and various contents of carbon fiber (CF) and carbon black (CB)

Total conductive admixture content (by mass of cement) (%)	Conductive admixture contents (by mass of cement)	Slump (mm)
1.0	0.5% CF + 0.5% CB	67 ± 7
1.0	1.0% CF	34 ± 4
3.5	1.5% CF + 2.0% CB	18 ± 2
3.5	3.5% CF	^a

^a Too low to be measured.

The maximum total conductive admixture content is 3.5% by mass of cement in this work, as the workability is too low when this content is exceeded. The high carbon black content of 15% (or more) by mass of cement in prior report [42] is probably due to the absence of silica fume, in contrast to the use of silica fume in this work. Silica fume has been previously reported to decrease the workability [47].

3.3. Strain sensing effectiveness

Figs. 2–4 show the results for the cement paste containing carbon black and silica fume, but no carbon fiber. The resistance decreased monotonically up to failure, at which it increased abruptly (Fig. 2). Moreover, it decreased reversibly upon loading in every stress cycle, such that the extent of the resistance decrease increased with increasing stress amplitude (Fig. 3). Upon cyclic loading at a fixed stress amplitude (Fig. 4), the resistance decreased reversibly

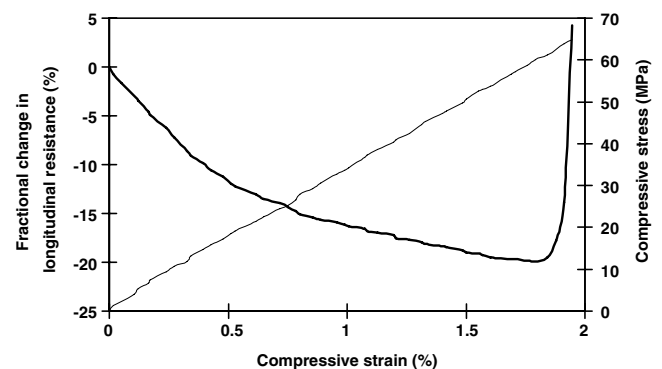


Fig. 2. Variation of the fractional change in resistance (thick curve) and of the compressive stress (thin curve) with compressive strain up to failure. The cement-based material contained carbon black (0.5% by mass of cement) but no carbon fiber.

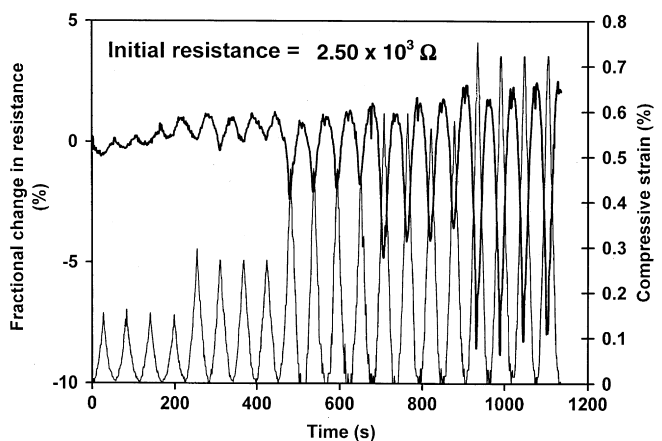


Fig. 3. Variation of the fractional change in resistance (thick curve) with time and of the compressive strain (thin curve) with time during repeated compressive loading at progressively increasing stress amplitudes such that four cycles were conducted at each stress amplitude. The cement-based material contained carbon black (0.5% by mass of cement) but no carbon fiber.

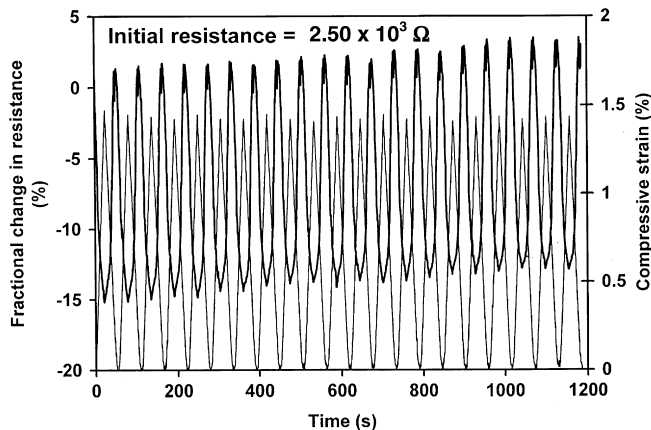


Fig. 4. Variation of the fractional change in resistance (thick curve) with time and of the compressive strain (thin curve) with time during repeated compressive loading at a fixed stress amplitude of 50 MPa. The cement-based material contained carbon black (0.5% by mass of cement) but no carbon fiber.

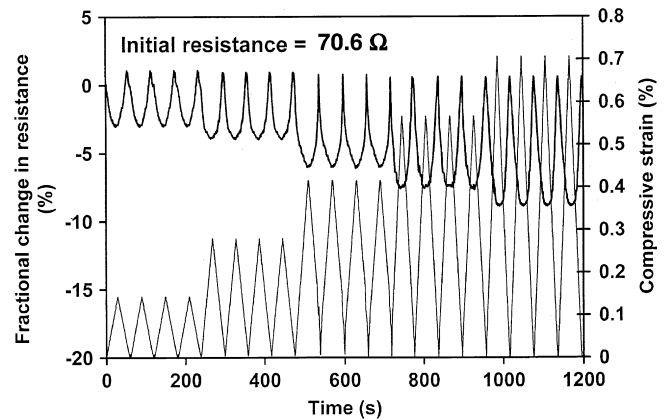


Fig. 6. Variation of the fractional change in resistance (thick curve) with time and of the compressive strain (thin curve) with time during repeated compressive loading at progressively increasing stress amplitudes such that four cycles were conducted at each stress amplitude. The cement-based material contained carbon black (0.5% by mass of cement) and carbon fiber (0.5% by mass of cement).

in a similar fashion, but the resistance baseline gradually increased as cycling progressed, indicating the presence of a small extent of irreversible resistance increase at the end of each cycle. A similar trend of resistance baseline increase was also observed in Fig. 3, indicating that the extent of irreversible resistance increase became more significant as the stress amplitude increased and also became more significant as cycling progressed from the first to the fourth cycle at each stress amplitude that corresponded to a strain amplitude exceeding 0.4%. The irreversible resistance increase may be partly due to electric polarization, which tends to be more substantial when the electrical resistivity of the cement-based material is higher [48]. The resistance is higher for cement containing carbon black in the absence of carbon fiber (Figs. 3 and 4) than cement containing carbon black in the presence of carbon fiber (Fig. 6).

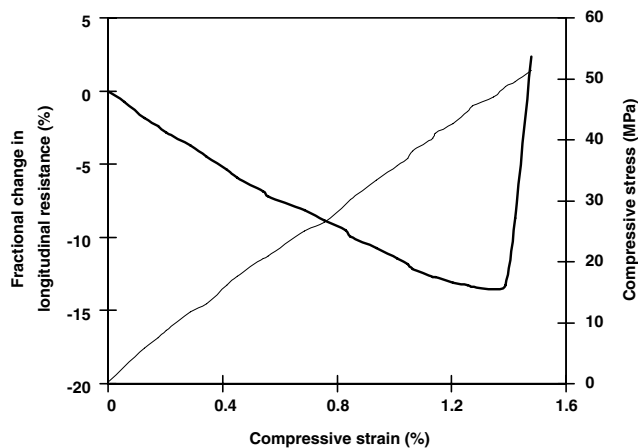


Fig. 5. Variation of the fractional change in resistance (thick curve) and of the compressive stress (thin curve) with compressive strain up to failure. The cement-based material contained carbon black (0.5% by mass of cement) and carbon fiber (0.5% by mass of cement).

Figs. 5 and 6 show the results for cement paste containing carbon black, carbon fiber and silica fume. The resistance decreased monotonically up to failure, at which it increased abruptly (Fig. 5). Moreover, it decreased very reversibly upon loading in every stress cycle (Fig. 6). The behavior is similar to that for carbon-black silica-fume cement paste (without fiber) (Fig. 3), except that the resistance baseline is more stable and the resistance noise level is lower. The lower noise level in Fig. 6 is associated with the larger extent of fractional resistance change at essentially the same strain amplitude. Thus, the addition of carbon fiber greatly enhances the strain sensing ability.

Table 3 shows the gage factor (fractional change in resistance per unit strain). Although the gage factor is much higher for the cement paste with both carbon black (0.5% by mass of cement) and carbon fiber (0.5% by mass of cement) than that with carbon black (0.5% by mass of cement) as the sole conductive admixture, it is much lower than the value of 330 [11] previously reported for the cement paste with carbon fiber (whether 0.5% or 1.0% by mass of cement) as the sole conductive admixture, all investigated under compression. This means that, for a total conductive admixture content of 1.0% by mass of cement, 50% partial replacement of carbon fiber by carbon black decreases the gage factor from 330 [11] to 17 (Table 3). It also means that, for a conductive admixture content of 0.5% by mass of cement, 100% replacement of carbon fiber by carbon black decreases the gage factor from 330 [11] to 2 (Table 3).

The large decrease in gage factor upon partial or total replacement of carbon fiber by carbon black is attributed to a difference in the mechanism behind the piezoresistivity. In relation to fiber bridging across microcracks, fiber push-in upon compression (fiber-pull-out upon tension) has been shown to be a possible origin of the piezoresistivity in carbon fiber cement [49]. However, this mechanism cannot apply to carbon black cement, due to the particulate (non-fibrous) nature of carbon black. The mechanism in

Table 3
Gage factor (under compressive loading at various stress amplitudes) and compressive properties of cement pastes with various proportions of carbon black (CB), carbon fiber (CF) and silica fume (SF)

SF content (by mass of cement)	CB content (by mass of cement)	CF content (by mass of cement)	Gage factors at various compressive strain amplitudes					Compressive strength (MPa)	Compressive modulus (GPa)	Compressive strain at failure (%)	Density (g/cm ³)
			5 MPa	10 MPa	15 MPa	20 MPa	25 MPa				
15%	0.5%	0	1.6 ± 0.1	2.2 ± 0.2	5.8 ± 0.3	9.5 ± 0.6	14 ± 1.3	64.8 ± 4.3	3.27 ± 0.26	1.98 ± 0.14	1.93 ± 0.09
15%	0.5%	0.5%	17.3 ± 2.9	16.6 ± 2.7	15.8 ± 1.6	14.4 ± 1.3	12.7 ± 1.1	51.4 ± 5.3	3.40 ± 0.31	1.52 ± 0.17	1.65 ± 0.11
15%	0	0.5%	327 ± 23 ^c	/	/	/	/	62.0 ± 2.3 ^a	21.1 ± 0.5 ^a	0.138 ± 0.002 ^a	/
15%	0	1.0%	332 ± 17 ^c	/	/	/	/	/	/	/	/
0	15%	0	/	/	/	/	60 ^b	46 ^b	10 ^b	0.5	/

^a From Ref. [42].

^b From Ref. [37], with the stress amplitude 45 MPa (not 25 MPa).

^c From Ref. [11], with the stress amplitude in the range 1.3 – 5.5 MPa (not 5 MPa).

the case of carbon black cement may relate to the increased proximity of the carbon black particles upon compression – as in the case of a carbon black polymer–matrix composite [50]. That the partial replacement of carbon fiber by carbon black is detrimental to the strain sensing behavior is probably due to the interference of the carbon black to the carbon fiber push-in (pull-out) piezoresistive mechanism.

When carbon black is used as the sole conductive admixture in the amount of 15% by mass of cement, the gage factor is 60 [42], which is much higher than the value of 14 obtained in this work for carbon black as the sole conductive admixture in the amount of 0.5% by mass of cement. Thus, an increase in carbon black content increases the gage factor. However, this increase may be partly due to the fact that silica fume is not used with carbon black in case of the gage factor of 60 [42] and that silica fume is used with carbon black in case of the gage factor of 14 (this work). At any rate, the gage factor of 60 obtained with carbon black as the sole conductive admixture in the amount of 15% by mass of cement [42] is much lower than the value of 330 for carbon fiber as the sole conductive admixture in the amount of 0.5% by mass of cement [11].

The gage factor depends on the stress amplitude. That the gage factor decreases with increasing stress amplitude has been previously shown for carbon fiber as the sole conductive admixture in the amount of 0.5% by mass of cement [13]. Combined use of carbon fiber and carbon black gives the same trend, as shown in Table 3. However, when carbon black is present as the sole conductive admixture, the dependence of the gage factor on the strain amplitude is particularly strong (Table 3 and Fig. 3). In this case, the gage factor increases with increasing stress amplitude. This significant variation in the gage factor complicates the strain sensing application and is attributed to the effect of minor damage on the piezoresistive effect; the higher the stress amplitude, the more is the extent of minor damage. The type of minor damage, which may be quite subtle, has not been identified.

3.4. Compressive properties

The compressive strength, modulus and strain at failure are respectively 62.0 ± 2.3 MPa, 21.1 ± 0.5 GPa and (0.138 ± 0.002)% for cement paste with carbon fiber as the sole conductive admixture in the amount of 0.5% by mass of cement [47]. Total replacement of the carbon fiber by carbon black essentially does not affect the compressive strength, but it decreases the modulus from 21 to 3 GPa and increases the strain at failure from 0.14% to 2% (Table 3). That total replacement of carbon fiber by carbon black essentially does not affect the compressive strength is consistent with prior report that the compressive strength is only 24% lower for carbon black (4.0% by mass of cement) than carbon fiber (2.0% by mass of cement) [32].

The compressive strength of 65 MPa (Table 3) for cement paste containing carbon black (0.5% by mass of

cement) and silica fume (15% by mass of cement) is higher than the value of 46 MPa previously reported for cement paste containing carbon black (15% by mass of cement) in the absence of silica fume [42]. This is consistent with the prior report that silica fume addition increases the compressive strength of cement paste [47]. The corresponding compressive modulus of 3 GPa (Table 3) is lower than the value of 10 GPa previously reported for cement paste containing carbon black (15% by mass of cement) in the absence of silica fume [42], even though silica fume is known to increase the modulus [47]. The corresponding compressive strain at failure of 2% (Table 3) is higher than the value of 0.5% previously reported for cement paste containing carbon black (15% by mass of cement) in the absence of silica fume [42], even though silica fume is known to decrease the strain at failure [47]. Thus, the difference between the compressive properties (Table 3) for cement paste containing carbon black (0.5% by mass of cement) and silica fume and those of prior work for cement paste containing carbon black (15% by mass of cement) in the absence of silica fume [42] cannot be only due to the silica fume in this work. The high carbon black content in prior work [42] may contribute to the high modulus and the low strain at failure. The effect of carbon black content on the mechanical properties is beyond the scope of this paper.

Table 3 also shows that the addition of carbon fiber to cement with carbon black decreases the compressive strength, strain at failure and density. Thus, the use of carbon black without carbon fiber is attractive for high compressive strength (due to the high density) and high compressive strain at failure.

4. Conclusion

Both carbon fiber and carbon black (used with silica fume in the amount of 15% by mass of cement) decrease the DC electrical resistivity and increase the EMI shielding effectiveness of cement, but carbon fiber is more effective than carbon black at the same mass content. Partial replacement (as much as 50%) of carbon fiber by carbon black lowers the cost, while maintaining the conductivity and the shielding effectiveness, thus making it attractive for deicing, grounding, cathodic protection and EMI shielding. Total replacement of carbon fiber by carbon black diminishes both the conductivity and the shielding effectiveness. Partial or total replacement of carbon fiber by carbon black is detrimental to strain sensing, as the gage factor is much lowered. On the other hand, partial replacement of carbon fiber by carbon black increases the workability, thereby allowing a higher total conductive admixture content to be attained. The maximum total conductive admixture content is 3.5% by mass of cement.

Total replacement of carbon fiber by carbon black greatly decreases the compressive modulus, though the compressive strength is maintained and the compressive strain at failure is increased. In contrast to fiber replacement, the addition of carbon fiber to cement with carbon

black decreases the compressive strength, strain at failure and density.

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