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Carbon-Fiber Cement-Based Materials for Electromagnetic Shielding

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Short carbon fiber is used as an admixture with silica fume to form cement-matrix composites. It is made from pitch or polyacrylonitrile (PAN). PAN-based fiber with a diameter of 7 μm is effective for providing electromagnetic interference (EMI) shielding (1 GHz), low electrical resistivity (DC), and high flexural strength and modulus. Its shielding ability is superior to that of previously studied pitch-based fiber with a diameter of 15 μm (6 × 10^{-4} in.). Thermally desized PAN-based fiber is less effective than the unsized counterpart for providing shielding, reflection, and low electrical resistivity, but it is more effective as a reinforcement. An increase in the fiber content increases the shielding effectiveness, decreases the resistivity; and increases the flexural strength and modulus. For each fiber content in percentage by mass of cement, the addition of sand causes a slight decrease of the shielding effectiveness; at the same fiber volume fraction, the shielding effectiveness is similar for cases with and without sand.

Keywords: carbon; electrical resistivity; electromagnetic shielding; fiber; mechanical properties; silica fume; sizing.

INTRODUCTION

There is an increasing need to protect electronics from the interference of electromagnetic radiation, particularly that in the radio frequency regime. Such radiation is emitted by cellular phones, microwave devices, and so on. The development of materials that can shield the radiation is greatly needed. Shielding is necessary for both the electronics and the radiation sources.

Most attention on electromagnetic interference (EMI) shielding materials has been focused on polymer-matrix composites that contain electrically conductive fillers, such as particles and short fibers.[1,2] Such composites are attractive for their moldability and the consequent suitability for packaging devices. Increasing attention is given to construction materials that can provide shielding, however, as needed for buildings that house sensitive electronics and for strategic structures such as nuclear reactors, power plants, hospitals, embassies, and military installations. It is desired to protect the electronics and deter electromagnetic spying.

By the incorporation of various admixtures (for example, electrically conductive particles or short fibers) in the cement mixture, cement-based materials that are effective for shielding have been achieved.[3] Examples of conductive particulate admixtures are graphite particles,[4-6] coke particles,[7] carbon black,[8] and copper-coated aluminosilicate microspheres.[9] Examples of conductive fiber admixtures are carbon fibers,[8,10,11] carbon nanofibers (originally known as carbon filaments),[12-14] stainless steel fibers,[15,16] and copper fibers.[16] Fly ash, which contains iron oxide, is less effective than the conductive admixtures.[17] Carbon fibers have also been used as an admixture in gypsum plaster to provide shielding.[18]

The highest shielding effectiveness reported for cement-based materials is for materials containing stainless steel fiber with a diameter of 8 μm (3 × 10^{-4} in.) and a length of 6 mm (0.2 in.) as an admixture.[15] In the case of cement paste, the effectiveness is 58 dB at 1 GHz, as attained using the steel fiber at 0.90 vol.%. In the case of mortar (with sand at a sand-cement ratio of 1.0), the highest effectiveness reported is 57 dB at 1 GHz, as attained using the steel fiber at 0.46 vol.%. This steel fiber is highly effective, due to its small diameter (the skin effect), high electrical conductivity, and perhaps some magnetic character. This fiber, however, is more expensive than carbon fiber.

A more cost-effective admixture is petroleum coke particles (less than 75 μm [3 × 10^{-3} in.] in size), which give shielding effectiveness 47 dB at 1 GHz when its content is 1 vol.%.[7] This means that coke is less effective than the steel fiber mentioned previously. The origin of the considerable effectiveness of the coke particles is unclear, as the electrical conductivity of the coke cement paste is low (in contrast to the high conductivity of the cement paste containing the steel fiber[15]). Furthermore, the effectiveness varies greatly with the source of the coke particles.

Another effective admixture is carbon nanofiber (originally known as carbon filament), with a diameter of 0.1 μm, [4 × 10^{-6} in.], which gives shielding effectiveness 30 dB at 1 GHz (0.5 vol.% in cement paste),[12,13] 35 dB at 1 GHz (1.0 vol.% in cement paste),[13] and 38 dB at 1 GHz (1.5 vol.% in cement paste).[13] This means that the coke mentioned previously is more effective than carbon nanofiber.

Much less expensive than carbon nanofiber is conventional carbon fiber (referred to as carbon fiber). Carbon fiber made from pitch with a diameter of 15 μm (6 × 10^{-4} in.) and a length of 5 mm (0.2 in.) gives shielding effectiveness 9 dB at 1 GHz (0.5% by mass of cement in cement paste, corresponding to 0.5 vol.%) and 13 dB at 1 GHz (1.0% by mass of cement in cement paste, corresponding to 1.0 vol.%).[8] Hence, carbon fiber is less effective than carbon nanofiber.

More effective than the pitch-based carbon fiber mentioned previously are graphite particles (0.7 to 0.8 μm, [2.8 × 10^{-5} to 3.1 × 10^{-5} in.] in average size), which give shielding effectiveness 10 dB at 1 GHz (0.5 vol.% in cement paste) and 22 dB at 1 GHz (0.92 vol.% in cement paste).[4] Less effective than the pitch-based carbon fiber is carbon black, which gives shielding effectiveness 9 dB at 1 GHz (1% by mass of cement in cement paste) and 12 dB at 1 GHz (2% by mass of cement in cement paste).[8] Carbon black is not as effective as carbon fiber as a reinforcement.[8]

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A combination of the pitch-based carbon fiber and carbon black can be as effective as the pitch-based carbon fiber alone at the same total conductive admixture content.[8] For example, the pitch-based carbon fiber (0.5% by mass of cement) and carbon black (0.5% by mass of cement) in cement paste gives shielding effectiveness 12 dB at 1 GHz, whereas the pitch-based carbon fiber alone at 1.0% by mass of cement gives 13 dB at 1 GHz.[8] The combination of the pitch-based carbon fiber (1.5% by mass of cement) and carbon black (2.0% by mass of cement) in cement paste gives shielding effectiveness 21 dB at 1 GHz.[8]

Pitch and polyacrylonitrile (PAN) are the two most common precursors of carbon fiber. Isotropic-pitch-based carbon fibers tend to be less expensive than PAN-based carbon fibers. Due to the wider use of PAN-based carbon fiber than pitch-based carbon fiber in polymer-matrix structural composites, however, PAN-based carbon fiber is more widely available than pitch-based carbon fiber. The electrical conductivity of a carbon fiber increases with an increasing degree of graphitization. PAN-based carbon fiber is less graphitizable than pitch-based carbon fiber, but graphitized pitch-based carbon fiber is expensive and is thus not cost-effective anyway. The pitch-based carbon fiber used in prior work[8,10] has not been graphitized. Furthermore, PAN-based carbon fiber tends to be smaller in diameter than pitch-based carbon fiber. For example, the diameter of PAN-based carbon fiber is typically 7 μm (3×10^{-4} in.),[11] in contrast to 15 μm (6×10^{-4} in.) for the pitch-based carbon fiber of prior work.[8,10]

Prior relevant work on cement containing PAN-based carbon fiber addressed the reflectivity rather than the shielding effectiveness and showed that the reflectivity at 8 to 18 GHz is enhanced by the surface treatment of the carbon fiber.[11] The surface treatment involved pyrolytic carbon deposition due to the decomposition of propylene in a furnace at 1100°C (2012°F).[11]

Prior work has addressed the flexural strength[19-23] and electrical resistivity[24] of cement containing PAN-based carbon fiber, which is effective for enhancing these properties. The fiber efficiency factor is defined as the ratio of the composite strength to the fiber strength, divided by the fiber volume fraction. The comparison of PAN-based and pitch-based carbon fibers in relation to the flexural strength of their cement-matrix composites has shown that PAN-based fiber (with a diameter of 7 μm [3×10^{-4} in.] and a ductility of 1.4%) is lower in the efficiency factor than the pitch-based fiber (with a diameter of 18 μm [7.1×10^{-4} in.] and a ductility of 2%).[19] The relatively low ductility of the PAN-based fiber contributes to causing a low efficiency factor.

Fibers commonly have a sizing (polymeric coating on the fiber surface) for improving the handleability, although fibers without sizing (that is, being unsized) are available. The sizing is particularly common for carbon fibers, which are quite brittle. The sizing is expected to be detrimental to the bond between the carbon fiber and the cement matrix. The removal of the sizing is known as desizing. The effect of the sizing on the effectiveness of carbon fiber in cement has not been previously addressed.

Because of the abovementioned differences between pitch-based and PAN-based carbon fibers and the absence of prior work on the shielding effectiveness of cement-based materials containing PAN-based carbon fibers, this work is aimed at evaluating the shielding effectiveness of cement-based materials containing PAN-based carbon fibers.

RESEARCH SIGNIFICANCE

This paper provides: 1) the first evaluation of the EMI shielding effectiveness of cement-based materials containing PAN-based carbon fiber (in contrast to the previously investigated pitch-based fiber, which is less widely available than PAN-based fiber); 2) the first comparative evaluation of unsized and desized carbon fibers (that is, two forms of carbon fiber without sizing) in terms of their effectiveness for improving functional and structural performance; 3) a systematic study of the effects of carbon-fiber volume fraction and sand on the shielding effectiveness; and 4) a correlation of the shielding effectiveness, electrical resistivity, and flexural properties.

EXPERIMENTAL INVESTIGATION

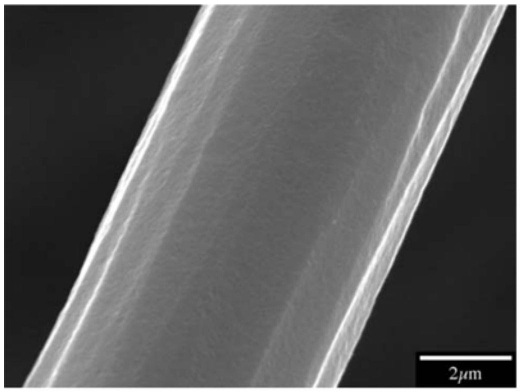
Two types of carbon fiber, designated Type A and Type B, are evaluated as described in Table 1. For the sake of comparison, information on the pitch-based carbon fiber in prior work is also shown in Table 1.[8,10] The Type A PAN-based carbon fiber (with a carbon content of 95%) is sized, thus requiring desizing. The Type B PAN-based carbon fiber (whose production is discontinued) is unsized, so desizing is not performed. Prior to using the fibers in cement, they are prepared as described in Table 2 for the purpose of desizing and/or ozone surface treatment. The ozone treatment involves exposure to ozone gas (0.6 vol.% in oxygen) and is for improving the wettability of fibers by water.[8]

Figure 1 shows scanning electron microscope (SEM) photographs of Type A and Type B carbon fibers and Type A fiber in the as-received form (without desizing). The Type A fiber (Fig. 1(a)) has a smaller diameter (approximately 6.4 μm, [2.5×10^{-4} in.]) than Type B (Fig. 1(b)) (approximately 7.3 μm, [2.9×10^{-4} in.]) due to carbon oxidation that presumably occurred to a limited degree during the desizing treatment of

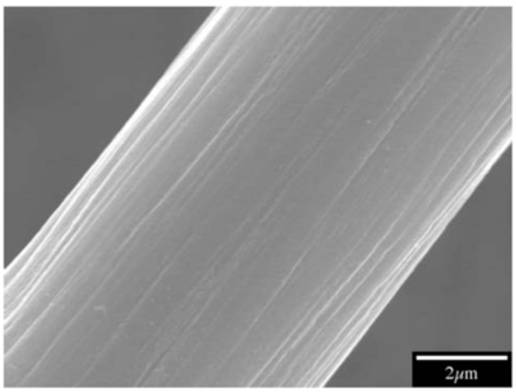
Table 1—Types of carbon fiber

	Fiber type	Source	Sizing	Nominal diameter, μm (10^{-4} in.)	Length, mm (in.)	Resistivity, 10^{-3} Ω.cm (10^{-3}Ω.in.)	Tensile strength, MPa (10^6 psi)	Tensile modulus, GPa (10^6 psi)	Elongation, %	Density, g/cm^3 (10^{-2} lb/in.^{3})
Prior work[8,10]	Pitch-based	Ashland*	Unsized	15 (5.9)	5 (0.2)	3.0 (1.2)	690 (0.10)	48 (7.0)	1.4	1.6 (5.8)
This work	Type A PAN-based	Zoltek	Urethane-based	6.4 (2.5)	8 (0.3)	1.55 (0.610)	3800 (0.55)	242 (35.1)	1.5	1.81 (6.5)
This work	Type B PAN-based	Zoltek	Unsized	7.3 (2.9)	8 (0.3)	1.55 (0.610)	3800 (0.55)	228 (33.1)	1.5	1.81 (6.5)

*Discontinued.



(a)



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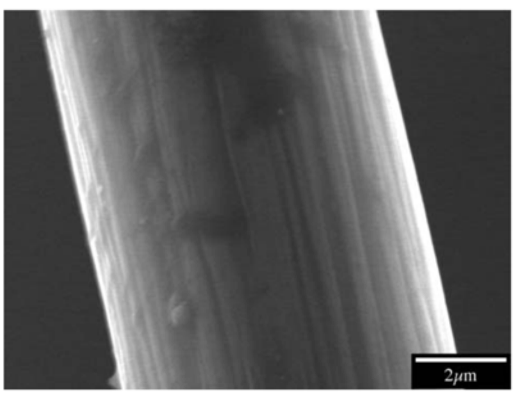

(c)

Fig. 1—SEM photographs of carbon fibers: (a) Type A carbon fiber; (b) Type B carbon fiber; and (c) Type A carbon fiber without desizing (as-received state). All photographs are at same magnification.

Type A. The variation in fiber diameter is large for Type A, presumably due to the variation in the extent of oxidation. Prior to the desizing treatment, the fiber (Fig. 1(c)) is approximately 7.7 μm (3.0×10^{-4} in.) in diameter. The surface microstructure also differs among these types of fibers. Striations (undulations) along the fiber axis are particularly clear on the surface of the Type B fiber. The presence of the sizing (Fig. 1(c)) makes these striations unclear. The carbon surface region removal associated with the desizing treatment also makes the striations unclear (Fig. 1(a)).

For Type A PAN-based carbon fiber, only the fiber content of 0.50% by mass of cement was used. Type B PAN-based carbon fiber in amounts of 0.50, 1.00, 1.50, and 2.00% by mass of cement were used. Type A is studied at only one fiber content because of the lower effectiveness of Type A compared to Type B in lowering the resistivity and providing shielding. In the case of cement paste (without aggregate), these fiber contents correspond to 0.50, 1.00, 1.50, and 2.00 vol.% of the cement paste; in the case of the mortar (with sand), they correspond to 0.24, 0.48, 0.72, and 0.96 vol.% of the mortar. In the case of the pitch-based fibers (15 μm, [6×10^{-4} in.], diameter, Table 1) in cement paste, the percolation threshold was between 0.5 and 1.0 vol.%.[25] In the case of pitch-based fibers (7 μm [3×10^{-4} in.] diameter) of prior work, it was between 0.4 and 0.8 vol.%, both in cement paste and in mortar with a sand-cement ratio of 1.0.[26] The percolation threshold depends on the fiber diameter, as expected.

Table 2—Methods of preparing carbon fiber prior to incorporation in cement mixture

	Fiber type	Step 1	Step 2
Prior work[8]	Pitch-based	Dry for 1 hour at 110°C (230°F)	Ozone treat for 10 minutes at 160°C (320°F)
This work	Type A PAN-based	Desize for 4 hours at 500°C (932°F)	Ozone treat for 10 minutes at 160°C (320°F)*
This work	Type B PAN-based	Dry for 1 hour at 110°C (230°F)	Ozone treat for 10 minutes at 160°C (320°F)

*Immediately after Step 1, fiber is cooled to 160°C (320°F) for ozone treatment.

The cement is a Type 1 portland cement. The sand is natural sand (100% passing 2.36 mm sieve, 99.9% SiO_2). The sand-cement ratio is 1.00 when sand is present. The water-cement ratio (*w/c*) is 0.35. A high-range water-reducing admixture was used in amounts ranging from 1.0 to 2.0% by mass of cement; the higher the fiber content, the greater the proportion of water-reducing admixture, as needed to maintain the slump at 75 to 120 mm (3.0 to 4.7 in.) (Table 3). No coarse aggregate was used.

Silica fume was used in the amount of 15% by mass of cement. The silica fume had a particle size of 0.03 to 0.5 μm (1×10^{-6} to 2×10^{-5} in.), with an average size of 0.2 μm (8×10^{-6} in.). Due to its small particle size, silica fume is effective in helping the fiber dispersion.[27] The methylcellulose was used in the amount of 0.4% by mass of cement. Methylcellulose is a water-soluble polymer that helps the fiber-matrix bonding.[28] The defoamer, used in the amount of 0.13% (% of specimen volume), was necessary to remove the air bubbles introduced by the presence of methylcellulose.

A rotary mixer with a flat beater was used for mixing. Methylcellulose was dissolved in water and then the defoamer and fibers were added and stirred by hand for approximately 2 minutes. Then, the methylcellulose mixture, cement, water, and silica fume were mixed for 5 minutes. After pouring the mixture 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. Three specimens of each composition were tested for each type of test, except that six specimens of each composition were tested for electrical resistivity.

For shielding testing, the attenuations upon reflection and transmission were measured using the coaxial cable method (the transmission line method). The setup consisted of a

Table 3—Water-reducing admixture proportion and slump for various carbon-fiber cement mixtures and cement-based material density after curing

PAN-based carbon fiber type	Fiber content			WR/cement,* %	Slump, mm (in.)		Density, g/cm³ (10⁻² lb/in.³)	
	Percent by mass of cement	Vol. %						
		Without sand	With sand		Without sand	With sand	Without sand	With sand
A	0.50	0.50	0.24	1.00	82 ± 5 (3.2 ± 0.2)	85 ± 3 (3.3 ± 0.1)	1.45 ± 0.12 (5.24 ± 0.43)	1.52 ± 0.06 (5.49 ± 0.22)
B	0.50	0.50	0.24	1.00	77 ± 3 (3.0 ± 0.1)	85 ± 6 (3.3 ± 0.2)	1.43 ± 0.05 (5.17 ± 0.18)	1.54 ± 0.10 (5.56 ± 0.36)
B	1.00	1.00	0.48	1.25	95 ± 4 (3.7 ± 0.2)	99 ± 5 (3.9 ± 0.2)	1.49 ± 0.10 (5.38 ± 0.36)	1.70 ± 0.04 (6.14 ± 0.14)
B	1.50	1.50	0.72	1.50	110 ± 7 (4.3 ± 0.3)	116 ± 5 (4.6 ± 0.2)	1.55 ± 0.10 (5.60 ± 0.36)	1.79 ± 0.09 (6.47 ± 0.33)
B	2.00	2.00	0.96	2.00	112 ± 4 (4.4 ± 0.2)	117 ± 5 (4.6 ± 0.2)	1.61 ± 0.06 (5.82 ± 0.22)	1.88 ± 0.12 (6.79 ± 0.43)

*WR is water-reducing admixture.

Table 4—Attenuation (dB) of ratio wave upon transmission (same as EMI shielding effectiveness)

PAN-based carbon fiber type	Fiber content			Specimen thickness, mm (in.)		Shielding effectiveness (dB)			
	Percent by mass of cement	Vol.%				1.0 GHz		1.5 GHz	
		Without sand	With sand	Without sand	With sand	Without sand	With sand	Without sand	With sand
A	0.50	0.50	0.24	4.1 ± 0.5 (0.16 ± 0.02)	4.2 ± 0.4 (0.17 ± 0.02)	19.2 ± 4.1	13.5 ± 3.5	18.4 ± 3.5	13.0 ± 4.1
B	0.50	0.50	0.24	4.3 ± 0.6 (0.17 ± 0.02)	4.3 ± 0.4 (0.17 ± 0.02)	26.9 ± 2.5	25.9 ± 3.4	25.7 ± 4.3	23.1 ± 1.5
B	1.00	1.00	0.48	4.1 ± 0.4 (0.16 ± 0.02)	4.2 ± 0.2 (0.17 ± 0.01)	29.0 ± 2.5	27.2 ± 2.9	28.5 ± 4.2	25.5 ± 3.5
B	1.50	1.50	0.72	4.0 ± 0.1 (0.15 ± 0.00)	4.1 ± 0.2 (0.16 ± 0.01)	31.5 ± 3.5	30.8 ± 4.5	29.5 ± 2.8	27.2 ± 3.5
B	2.00	2.00	0.96	4.2 ± 0.4 (0.17 ± 0.02)	4.0 ± 0.2 (0.16 ± 0.01)	34.0 ± 2.8	32.6 ± 4.3	33.0 ± 4.2	30.5 ± 3.3

shielding effectiveness tester with its input and output connected to a network analyzer. A calibration kit was used to calibrate the system. The frequency was either 1.0 or 1.5 GHz, with the upper limit of the frequency imposed by the specimen dimensions. The specimen placed in the center plane of the tester (with the input and output of the tester on the two sides of the specimen) is in the form of an annular ring of an outer diameter of 97 mm (3.8 in.) and an inner diameter of 29 mm (1.1 in.). Silver paint was applied at both inner and outer edges of each specimen and at the vicinity of the edges to make electrical contact with the inner and outer conductors of the tester.[29] The sample thickness, as measured for each specimen, was approximately 4.3 mm (0.17 in.).

The DC volume electrical resistivity was measured using a multimeter and the four-probe method. In this method, four electrical contacts were applied by silver paint around the whole perimeter at four planes perpendicular to the length of the specimen (60 x 12 x 11 mm [2.4 x 0.47 x 0.43 in.]). The four planes are symmetrical around the midpoint along the length of the specimen, such that the outer contacts (for passing current) are 50 mm (2.0 in.) apart and the inner contacts (for measuring the voltage) were 30 mm (1.2 in.) apart.

The flexural strength was measured under three-point bending, with the specimen in the shape of a beam with dimensions 160 x 40 x 40 mm (6.3 x 1.6 x 1.6 in.). The span was 140 mm (5.5 in.). A hydraulic mechanical testing system was used at a controlled displacement speed of 0.5 mm/min (0.02 in./min).

EXPERIMENTAL RESULTS AND DISCUSSION

The density of the cured specimens (Table 3) was slightly higher in the presence of sand. The density was similar for specimens with Type A and Type B fibers at the same volume fraction. The density was essentially independent of the fiber content.

The EMI shielding effectiveness (Table 4) was considerably higher for Type B fiber specimens than Type A fiber specimens at the same fiber volume fraction, whether sand is present or not. An increase in the Type B fiber content increases the shielding effectiveness, but the effect is not significant. For each fiber content in percentage by mass of cement, the addition of sand caused a slight decrease of the shielding effectiveness. This is attributed to the decrease in the fiber volume fraction when sand is added. At the same fiber volume fraction, the shielding effectiveness is similar with and without sand, as shown for the fiber volume fraction of 0.5%, for which the shielding effectiveness at 1.0 GHz was 26.9 ± 2.5 dB without sand and 27.2 ± 2.9 dB with sand, and also shown for the fiber volume fraction of 1.0%, for which the shielding effectiveness at 1.0 GHz was 29.0 ± 2.5 dB without sand and 32.6 ± 4.3 dB with sand. The results were similar at 1.0 and 1.5 GHz. Figure 2 shows that the shielding effectiveness at 1.0 GHz increases with increasing fiber volume fraction, with the presence of sand having little (if any) effect on the shielding effectiveness at a given fiber volume fraction.

Pitch-based carbon fiber gives a shielding effectiveness of 9 dB at 1 GHz (0.5% by mass of cement in cement paste, corresponding to 0.5 vol.%) and 13 dB at 1 GHz (1.0% by mass of cement in cement paste, corresponding to 1.0 vol.%).[8]

The comparison of these data with those in Table 4 shows that the PAN-based fiber, whether Type A or B, is more effective than the pitch-based fiber for providing shielding. The superiority of the PAN-based fiber is partly due to the smaller diameter of the PAN-based fiber (7 μm [3×10^{-4} in.]) compared to the pitch-based fiber (15 μm [6×10^{-4} in.]).

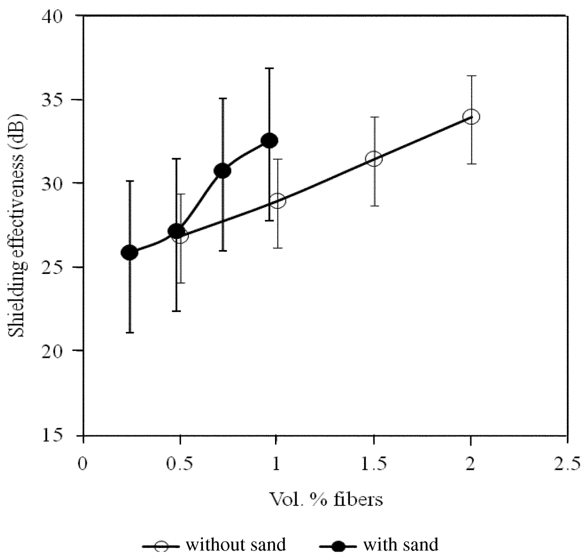

Fig. 2—Effect of Type B PAN-based carbon-fiber volume fraction on EMI shielding effectiveness for cement paste (without sand) and mortar (with sand). Each curve merely connects the points.

This explanation is supported by prior work, which shows that a smaller diameter gives a lower percolation threshold.[25,26] Fiber of a smaller diameter provides a larger fiber-cement interface area per unit volume of the composite. Due to the skin effect (the phenomenon in which the electromagnetic radiation only penetrates the near-surface region of a conductor) and the reflection mechanism of shielding, a larger interface area promotes shielding.

Table 5 shows that the attenuation upon reflection is lower for the Type B fiber specimens than the Type A fiber specimens. This difference occurs in spite of the smaller diameter of the Type A fiber. This means that the reflectivity is higher for the Type B fiber specimens. The higher reflectivity for Type B is probably associated with the clearer surface microstructure of Type B (Fig. 1(b)) because the presence of a surface layer that is poorly ordered carbon would have decreased the reflectivity. The higher reflectivity is consistent with the higher shielding effectiveness shown for the Type B fiber specimens in Table 4. In other words, the increase in reflectivity contributes to causing the higher shielding effectiveness for the Type B case.

An increase in the Type B fiber content essentially does not affect the attenuation upon reflection; the effect, if any, is overshadowed by the data scatter. At the same fiber content in percentage by mass of cement, the addition of sand essentially does not affect the attenuation upon reflection; the effect, if any, is overshadowed by the data scatter.

Table 6 shows that the electrical resistivity is much lower for Type B than Type A specimens at the same fiber volume fraction, whether sand is present or not. This difference, which occurs in spite of the smaller diameter of the Type A

Table 5—Attenuation (dB) of radio wave upon reflection. (The smaller is the attenuation upon reflection; the greater is reflectivity)

PAN-based carbon fiber type	Fiber content			Specimen thickness, mm (in.)		Shielding effectiveness (dB)			
		Vol.%				1.0 dB		1.5 dB	
	% by mass of cement	Without sand	With sand	Without sand	With sand	Without sand	With sand	Without sand	With sand
A	0.50	0.50	0.24	4.1 ± 0.5 (0.16 ±0.02)	4.2 ± 0.4 (0.17 ± 0.02)	3.05 ± 0.11	3.51 ± 0.59	2.86 ± 0.26	3.14 ± 0.82
B	0.50	0.50	0.24	4.3 ± 0.6 (0.17 ± 0.02)	4.3 ± 0.4 (0.17 ± 0.02)	2.69 ± 0.12	2.04 ± 0.18	2.25 ± 0.15	2.54 ± 0.41
B	1.00	1.00	0.48	4.1 ± 0.4 (0.16 ± 0.02)	4.2 ± 0.2 (0.17 ± 0.01)	2.45 ± 0.34	2.63 ± 0.45	2.56 ± 0.22	2.45 ± 0.12
B	1.50	1.50	0.72	4.0 ± 0.1 (0.15 ± 0.00)	4.1 ± 0.2 (0.16 ± 0.01)	2.22 ± 0.22	2.34 ± 0.32	2.78 ± 0.19	2.64 ± 0.20
B	2.00	2.00	0.96	4.2 ± 0.4 (0.17 ± 0.02)	4.0 ± 0.2 (0.16 ± 0.01)	2.32 ± 0.14	2.27 ± 0.20	2.55 ± 0.15	2.34 ± 0.11

Table 6—Electrical resistivity

PAN-based carbon fiber type	Fiber content			Electrical resistivity, Ω.cm (Ω.in.)	
		Vol. %			
	% by mass of cement	Without sand	With sand	Without sand	With sand
A	0.50	0.50	0.24	$(5.82 \pm 0.68) \times 10^4$ [(2.29 ± 0.27) x 10^4]	$(8.15 \pm 0.55) \times 10^4$ [(3.21 ± 0.22) x 10^4]
B	0.50	0.50	0.24	$(1.54 \pm 0.52) \times 10^3$ [(0.61 ± 0.20) x 10^3]	$(5.27 \pm 0.43) \times 10^3$ [(2.07 ± 0.17) x 10^3]
B	1.00	1.00	0.48	$(6.62 \pm 0.42) \times 10^2$ [(2.61 ± 0.17) x 10^2]	$(1.41 \pm 0.33) \times 10^3$ [(5.55 ± 1.30) x 10^2]
B	1.50	1.50	0.72	$(2.30 \pm 0.63) \times 10^2$ [(0.91 ± 0.25) x 10^2]	$(6.56 \pm 0.25) \times 10^2$ [(2.58 ± 0.10) x 10^2]
B	2.00	2.00	0.96	$(4.33 \pm 0.46) \times 10^1$ [(1.70 ± 0.18) x 10^1]	$(7.89 \pm 0.55) \times 10^1$ [(3.11 ± 0.22) x 10^1]

fiber, is probably associated with the clearer surface microstructure of Type B (Fig. 1(b)) because the presence of a surface layer that is poorly ordered carbon would have increased the contact resistivity between the fiber and the cement matrix.

An increase of the Type B fiber content decreases the resistivity monotonically, such that the effect is particularly large between fiber contents of 1.5 and 2.0% by mass of cement (that is, between 1.5 and 2.0 vol.%), whether sand is present or not. This suggests that the percolation threshold is between 1.5 and 2.0 vol.% when sand is absent, and is between 0.72 and 0.96 vol.% when sand is present. This implies that the presence of sand facilitates percolation, probably due to the double percolation that can occur in the presence of sand. Double percolation refers to percolation of the fiber in the cement paste, in addition to the percolation of the cement paste in the mortar.[30] Due to the volume occupied by the sand, the presence of sand causes the fibers to be localized to the cement paste part of the mortar, so that, for the same overall fiber volume fraction, the fiber volume fraction in the cement paste is higher in the presence of sand. As a consequence, the presence of sand allows percolation to occur at a relatively low overall fiber volume fraction. At the same fiber content in percentage by mass of cement, the presence of sand increases the resistivity. At the same fiber volume fraction of 1%, the presence of sand decreases the resistivity greatly from $(6.62 \pm 0.42) \times 10^2$ to $(7.89 \pm 0.55) \times 10^1$ Ω.cm [$(2.61 \pm 0.17) \times 10^2$ to $(3.11 \pm 0.22) \times 10^1$ Ω.in.]. At the same fiber volume fraction of 0.5%, the presence of sand essentially does not affect the resistivity, as the change is from $(1.54 \pm 0.52) \times 10^3$ to $(1.41 \pm 0.33) \times 10^3$ Ω.cm [$(0.61 \pm 0.20) \times 10^3$ to $(5.55 \pm 1.30) \times 10^2$ Ω.in.]. The effect of sand at a high fiber volume fraction of 1% is because percolation in the cement paste is promoted by the presence of sand, that is, the presence of sand enables double percolation. The absence of the effect of sand at a low fiber volume fraction of 0.5% is because this low fiber volume fraction is inadequate for percolation in the cement paste (whether sand is present or not). Figure 3 shows that the resistivity decreases with increasing fiber volume fraction, whether sand is present or not. The decrease, however, is more significant for the same range of fiber volume fraction change when sand is present. At the same fiber volume fraction, the presence of sand tends to decrease the resistivity.

Figure 4 shows that a high shielding effectiveness correlates with a low resistivity. The correlation is particularly strong when cement-based materials with the same type of fiber (Type B) are compared, with the correlation curve essentially unaffected by the presence of sand. The relatively small effect of fiber volume fraction on the shielding effectiveness is in contrast to the large effect of fiber volume fraction on the resistivity. This contrast is because electrical connectivity is more important for electrical conduction than shielding.

Table 7 shows that the flexural strength and modulus are slightly lower for Type B than Type A specimens at the same fiber volume fraction, though the effect is more substantial for the strength than the modulus. An increase of the Type B fiber content increases the flexural strength and modulus monotonically, whether sand is present or not, such that the effect on the strength is particularly large when the fiber content is increased from 0.5 to 1.0% by mass of cement. The effect of the fiber content on the modulus is small compared to the effect on the strength.

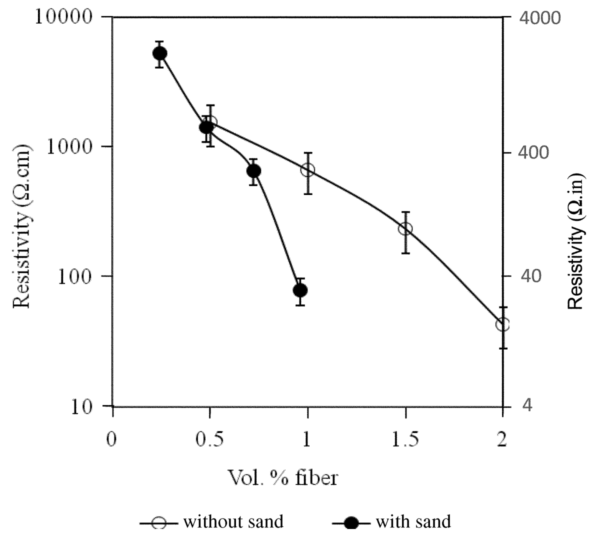

Fig. 3—Effect of Type B PAN-based carbon-fiber volume fraction on electrical resistivity (log scale) of cement paste (without sand) and mortar (with sand). Each curve merely connects the points.

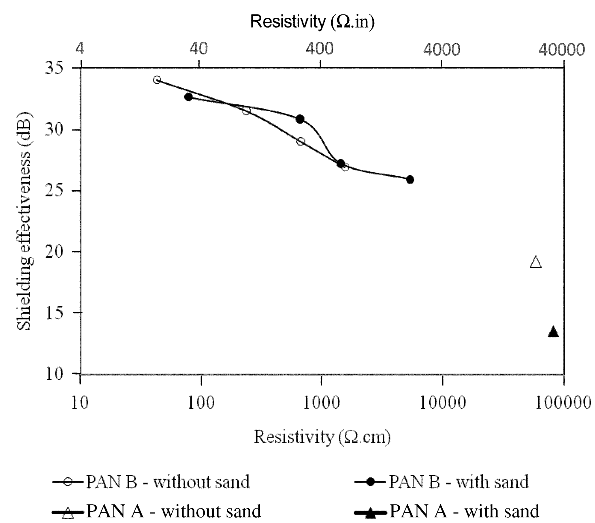

Fig. 4—Correlation of shielding effectiveness and electrical resistivity (log scale) for various cement-based materials, that is, cement paste (without sand) and mortar (with sand). In each case, specimens include those that contain Type B PAN-based carbon fiber at 0.5 to 2.0% by mass of cement and those that contain Type A PAN-based carbon fiber at 0.5% by mass of cement. Each curve merely connects the points.

At the same fiber content in percentage by mass of cement, the addition of sand increases the flexural strength slightly. This is due to the reinforcing ability of the sand, which is observed weakly in the presence of the dilution effect of sand on the reinforcing provided by the fiber. At the same fiber volume fraction, the presence of sand increases the strength substantially, as shown for fiber volume fractions of 0.5% (7.49 ± 0.12 MPa [1.04 ± 0.02 ksi] without sand and 11.40 ± 0.09 MPa [1.65 ± 0.01 ksi] with sand) and 1.0% (11.24 ± 0.12 MPa [1.63 ± 0.02 ksi] without sand and 14.75 ± 0.14 MPa [2.14 ± 0.02 ksi] with sand). This is due to the reinforcing ability of the sand, as observed strongly in the absence of a

Table 7—Flexural properties

PAN-based carbon fiber type	Fiber content: Percent by mass of cement	Fiber content: Vol. %, Without sand	Fiber content: Vol. %, With sand	Flexural strength, MPa (ksi): Without sand	Flexural strength, MPa (ksi): With sand	Flexural modulus, GPa (Msi): Without sand	Flexural modulus, GPa (Msi): With sand	Flexural strain* at maximum stress: Without sand	Flexural strain* at maximum stress: With sand
A	0.50	0.50	0.24	8.15 ± 0.15 (1.18 ± 0.02)	8.36 ± 0.18 (1.21 ± 0.03)	2.11 ± 0.02 (0.306 ± 0.003)	2.09 ± 0.03 (0.303 ± 0.004)	0.0026 ± 0.0001	0.0027 ± 0.0001
B	0.50	0.50	0.24	7.49 ± 0.12 (1.04 ± 0.02)	7.84 ± 0.16 (1.14 ± 0.02)	1.98 ± 0.01 (0.287 ± 0.001)	2.04 ± 0.02 (0.296 ± 0.003)	0.0020 ± 0.0003	0.0025 ± 0.0001
B	1.00	1.00	0.48	11.24 ± 0.12 (1.63 ± 0.02)	11.40 ± 0.09 (1.65 ± 0.01)	2.16 ± 0.04 (0.313 ± 0.006)	2.15 ± 0.02 (0.312 ± 0.003)	0.0021 ± 0.0002	0.0033 ± 0.0002
B	1.50	1.50	0.72	12.89 ± 0.15 (1.87 ± 0.02)	13.64 ± 0.13 (2.00 ± 0.02)	2.44 ± 0.04 (0.354 ± 0.006)	2.22 ± 0.03 (0.322 ± 0.004)	0.0024 ± 0.0001	0.0031 ± 0.0003
B	2.00	2.00	0.96	14.19 ± 0.12 (2.06 ± 0.02)	14.75 ± 0.14 (2.14 ± 0.02)	2.63 ± 0.03 (0.381 ± 0.004)	2.43 ± 0.04 (0.352 ± 0.006)	0.0025 ± 0.0002	0.0034 ± 0.0002

*Magnitude of longitudinal strain at surface.

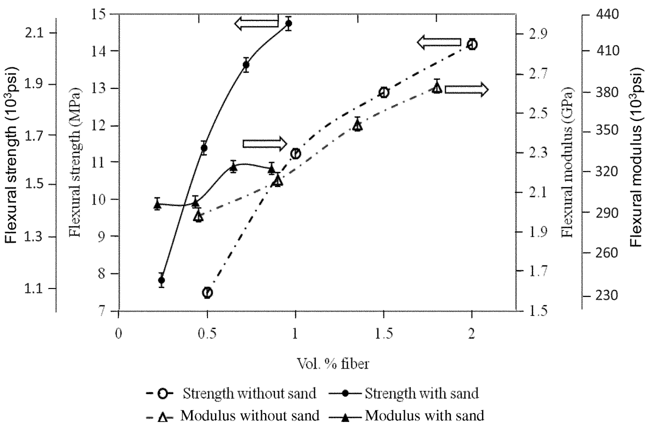

Fig. 5—Effect of Type B PAN-based carbon fiber volume fraction on flexural strength and modulus of cement paste (without sand) and mortar (with sand). Each curve merely connects the points.

dilution effect of the sand when the fiber volume fraction is fixed.

At the same fiber content in percentage by mass of cement, the addition of sand affects the flexural modulus only slightly, if at all. At the same fiber volume fraction, the presence of sand increases the modulus, as shown for fiber volume fractions of 0.5% (1.98 ± 0.01 GPa [0.287 ± 0.001 Msi] without sand and 2.15 ± 0.02 GPa [0.312 ± 0.003 Msi] with sand) and 1.0% (2.16 ± 0.04 GPa [0.313 ± 0.006 Msi] without sand and 2.43 ± 0.04 GPa [0.352 ± 0.006 Msi] with sand). The explanation is the same as that for the flexural strength.

That the sand addition helps the flexural properties but degrades the electrical properties is expected from the fact that sand is not conductive and acts mainly as a reinforcement. This finding suggests that the optimum concrete mixture design for mechanical performance and that for electrical performance may be different.

Figure 5 clearly shows that the flexural strength and modulus are both increased by the presence of sand, for a given fiber volume fraction. The substantial and positive effects of sand on the strength and modulus at the same fiber volume fraction are due to: 1) the reinforcing ability of the sand; and 2) the increased fiber volume fraction in the cement paste part of the composite when sand is present.

At the same fiber volume fraction, the addition of sand increases the shielding effectiveness and decreases the resistivity but increases the flexural strength and modulus. The effects of the shielding and the resistivity are because the presence of sand allows percolation to occur at a relatively low fiber volume fraction. The effects on the flexural strength and modulus are mainly because of the reinforcing ability of the sand. Percolation affects the electrical properties much more than the mechanical properties.

The flexural strain at the maximum stress is similar for Type B and Type A specimens at the same fiber volume fraction. The effect of the fiber content on the strain at maximum stress is essentially absent when sand is absent. When sand is present, the strain at the maximum stress tends to increase with the fiber content, such that the increase is clearest when the fiber content is increased from 0.5 to 1.0% by mass of cement. For Type B, at the same fiber content in percentage by mass of cement, the presence of sand increases the strain at the maximum stress. At the same Type B fiber content in volume fraction, the presence of sand increases significantly the strain at the maximum stress, as shown for fiber volume fractions of 0.5% (0.0020 ± 0.0003 without sand and 0.0033 ± 0.0002 with sand) and 1.0% (0.0021 ± 0.0002 without sand and 0.0034 ± 0.0002 with sand).

Figure 6 shows that the flexural strength increases with the fiber volume fraction, whether sand is present or not. The curve of flexural stress versus midspan deflection (as indicated by the stroke or displacement, with the displacement meaning that of the actuator of the mechanical testing system) has a tail after the highest stress has been reached. This tail occurs for all fiber volume fractions, whether sand is present or not. The deflection at the peak stress tends to be higher in the presence of sand. In addition, the tail extends to higher deflection in the presence of sand. Hence, the presence of sand enhances the toughness.

The slightly inferior reinforcing ability of Type B fiber than Type A fiber correlates with the substantial superiority of Type B fiber for providing shielding and low resistivity. This suggests that there is less interfacial material (for example, poorly ordered carbon) at the fiber-cement interface for Type B than Type A, as supported by Fig. 1. The interfacial material apparently enhances the fiber-cement bond, thereby increasing the reinforcing ability of the fiber. The interfacial material also increases the contact electrical resistivity of the fiber-cement interface, however, thereby increasing the volume electrical resistivity of the composite and decreasing the shielding effectiveness of the composite.

CONCLUSIONS

A PAN-based carbon fiber with a diameter of 7 μm (3 × 10^{-4} in.) is effective for providing shielding, low electrical

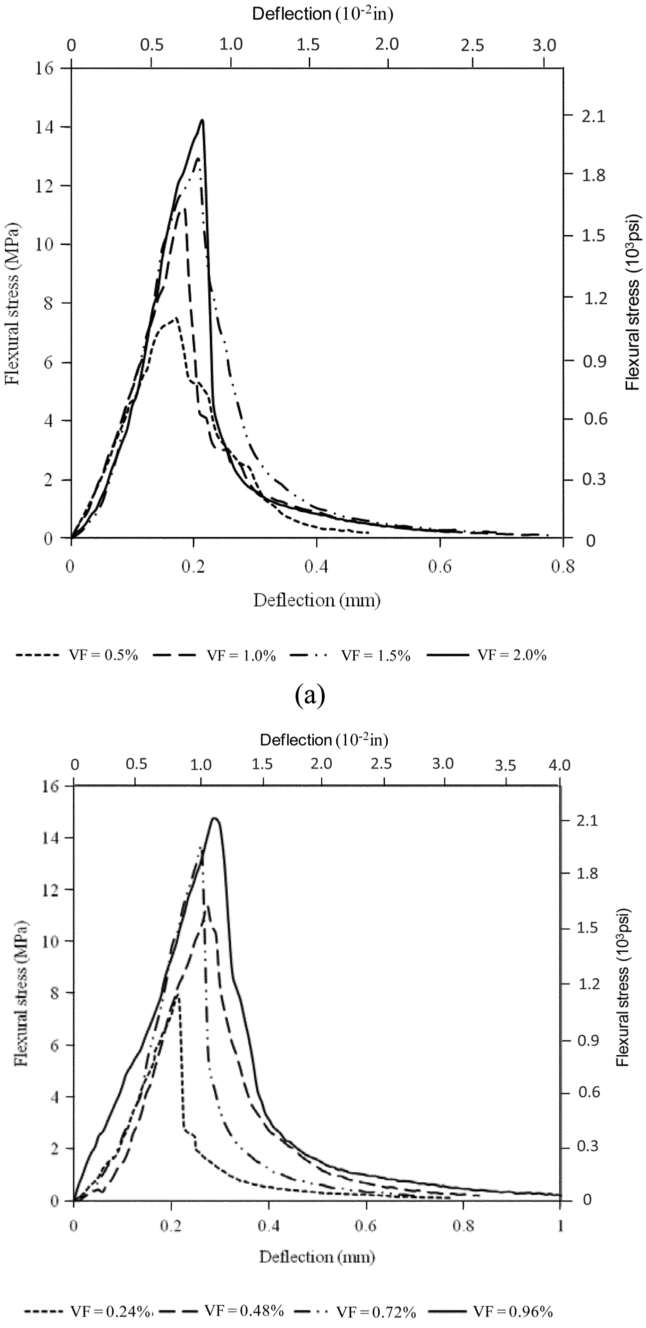

Fig. 6—Flexural stress versus midspan deflection (as indicated by stroke or displacement) during flexural testing: (a) cement paste (without sand); and (b) mortar (with sand). VF is fiber-volume fraction. Type B PAN-based carbon fiber is used.

resistivity, and high flexural strength and modulus to cement-based materials. Its ability to provide shielding is superior to that of pitch-based carbon fiber with a diameter of 15 μm (6×10^{-4} in.). The shielding effectiveness 30 dB at 1 GHz is provided by cement paste containing 1 vol.% Type B PAN-based carbon fiber (unsized). Type A PAN-based carbon fiber (desized) is less effective than Type B PAN-based carbon fiber for providing shielding, reflection, and low electrical resistivity; but it is more effective as a reinforcement. This difference in performance is attributed to a difference in the fiber surface structure. There appears to be more highly ordered carbon on the surface of Type B fiber than Type A fiber. An increase in the fiber content increases the shielding effectiveness, decreases the resistivity, and increases the flexural strength and modulus.

For each fiber content in percentage by mass of cement, the addition of sand causes slight decrease of the shielding effectiveness. This is attributed to the decrease in the fiber volume fraction when sand is added. At the same fiber volume fraction, the shielding effectiveness is similar for cases with and without sand. The relatively small effect of fiber volume fraction on the shielding effectiveness is in contrast to the large effect of fiber volume fraction on the resistivity.

At the same fiber content in percentage by mass of cement, the presence of sand increases the resistivity. At the same fiber volume fraction of 1%, the presence of sand decreases the resistivity greatly. At the same fiber volume fraction of 0.5%, the presence of sand essentially does not affect the resistivity.

An increase in the fiber content increases both the flexural strength and modulus, though the effect on the strength is greater than that on the modulus. At the same fiber content in percentage by mass of cement, the addition of sand slightly increases the flexural strength. At the same fiber volume fraction, however, the presence of sand increases the strength substantially.

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