critical dimensions of the molecules, especially when their initial concentration in the gas-air flow is low. Table 3 shows that increasing degree of activation results in a regular increase of the duration of the protective action of the adsorbent layer with respect to benzyl vapor and the dynamic adsorption capacity with respect to benzyl vapors is higher than for industrial carbon adsorbents. The duration of the protective fraction with respect to ethylchloride vapor also increases.

Tests were carried out on the resultant adsorbents with sorption cleaning of effluents (from the discharge stream of a roasting plant) with an arsenic content of 30.4 mg/dm^3. The kinetic characteristics, Table 3, were recorded by the method of constant concentrations of the target components and the salt composition with the solution changed under the static conditions with agitation in a mixer. The ratio of the sorbent and the solution was 1:500. Arsenic was determined by the photocalorimetric method using silver diethyldithiocarbamate (Table 3).

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Submicron-diameter-carbon-filament cement-matrix composites

XULI FU and D.D.L. CHUNG

Composite Materials Research Laboratory, SUNY Buffalo, Buffalo, NY 14260-4400, USA

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Submicron-diameter carbon filaments made catalytically from carbonaceous gases [1,2] are characterized by being discontinuous and naturally bent. This morphology has made these filaments not particularly attractive as a reinforcement for advanced composites, compared to conventional carbon fibers, which have diameter around 10 μm, can be continuous and are made from pitch or polymers [3-5]. For advanced composites, such as polymer-matrix composites for aerospace structures, continuous fibers are required in order to achieve sufficient strength and modulus. On the other hand, cement-matrix composites, such as concrete for civil structures, require low cost and prefer processability by mixing with cement, water, sand and other ingredients. For low cost and processability, short fibers are preferred to continuous fibers, even though they are less effective than continuous fibers as a reinforcement. Therefore, submicron-diameter carbon filaments, which are discontinuous, are suitable for use as a reinforcement in cement-matrix composites [6].

The interface between the reinforcement and the matrix in a composite is critical to the effectiveness of the reinforcement. For a reinforcement with a small diameter, the interface area per unit volume of the composite is large for a give volume fraction of the reinforcement. Under this situation, the quality of the interface is even more critical. In order to improve the interface quality, the reinforcement may be surface treated. This paper provides a surface treatment method for the submicron diameter carbon filaments. The treatment results in significant improvement of the mechanical properties of the carbon filament cement-matrix composites.

An application of discontinuous carbon fibers is as a filler in composite materials used for electromagnetic interference (EMI) shielding. Discontinuous fibers are used for this application [7] because they allow composite fabrication by injection molding and other conventional techniques for shaping polymers. Due to the skin effect, electromagnetic radiation at high frequencies (e.g., 1 GHz) interacts only with the near surface region of an electrical conductor. Therefore, at a given volume fraction of fibers in a composite, fibers with a smaller diameter are more effective for EMI shielding [6, 8-10]. Indeed, the submicron-diameter carbon filaments have been shown to be attractive for EMI shielding in a cement matrix [6] as well as a polymer matrix [8]. The shielding is mainly due to reflection rather than absorption, as shown in this work for a cement matrix. By using 1.5 vol.% carbon filaments in a cement matrix, we have attained in this work an EMI shielding effectiveness of 40 dB at 1 GHz. This is the highest shielding effectiveness ever attained for a cement-matrix composite. This level of shielding effectiveness would have required 10 vol.% carbon filaments (same type) if the matrix were a polymer (polyether sulfone) [11]. Concrete capable of EMI shielding is useful for structures that house electronics.

The reflection of radio waves or microwaves is an ability that is desired for waveguides and for electromagnetic detection. For concrete, electromagnetic detection is particularly relevant, since reflecting concrete may be used for lateral guidance in automatic highways. Current technology uses magnetic sensors together with magnetic highway markings (embedded magnets) to provide lateral guidance, and uses radar to monitor the vehicle position relative to other vehicles in its lane for the purpose of longitudinal guidance [12-14]. An alternate lateral guidance technology uses concrete that reflects radio wave electromagnetic radiation as highway marking, which is either in the middle or at the two sides of each lane. The marking is sensed by radio wave electromagnetic radiation emitted by each vehicle, thereby achieving lateral guidance. In other words, the vehicle has a transmitter that emits the radiation straight down to the reflecting concrete, the radiation is reflected by the concrete and detected by a detector in the vehicle. Compared to the magnetic technology, the attractions of the electromagnetic technology are low material cost, low labor cost, low peripheral electronic cost, good mechanical properties, good reliability, and high durability. This paper shows that submicron-diameter carbon-filament cement-matrix composites are effective for reflecting radio waves, in contrast to plain cement, which is a poor reflector.

Cement paste made from portland cement (Type I) from Lafarge Corp. (Southfield, MI) was used for the cementitious material. The admixtures used include (i) latex, a styrene butadiene copolymer (Dow Chemical Co., Midland, MI 460NA) with the polymer making up about 48% of the solution and with styrene and butadiene in the weight ratio 66:34, such that the latex (20% by weight of cement) was used along with an antifoam (Dow Corning Corp., Midland, MI, #2210, 0.5% by weight of latex), (ii) methylcellulose (Dow Chemical Corp., A15-LV, 0.4% by weight of cement), which was used along with a defoamer (Colloids Inc., Marietta, GA, Colloids 1010, 0.13 vol.%), (iii) silica fume (EMS 965, Elkem Materials Inc., Pittsburgh, PA, 15% by weight of cement), and (iv) carbon filaments, which were of diameter 0.1 μm and length >100 μm, and electrical resistivity 10^{-3} Ω.cm (estimate based on the resistivity of a filament compact, as single filament resistivity measurement was impossible), as obtained from Applied Sciences Inc. (Cedarville, Ohio). Methylcellulose, silica fume and latex serve to help the fiber dispersion [15]. The combined use of silica fume (average particle size 0.15 μm; particle size range 0.03 - 0.5 μm; 94% SiO_2) and methylcellulose (a surfactant) is particularly effective [15,16]. The filaments were used in amounts of 0.5, 1.0 and 1.5% by weight of cement; these amounts corresponded to filament volume fractions of 0.51, 1.0 and 1.5% respectively. The filaments had not been surface treated, unless noted otherwise. Surface treatment was performed by exposure to ozone (O_3) gas (0.3 vol.%, in air) for 10 minutes at 160°C. Prior to O_3 exposure, the filaments had been dried at 110°C in air for 1 hour. The water reducing agent was a sodium salt of a condensed naphthalenesulfonic acid (TAMOL SN, Rohm and Haas Co., Philadelphia, PA) used in amounts to maintain the slump at around 170 mm. No aggregate (whether fine or coarse) was used.

A Hobart mixer with a flat beater was used. For cement pastes containing latex, the latex, antifoam and filaments were first mixed by hand for about 1 min. Then this mixture, cement and water were mixed in the Hobart mixer for 5 minutes. For pastes containing methylcellulose, the methylcellulose was dissolved in water and then filaments and the defoamer were added and stirred by hand for about 2 minutes. Then this mixture, cement, water and silica fume (if applicable) were mixed in the mixer for 5 minutes. After pouring the mix into oiled molds, an external vibrator was used to 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 = 40%) for 28 days. All testing was performed at 28 days.

The attenuations upon reflection and transmission were measured using the coaxial cable method. The set-up consisted of an Elgal (Israel) SET 19A shielding effectiveness tester with its input and output connected to a Hewlett-Packard (HP) 8510A network analyzer. An HP APC-7 calibration kit was used to calibrate the system. The frequency was 1 GHz. The sample 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 32 mm. The sample thickness ranged from 3.6 to 4.4 mm.

The DC volume electrical resistivity was measured by the four-probe method (outer two probes for passing current and inner two probes for voltage measurement), using silver paint for the electrical contacts, which were applied around the perimeter of the specimen (160 x 40 x 40 mm) in four parallel planes perpendicular to the current direction (along the longest dimension of the specimen).

Tensile testing was performed on dogbone shaped specimens. The specimen cross section was 30 x 20 mm in the narrow part of the dogbone shape. The Sintech 2/D screw action mechanical testing system was used at a cross head speed of 1.27 mm/min. The strain was measured by using a strain gage attached to the narrow part of the dogbone shaped specimen. The strain allowed determination of the tensile modulus and ductility. For compressive testing according to ASTM C109-80, specimens were prepared by using a 2 x 2 x 2 in (5.1 x 5.1 x 5.1 cm) mold. Compression testing was performed using a hydraulic material testing system (MTS). The cross head speed was 1.27 mm/min.

By using 0.1 μm diameter carbon filaments (0.5-1.5 vol.%) as an admixture in cement paste, the reflectivity is 24-37 dB higher than the transmissivity, and reflectivity 10 dB higher than conventional cement paste (without admixture) has been attained (Table 1). The reflectivity is mostly due to the filaments, which strongly reflect. The intensity absorbed is negligible compared to that reflected. In contrast, without the filaments, the reflectivity is 3 - 11 dB lower than the transmissivity. As shown in Table 1, the attenuation upon reflection decreases (i.e., the reflectivity increases), the attenuation upon transmission (due to both reflection and absorption) increases (i.e., the transmissivity decreases), and the DC electrical resistivity decreases with increasing filament volume fraction. For Formula A (with methylcellulose and silica fume) or B (with latex), even at a filament volume fraction of just 0.5% (corresponding to 0.5% by weight of cement), the reflectivity is 29 dB higher than the transmissivity and the reflectivity is 10 dB higher than conventional cement paste. With both cost and performance considered, a carbon filament volume fraction of 0.5% is recommended. By using conventional carbon fibers (5 mm long, 10 μm diameter, based on isotropic pitch, from Ashland Petroleum Co., Ashland, KY, in the amount of 4 vol.%) instead of the carbon filaments, the reflectivity is even less than that of the cement paste with 0.5 vol.% carbon filaments. Thus, the carbon filaments of diameter 0.1 μm are much more effective than the carbon fibers of diameter 10 μm in providing radio wave reflecting concrete.

Admixtures such as methycellulose (0.4% by weight of cement) together with silica fume (15% by weight of cement), or latex (20% by weight of cement) are needed to help the dispersion of the filaments. As shown in Table 1, when filaments are present, both formulae A and B give similar attenuation, though Formula A gives lower resistivity than Formula B for the same filament volume fraction. The higher resistivity for Formula B is partly due to the higher filament/cement contact resistivity [17]. This contact resistivity affects the volume resistivity more than the attenuation, because

Table 1 Attenuation upon reflection and transmission* at 1 GHz and electrical resistivity of cement pastes. Formulation A has methylcellulose and silica fume. Formulation B has latex. Formulation C has no admixture.

Filament vol.%	Formulation	Attenuation (dB)		Sample thickness (mm)	Resistivity (Ω.cm)
		Reflection	Transmission		
0	C	11	0.4	3.6	1.62×10^5
0	A	13	1.9	4.4	2.32×10^5
0	B	7.1	4.5	3.8	2.75×10^5
0.5	C	1.8	26	4.0	1.93×10^4
0.5	A	1.3	30	3.9	1.34×10^4
0.5	B	1.3	30	4.1	8.14×10^4
1.0	A	1.1	35	3.7	1.21×10^4
1.0	B	0.9	36	3.9	7.82×10^4
1.5	A	0.8	38	3.8	1.08×10^4
1.5	B	0.7	40	4.0	7.41×10^4

*A high attenuation upon reflection means a low reflectivity. A high attenuation upon transmission means a low transmissivity and a high EMI shielding effectiveness.

connectivity is more important for conduction than for attenuation. The higher resistivity for Formula B is also partly due to the lower degree of fiber dispersion [15]. The slightly higher reflectivity for Formula B compared to Formula A is at least partly due to the larger sample thickness for Formula B at each filament volume fraction. Formula C is less attractive than Formula A or B, as shown by the low reflectivity and high transmissivity compared to Formula A or B at the same filament volume fraction. Because latex (20% by weight of cement) is expensive, Formula A is recommended.

For polyether sulfone (PES) matrix composites using the same filaments as this work, the volume resistivity is 3.78 and 0.368 Ω.cm at 7 and 13 vol.% filaments respectively and the shielding effectiveness (measured using the experimental set-up of this paper) is 32 and 54 dB at 7 and 13 vol.% filaments respectively [11]. Thus, to attain around 40 dB shielding in a PES-matrix composite, around 10 vol.% filaments are needed and this corresponds to a volume resistivity between 0.368 and 3.78 Ω.cm. In contrast, the volume resistivity of a cement-matrix composite exhibiting a shielding effectiveness of 40 dB is from 1×10^4 to 7×10^4 Ω.cm (depending on the formulation). High shielding effectiveness is exhibited by the cement-matrix composites in spite of the high volume resistivity.

Measurement of the volume resistivity as a function of the filament volume fraction shows that the percolation threshold is around 10% for PES as matrix [11] and more than 1.5% for cement as matrix (this work). Thus, a PES-matrix composite containing around 10 vol.% filaments is at or near the percolation threshold, whereas a cement-matrix composite containing 1.5 vol.% filaments is below the percolation threshold. The high resistivity of the cement-matrix composites is due to their being below the percolation threshold. The low resistivity of the PES-matrix composites is due to their being near the percolation threshold. Although the cement-matrix composites are below the percolation threshold, the cement matrix is slightly conducting (10^5 Ω.cm, Table 1) whereas the PES matrix is insulating (10^{10} Ω.cm [11]) and, as a consequence, there is a certain degree of electrical connectivity between the filaments in a cement-matrix composite below the percolation threshold. This connectivity is not sufficient for percolation, but enough for enhancing the shielding effectiveness. Furthermore, the cement matrix has slight absorptivity (Table 1). As a result, the cement-matrix composites of high volume resitivity (10^4 Ω.cm) exhibited shielding effectiveness that was as high as the PES-matrix composites of low volume resistivity (1 Ω.cm).

The results of this work on cement-matrix composites support the attraction of using a polymer matrix that is inherently slightly conducting in order to attain a composite of high shielding effectiveness. However, cement is much less expensive than any polymer, particularly the conducting polymers.

Surface treatment of the carbon filaments with ozone prior to incorporation of the filaments in concrete increases the surface oxygen concentration, thereby improving wettability by water and increasing the bond strength between filament and cement paste, as shown for the case of conventional carbon fibers [17-19]. As a result, the tensile strength, modulus and ductility and the compressive strength, modulus and ductility of cement paste are all increased by the ozone treatment of the carbon filaments, as shown in Table 2. Although the carbon filaments are not as effective as the conventional carbon fibers (5 mm long, 10 μm diameter, based on isotropic pitch, from Ashland Petroleum Co., Ashland, KY) as a reinforcement [18], they still reinforce, as shown by the low values of the tensile strength, tensile ductility and compressive modulus of the plain cement paste compared to the pastes with filaments in Table 2.

In conclusion, EMI shielding has been achieved using cement pastes with discontinuous 0.1 μm-diameter carbon filaments, such that the shielding effectiveness is 30, 36 and 40 dB (1 GHz) at 0.5, 1.0 and 1.5 vol.% filaments respectively (all below the percolation threshold), the shield thickness is 4 mm, and the volume electrical resistivity is 10^4 Ω.cm. In contrast, these filaments in a PES matrix require 10 vol.% (around the percolation threshold) for reaching 40 dB of shielding effectiveness. The high shielding effectiveness of a cement-matrix composite below the percolation threshold is due to the slightly conducting nature of the cement matrix (10^5 Ω.cm) providing some connectivity between the filaments and due to the slight absorptivity of the cement matrix. This connectivity is not enough for

Table 2 Effect of ozone treatment on the tensile and compressive properties of cement paste.

	P	+F	+F+M	+F+M+SF	+F+L
Tensile strength (MPa)					
Untreated	0.91(±2.7%)	1.23(±1.9%)	1.52(±2.5%)	1.67(±3.1%)	2.86(±3.2%)
Treated	0.91(±2.7%)	1.37(±2.2%)	1.73(±2.4%)	1.83(±2.7%)	2.98(±2.1%)
Tensile modulus (GPa)					
Untreated	11.2(±2.1%)	12.4(±1.9%)	8.7(±2.3%)	12.8(±1.2%)	6.8(±1.2%)
Treated	11.2(±2.1%)	13.8(±2.0%)	10.8(±1.7%)	15.2(±2.8%)	10.6(±2.8%)
Tensile ductility (%)					
Untreated	0.0041(±1.9%)	0.0090(±2.5%)	0.0160(±2.1%)	0.0140(±1.8%)	0.0360(±2.2%)
Treated	0.0041(±1.9%)	0.0120(±1.8%)	0.0201(±3.2%)	0.0210(±3.0%)	0.0425(±1.9%)
Compressive strength (MPa)					
Untreated	57.9(±3.2%)	40.9(±2.1%)	41.6(±2.8%)	47.2(±2.8%)	43.3(±2.0%)
Treated	57.9(±3.2%)	42.5(±1.5%)	43.5(±2.0%)	48.6(±3.0%)	45.1(±2.8%)
Compressive modulus (GPa)					
Untreated	2.92(±2.3%)	5.75(±1.2%)	3.52(±1.8%)	3.55(±1.4%)	3.72(±2.3%)
Treated	2.92(±2.3%)	6.47(±2.2%)	4.12(±3.1%)	4.16(±2.6%)	4.46(±1.6%)
Compressive ductility (%)					
Untreated	1.72(±2.2%)	1.12(±2.1%)	1.23(±1.7%)	1.29(±2.2%)	1.33(±1.5%)
Treated	1.72(±2.2%)	1.20(±2.1%)	1.27(±2.2%)	1.31(±2.7%)	1.45(±2.3%)

Note: P = plain (no admixture), F = filament (0.5% by weight of cement, or 0.51 vol.%), M = methylcellulose (0.4% by weight of cement), SF = silica fume (15% by weight of cement), and L = latex (20% by weight of cement).

percolation, but enough for enhancing the shielding effectiveness.

This paper provides radio wave reflecting concrete, which is potentially useful for lateral guidance in automatic highway technology. It contains 0.1 μm-diameter carbon filaments as an admixture. The radiation absorbed is negligible compared to that reflected. The reflectivity at 1 GHz is 10 dB higher for radio wave reflecting cement paste containing 0.5 vol.% filaments compared to conventional cement paste (without filaments). With the filaments, the reflectivity is 29 dB higher than the transmissivity. Without the filaments, the reflectivity is 3 - 11 dB lower than the transmissivity.

The filaments not only provide the cement paste with the ability to reflect electromagnetic radiation, it also reinforces the cement paste under tension, especially if the filaments have been treated with ozone prior to incorporation in the concrete. The compressive strength is decreased by the filaments, although the effect of the filaments on the compressive strength is much less than that on the tensile strength.

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