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Colloidal graphite as an admixture in cement and as a coating on cement for electromagnetic interference shielding

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Abstract

A water-based colloid of submicron graphite particles is an effective admixture for enhancing the EMI shielding effectiveness of cement paste, though it is ineffective for lowering the electrical resistivity. As an admixture, it is more effective for shielding than 15-μm-diameter discontinuous carbon fibers, though it is less effective than 0.1-μm-diameter discontinuous carbon filaments. A shielding effectiveness of 22 dB at 1 GHz is reached by cement paste at a solid graphite content of 0.92 vol.%, compared to a value of 11 dB for a coating made from the graphite colloid and a value of 14 dB for graphite-colloid-coated cement paste (without admixture).

Keywords: Electrical properties; Admixture; Cement paste

1. Introduction

EMI shielding [1–4] is in critical demand due to the interference of wireless (particularly radio frequency) devices with digital devices and the increasing sensitivity and importance of electronic devices. Shielding is particularly needed for underground vaults containing power transformers and other electronics that are relevant to electric power and telecommunication. It is also needed for deterring electromagnetic forms of spying.

Polymer–matrix composites containing electrically conductive fillers are widely used for the shielding of electronics. In contrast to a typical polymer matrix, which is electrically insulating, the cement matrix is slightly conductive. Therefore, the use of a cement matrix allows some degree of electrical connectivity among the conductive filler units, even when the filler volume fraction is below the percolation threshold. As electrical connectivity helps shielding, the cement matrix is attractive for the development of composite materials for shielding.

Electrically conductive admixtures in the form of discontinuous fibers [5–8] have been previously used in cement for providing EMI shielding. Although the fibers are effective, they are expensive and, in contrast to particles, have the tendency to cling together.

Colloidal graphite is fine graphite powder suspended in a liquid carrier (such as water and alcohol), usually together with a small amount of a polymeric binder. A small particle size of the powder is necessary for formation of a stable and workable colloid. After application of colloidal graphite on a surface by painting or related methods, the liquid carrier evaporates, thus allowing the graphite particles to be essentially in direct contact. The resulting coating is used for shielding in television scopes, in addition to being used as a lubricant. However, colloidal graphite has not been used on or in cement-based materials. Furthermore, there has been no report on the EMI shielding effectiveness of colloidal graphite, except for limited information in a commercial sales document [10].

The cost of graphite powder increases with decreasing particle size. However, due to the skin effect, the effectiveness of graphite powder (at a given volume fraction) for shielding is expected to increase with decreasing particle size. In spite of the relatively high cost of fine graphite powder, the cost is still low compared to that of carbon fibers or submicron-diameter carbon filaments. In this paper, the term "filaments" refers to those of diameter less than 1 μm, whereas the term "fibers" refers to those of diameter at least 1 μm.

This paper addresses the use of graphite colloid as an admixture in cement and as a coating on cement for provid-

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ing shielding. For the sake of comparison, this paper also addresses the shielding effectiveness of a colloidal graphite coating on Mylar, which is known for its electromagnetic transparency. Previous development of concrete for EMI shielding did not involve colloids, but only dry solid admixtures such as 15-μm-diameter carbon fibers [9], 0.1-μm-diameter carbon filaments [6], and 8-μm-diameter stainless steel fibers [8]. Colloids are attractive due to the submicron particles in them and the good dispersion of these particles, as attained by the use of surfactants. A small particle size is advantageous for EMI shielding due to the skin effect and the increased tendency for percolation. Furthermore, colloids are attractive for the cement mixing process due to their high fluidity. In addition, colloids can be used as a coating material, which can be applied to existing structures.

Because electrical resistivity is a basic quantity that describes the electrical conduction behavior, this paper includes measurement of electrical resistivity.

2. Experimental methods

The cement used was portland cement (Type I) from Lafarge (Southfield, MI). The water–cement ratio was 0.35. A water-reducing agent (a sodium salt of a condensed naphthalenesulfonic acid, TAMOL SN, Rohm and Haas, Philadelphia, PA) was used in the amount of 1.00% by mass of cement for all specimens. No aggregate was used, whether fine or coarse.

The colloidal graphite used in this work was a 9 lb/gallon (1 g/cm^3) dispersion of 22 wt.% graphite particles of average size 0.7–0.8 μm in deionized water (Grafo Hydrograf A M2 from Fuchs Lubricant, Emlenton, PA). The dispersion contains a starch-type binder. The density of solid graphite is 2.26 g/cm^3.

For shielding testing, the attenuations upon reflection and transmission were measured using the coaxial cable method (the transmission line method) (Fig. 1). The setup consisted of an Elgal (Israel) SET 19A shielding effectiveness tester with its input and output connected to a Hewlett-Packard (HP) 8510A network analyzer [10]. An HP APC-7 calibration kit was used to calibrate the system. The frequency was up to 1.5 GHz, as limited 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) was in the form of an annular ring of outer diameter 97 mm and inner diameter 29 mm. Silver paint was applied at both inner and outer edges of each specimen and near the edges to make electrical contact with the inner and outer conductors of the tester [11].

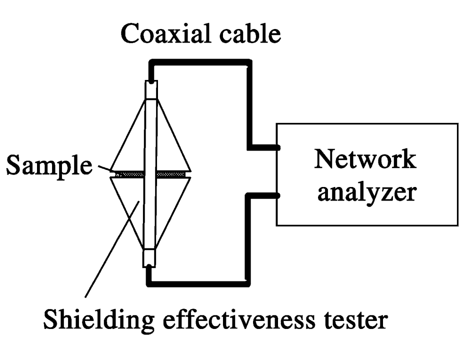

Fig. 1. EMI shielding effectiveness testing setup.

In the use of the colloid as an admixture, the water in the colloid was considered in the water–cement ratio mentioned earlier. The colloid was used as an admixture in proportions corresponding to the graphite solid amounting to 0.50% and 1.00% by mass of cement (corresponding to 0.46 and 0.92 vol.%, respectively). In the use of the colloid as a coating, the colloid was applied manually on one side of a specimen of cement paste (without admixture, in the form of an annular ring of dimensions mentioned above) and on one side of a Mylar sheet (60 μm thick, which had been cut to be an annular ring of dimensions mentioned earlier). After drying in air for at least 2 h, silver paint was applied, as mentioned earlier. The coating thickness was 0.3–0.4 mm after drying for both types of substrate, as measured by using a micrometer before and after coating.

The DC resistivity was measured using the Keithley 2001 multimeter and the four-probe method. In this method, four electrical contacts were applied by silver paint at four planes perpendicular to the length of the specimen ($75 \times 15 \times 15$ mm). The four planes were symmetrical around the midpoint along the length of the specimen, such that the outer contacts (for passing current) were 65 mm apart and the inner contacts (for measuring the voltage in relation to resistivity determination) were 55 mm apart.

3. Results and discussion

3.1. Graphite colloid as an admixture

Table 1 shows that the EMI shielding effectiveness (same as the attenuation upon transmission) increases significantly with increasing graphite content, whereas the attenuation upon reflection decreases slightly. This means that the graphite enhances the shielding effectiveness mainly by increasing the reflectivity.

The electrical resistivity is decreased by the graphite addition, but remains in the same order of magnitude. This implies that the graphite contents used are below the percolation threshold. In spite of this, the improvement of the shielding effectiveness due to the graphite is substantial.

Compared to 0.1-μm-diameter carbon filaments at a similar volume fraction [6], graphite (from graphite colloid) is less effective (22 vs. 35 dB at 1 GHz) for shielding, due to its size being large compared to the filament diameter, and is also less effective for lowering the resistivity (2×10^5 vs. 1×10^4 Ω cm), due to its particulate nature and consequent low aspect ratio. Compared to 15-μm-diameter carbon fibers

Table 1
Attenuation upon transmission (same as the shielding effectiveness), attenuation upon reflection and DC electrical resistivity of cement pastes with various graphite contents and of cement paste coated with graphite colloid

Graphite (vol.%)	Specimen thickness (mm)	Attenuation upon transmission (dB)		Attenuation upon reflection (dB)		Resistivity (10^5 Ω cm)
		1.0 GHz	1.5 GHz	1.0 GHz	1.5 GHz	
0	4.36 ± 0.37	4.00 ± 0.05	2.42 ± 0.07	4.95 ± 0.11	7.96 ± 0.30	8.2 ± 0.6
0.46	4.37 ± 0.23	10.31 ± 0.30	12.34 ± 0.17	4.01 ± 0.22	3.86 ± 0.26	2.3 ± 0.4
0.92	4.40 ± 0.38	22.31 ± 0.35	25.61 ± 0.22	3.89 ± 0.43	3.57 ± 0.35	1.6 ± 0.6
/	0.34 ± 0.11 *	14.26 ± 0.18	15.33 ± 0.15	4.86 ± 0.30	6.76 ± 0.38	/

Errors were based on measurement of six specimens of each type.

* Coating thickness. Substrate thickness is 4.33 ± 0.26 mm.

at a similar volume fraction [9], graphite (from graphite colloid) is more effective for shielding (22 vs. 15 dB at 1 GHz), due to its small particle size compared to the fiber diameter, but is less effective for lowering the resistivity (2×10^5 vs. 7×10^2 Ω cm), due to its particulate nature and consequent low aspect ratio. Hence, a high shielding effectiveness does not imply a high electrical conductivity.

The particulate nature of the graphite is expected to result in a high value of the percolation threshold (i.e., minimum volume fraction for attaining percolation), thereby diminishing the effectiveness for lowering the resistivity compared to carbon fibers or filaments. In spite of the poor effectiveness for lowering the resistivity, the graphite is effective for shielding, presumably due to the small particle size, the skin effect and the high crystallinity of the graphite.

3.2. Graphite colloid as a coating

Table 1 also shows the effect of the application of a graphite colloid (same as the colloid used as an admixture in Section 3.1) coating on the EMI shielding effectiveness of plain cement paste (i.e., cement paste without the graphite admixture). The coating is of thickness 0.34 ± 0.11 mm. It causes the attenuation upon transmission at 1 GHz to be increased from 4.0 to 14.3 dB, while having little effect on the attenuation upon reflection. Hence, the coated cement paste is as effective for shielding as cement paste containing graphite admixture in an amount between 0.46 and 0.92 vol.%, but is less effective for reflection than cement paste containing 0.46 vol.% graphite admixture. This means that graphite reflects better when it is dispersed in cement than when it is agglomerated, partly due to the skin effect and partly due to the electrical connectivity provided by the cement matrix, which is conductive. The high attenuation upon transmission for the coated cement paste is probably due to multiple reflections among the graphite particles in the coating.

The attenuation upon transmission and that upon reflection at 1 GHz are 10.8 and 4.1 dB, respectively, for graphite-colloid-coated Mylar, compared to corresponding values of 0.7 and 21.6 dB, respectively, for the bare Mylar substrate. Hence, the Mylar substrate contributes little to the shielding and the coating of thickness 0.3–0.4 mm is comparable in shielding effectiveness and reflectivity to cement paste of thickness 4.4 mm and containing 0.46 vol.% graphite admixture. However, the coating is much inferior to cement paste containing 0.92 vol.% graphite admixture.

Comparison between coated cement paste and coated Mylar shows that the coating on Mylar reflects better than that on cement paste. This may be due to the relative smoothness of the Mylar surface compared to the cement paste surface.

Although the graphite colloid coating on cement paste is quite effective for shielding and can be conveniently applied to existing structures, it suffers from its tendency to be damaged by scratching, wear and abrasion.

4. Conclusion

A water-based colloid of graphite particles of average size 0.7–0.8 μm is an effective admixture for enhancing the EMI shielding effectiveness of cement paste. The shielding effectiveness (1 GHz) is 22 dB at a solid graphite content of 0.92 vol.%, compared to 15 dB for 15-μm-diameter carbon fibers and 35 dB for 0.1-μm-diameter carbon filaments, both at similar volume fractions. The graphite as an admixture in cement increases the shielding effectiveness from 4 to 22 dB, while reducing the attenuation upon reflection from 5 to 4 dB. A coating of thickness 0.3 mm and made from the graphite colloid exhibits a shielding effectiveness of 11 dB—comparable to that of cement containing 0.46 vol.% solid graphite admixture. Cement paste with this coating exhibits a shielding effectiveness of 14 dB. Compared to carbon fibers and filaments, the graphite colloid as an admixture is ineffective for lowering the resistivity of cement.

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