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is impossible to restore those parameters from one measured $A_\varphi$ value. Extinction angles are ambiguous functions, as practically demonstrated [12]. However, as they are easy to obtain, it is reasonable to use them keeping in mind that they are not a useful parameter for any quantitative conclusions but for coarse estimations of the texture of deposits [2,4,5,12,13].

The main results of this study can be summarized as follows.

1. The discrepancy between the extinction angles of crystalline graphite and pyrolytic carbon deposits stems from the comparison of values measured for different material geometries. The use of the correct expressions obtained completely removes this disagreement.

2. The optical parameters of pyrolytic carbon deposits including the $A_\varphi$ value are defined by its texture approaching the ideal structure of graphite [13]. The calculated values for optical parameters of graphite are $A_\varphi = 17.9^\circ$ for a single crystal and $A_\varphi = 27.4^\circ$ for concentrically shaped deposits.

3. The analysis of the extinction angles indicated that although $A_\varphi$ values are easy to obtain, they are practically meaningless for any quantitative estimation of investigated systems as they are ambiguous functions of the optical parameters. However, the measurement of extinction angles can be convenient for a qualitative description. The modification of measurement methods for the determination of physically meaningful values will be proposed elsewhere [6].

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References


Coke powder as an admixture in cement for electromagnetic interference shielding

Jingyao Cao, D.D.L. Chung*

Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY 14260-4400, USA

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*Corresponding author. Tel.: +1-716-645-2593; fax: +1-716-645-3875.
E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

Petroleum coke is used as an electrode material for the production of aluminum [1], a sorbent for bitumen and naphtha [2], a collector for heavy metals [2], a raw
material for making graphite and steel, a fuel [3], an electrically conducting filler in concrete [4,5], polymer–concrete [6] or asphalt [7–10] overlays in cathodic protection of steel reinforcing bars in concrete, and an electrically conductive filler in concrete for deicing through resistance heating [11–13], in addition to other applications [14]. This paper provides a new application, namely the use of coke powder as an electrically conductive filler in concrete for electromagnetic interference (EMI) shielding.

EMI shielding [15–18] 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 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, a cement matrix allows electrical connectivity among the conductive filler units, even when the filler volume fraction is below the percolation threshold. Electrical connectivity helps shielding.

Due to their electrical conductivity and chemical resistance, carbons are suitable for use as an electrically conductive filler in composite materials. EMI shielding is one of the main applications of conventional short carbon fibers [19]. Due to the small diameter and the skin effect, carbon filaments (catalytically grown, of diameter 0.1 µm) are more effective at the same volume fraction in a composite than conventional short carbon fibers for EMI shielding, as shown for both thermoplastic [20,21] and cement [22,23] matrices. In this paper, filaments refer to those of diameter < 1 µm, whereas fibers refer to those of diameter 1 µm or more. Carbon filaments at 0.54 vol.% in a cement paste give an effectiveness of 26 dB at 1.5 GHz [22], whereas carbon fibers (isotropic pitch based, 3 mm long) at 0.84 vol.% in a mortarl give an effectiveness of 15 dB at 1.5 GHz [23]. The highest two values of EMI shielding effectiveness previously reported in cement–matrix composites are 40 dB, as attained in cement paste containing 1.5 vol.% carbon filaments [24], and 70 dB, as attained in cement paste containing 0.72 vol.% stainless steel fibers of diameter 8 µm and length 6 mm [25]. All these previous shielding effectiveness measurements and those of this paper were made with the same fixture and about the same sample thickness.

EMI shielding using carbons is mainly by reflection rather than absorption, due to the high reflectivity. The high radio wave reflectivity allows the use of a carbon–cement composite for lateral guidance in automatic highways [26].

This paper reports on the effectiveness of coke–cement composites for EMI shielding. Compared to carbons previously used as fillers for shielding, namely carbon fibers and filaments, coke is much less expensive. Compared to graphite, coke is less brittle due to its noncrystallinity, though it is less conductive. Moreover, coke’s particulate nature facilitates dispersion, in contrast to the fibers and filaments, which tend to cling together. On the other hand, coke powder has a much smaller aspect ratio than fibers or filaments and a large aspect ratio facilitates connectivity of the carbon filler in the composite. Because the electrical resistivity is a basic quantity that describes the electrical conduction behavior, this paper includes measurement of the electrical resistivity.

The cement used was portland cement (Type I) from Lafarge (Southfield, MI, USA). 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, USA) was used in the amount of 1.00% by mass of cement for all specimens. No aggregate was used, whether fine or coarse.

The petroleum coke powder was No. 9 carbon from Superior Graphite (Chicago, IL, USA) with a density of 2.1 g/cm³. At least 90% passed through 200 U.S. mesh. The coke powder was used as fillers for shielding, namely carbon fibers and filaments, coke is much less expensive. Compared to graphite, coke is less brittle due to its noncrystallinity, though it is less conductive. Moreover, coke’s particulate nature facilitates dispersion, in contrast to the fibers and filaments, which tend to cling together. On the other hand, coke powder has a much smaller aspect ratio than fibers or filaments and a large aspect ratio facilitates connectivity of the carbon filler in the composite. Because the electrical resistivity is a basic quantity that describes the electrical conduction behavior, this paper includes measurement of the electrical resistivity.

A rotary mixer with a flat beater was used for mixing. Cement, water and coke powder (if applicable) were mixed for 5 min. After pouring into oiled molds, an external electrical vibrator was used to facilitate compaction and decrease the number of air bubbles. The samples were demolded after 1 day and cured at room temperature (relative humidity = 100%) for 28 days.

The attenuations upon reflection and transmission were measured using the coaxial cable method [21]. 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 either 1.0 or 1.5 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 an annular ring of outer diameter 97 mm and inner diameter 28 mm. The sample thickness was measured for each specimen, but it was around 4.4 mm.

DC volume electrical resistivity was measured using a 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 perpendicular to the length of the specimen (150×12×11 mm). The four planes were symmetrical around the midpoint.
Table 1 shows the EMI shielding effectiveness (i.e., attenuation upon transmission) is greatly increased by coke powder addition. The increase of the shielding effectiveness with coke volume fraction becomes more gradual as the coke volume fraction increases beyond 1.02%. The shielding effectiveness reaches 49 dB (1.5 GHz) at 0.51 vol.% coke powder, in contrast to 38 dB (1.5 GHz) at 0.90 vol.% steel fibers (8 µm diameter) [25] and 35 dB at 1.02 vol.% carbon filaments [24]. Hence, coke powder is superior to carbon filaments, but inferior to steel fibers in the shielding effectiveness.

Table 1 also shows that the electrical resistivity is decreased by only one order of magnitude by coke powder addition. The main decrease occurs between 0 and 0.51 vol.% coke. Beyond 1.02 vol.% coke, the decrease is gradual. The percolation threshold is beyond 9.18 vol.% coke.

The resistivity is $4 \times 10^4 \ \Omega \ \text{cm}$ at 1.02 vol.% coke powder, in contrast to 40 Ω cm at 0.90 vol.% steel fibers (8 µm diameter) [25] and $1 \times 10^4 \ \Omega \ \text{cm}$ at 1.0 vol.% carbon filaments [24]. The resistivity is $7 \times 10^4 \ \Omega \ \text{cm}$ at 0.51 vol.% coke powder, in contrast to 38 Ω cm at 0.45 vol.% steel fibers (8 µm diameter) [25] and $1 \times 10^4 \ \Omega \ \text{cm}$ at 0.5 vol.% carbon filaments [24]. Hence, steel fibers are much more effective than coke powder or carbon filaments for decreasing the electrical resistivity of cement paste. Moreover, carbon filaments are slightly more effective than coke powder for decreasing the resistivity.

The high shielding effectiveness of cement paste containing steel fibers is consistent with its low electrical resistivity. Steel is much more conductive than carbon. The high conductivity makes the steel fibers outstanding for shielding, in spite of the large diameter compared to that of the carbon filaments.

Although carbon filaments are slightly more effective than coke powder for decreasing the resistivity, they are less effective than coke powder for shielding, in spite of their small diameter (0.1 µm). The lower resistivity rendered by carbon filaments is attributed to the high aspect ratio of the filaments and the importance of electrical conduction path connectivity for electrical conductivity. The higher shielding effectiveness rendered by coke powder may be due to better dispersion, as expected from its particulate nature.

In conclusion, coke powder is effective as an admixture in cement for EMI shielding by reflection mainly. It is more effective than carbon filaments (0.1 µm diameter), but less effective than steel fibers (8 µm diameter). Shielding effectiveness values of 45 and 49 dB are attained at 1.5 GHz by using coke powder at 0.51 and 1.02 vol.% respectively. Addition of coke beyond 1.02 vol.% gave little further gain in the shielding effectiveness or electrical conductivity. Coke powder is less effective than carbon filaments or steel fibers at similar volume fractions for reducing the electrical resistivity of cement paste.

References

Carbon fiber mats as resistive heating elements

Taejin Kim, D.D.L. Chung*

Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY 14260-4400, USA

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Continuous carbon fibers are widely used as reinforcement in lightweight structural composite materials, particularly polymer–matrix composites. A less expensive form of carbon fiber is short (discontinuous) fibers, which can be made into a porous mat by the use of a small amount of an organic binder. The fibers in a mat are usually randomly oriented in two dimensions. They are made by wet-forming, as in papermaking. Applications of carbon fiber mats include electromagnetic interference (EMI) shielding [1,2], lightning protection [2], electrical grounding, fuel cell electrodes, composite reinforcement [3,4] and deicing (i.e. using the mat as a resistance heating element [5], which can be incorporated in or on a structural composite). As many of these applications benefit from a high electrical conductivity, metal coated carbon fibers are often used for mats. A common metal for this purpose is nickel [2], due to its resistance to oxidation and corrosion.

Graphite has long been used as a heating element. In addition to graphite in monolithic form [6], pyrolytic graphite deposited on boron nitride has been used [7]. Furthermore, polymer–matrix composites containing carbon fibers [8] or carbon black [9], and carbon–matrix composites [10] have been used. Flexibility or shape conformability of the heating element is desirable for many applications, such as the deicing of aircraft [11,12] and the heating of floors, pipes and boilers. Carbon fiber mat is thus attractive. It is also attractive because it is in a sheet form, is corrosion resistant, and can be incorporated in a structural composite. In contrast, conventional graphite requires expensive machining to attain the shape required for the heating element. This paper evaluates the effectiveness of carbon fiber mats as heating elements. Although their use as heating elements has been briefly reported [5], evaluation of their effectiveness has received little attention.

This paper addresses a carbon fiber mat with bare fibers (no metal coating) and one with metal (Ni–Cu–Ni) coated fibers. The trilayer (Ni–Cu–Ni) form of the coating is a technologically common form which takes advantage of the low electrical resistivity of copper and the superior oxidation resistance of nickel.

*Corresponding author. Fax: +1-716-645-3875.
E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).