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Improving colloidal graphite for electromagnetic interference shielding using 0.1 μm diameter carbon filaments

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Colloidal graphite is fine graphite powder suspended in a liquid carrier (such as water and alcohol), together with a small amount of a polymeric binder. After application of colloidal graphite to a surface, the carrier evaporates, thus allowing the graphite particles to be essentially in direct contact with each other. The resulting coating is effective for electromagnetic interference (EMI) shielding. It is commonly used for shielding in the cathode ray tubes of televisions. In spite of this application and the growing demand of EMI shielding materials, there has been no report on the EMI shielding effectiveness of colloidal graphite, except for limited information in a commercial sales document [1]. Prior research on colloidal graphite has focused on its performance as a lubricant [2,3].

EMI shielding refers to the reflection and/or absorption of electromagnetic radiation by a material, which thereby acts as a shield against the penetration of the radiation. As electromagnetic radiation, particularly that at high frequencies (e.g. radio waves, such as those emanating from cellular phones) tends to interfere with electronics (e.g. computers), shielding of both electronics and radiation source is needed [4–12].

The primary mechanism of shielding is usually reflection. For reflection of the radiation by the shield, the shield must have mobile charge carriers (electrons or holes) which interact with the electromagnetic fields in the radiation. As a result, the shield tends to be electrically conducting, although a high conductivity is not required. However, electrical conductivity is not the scientific criterion for shielding, as conduction requires connectivity in the conduction path (percolation in the case of a composite material containing a conductive filler), whereas shielding does not. Although shielding does not require connectivity, it is enhanced by connectivity.

Metals are by far the most common materials for shielding. They can be in bulk and coating (by plating) forms [13,14]. Carbon materials are also effective for shielding [15], as reported for carbons in the form of composite materials [16–27] and flexible graphite [28].

Colloidal graphite in prior work has used graphite particles. However, the use of 0.1 μm diameter carbon filaments [29], which are catalytically made from carbonaceous gases such as methane, is attractive for shielding due to the small diameter and large aspect ratio. The small diameter is advantageous for formation of a stable colloid and for shielding (due to the skin effect). The large aspect ratio is advantageous for shielding and for enhancing the toughness of the resulting coating. The effectiveness of these filaments for shielding has been shown in polymer–matrix and cement–matrix composite materials [17,19,21,23]. This paper addresses the use of these filaments in combination with graphite particles to formulate colloids for use in shielding.

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 19A shielding effectiveness tester with its input and output connected to a Hewlett-Packard (HP) 8510A network analyzer [30]. 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

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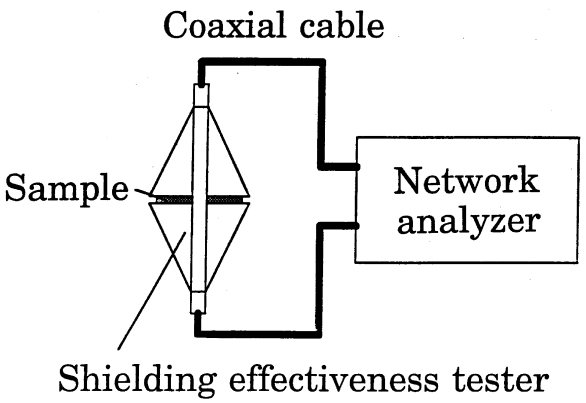

Fig. 1. EMI shielding effectiveness testing set-up.

diameter 97 mm and inner diameter 29 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 [30].

The DC volume electrical resistivity is a common fundamental property for material characterization, although shielding is an AC behavior. Therefore, the DC resistivity was measured using a 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. The four planes were symmetrical around the mid-point along the length of the specimen, such that the outer contacts (for passing current) were 80 mm apart and the inner contacts (for measuring the voltage in relation to resistivity determination) were 60 mm apart.

Colloidal graphite used in this work was a dispersion of 22 wt.% graphite particles of average size 0.7–0.8 μm in water, containing a starch-type binder (Grafo Hydrograf A M2; Fuchs Lubricant Co., Emlenton, PA, USA). Another colloidal graphite used was Electrodag EB-019 (Acheson Colloids Co., Port Huron, MI, USA), which was a dispersion of 27 wt.% graphite particles and 4 wt.% carbon black in water, without any binder. A polyvinyl alcohol binder (PVA, AIRVOL WS-53NF, Air Products & Chemicals, Allentown, PA, USA) was optionally used with the EB-019 colloid.

Carbon filaments used as an additive to colloidal graphites were 0.1 μm in diameter and >100 μm in length, as made catalytically from methane gas by Applied Sciences Inc. (Cedarville, OH, USA). The filaments had not been graphitized.

Carbon filaments in amounts of 15–35% by weight were added to colloidal graphites and mixed using a kitchen blender. The occurrence of some degree of filament breakage during the mixing was possible, but it had not been ascertained. The colloidal graphites without carbon filaments and with various contents of carbon filaments were applied to one side of a Mylar sheet (60 μm thick) which had been cut to be an annular ring of dimensions mentioned above. After drying in air for at least 2 h, silver paint was applied, as mentioned above. Mylar was chosen as the substrate material due to its electromagnetic transparency. The coating thickness was 0.3–0.4 mm after drying for all water-based colloids and was 0.1 mm after drying for the alcohol-based colloid.

Table 1 shows that the Mylar substrate contributes little to the shielding and that the EMI shielding effectiveness (same as the attenuation upon transmission) increases monotonically with increasing carbon filament content, while the attenuation upon reflection decreases. This means that the carbon filaments enhance the shielding

Table 1
EMI shielding effectiveness (same as attenuation upon transmission) and attenuation upon reflection at 1 GHz

Material on Mylar	Attenuation upon transmission (dB)	Attenuation upon reflection (dB)
None	0.7	21.6
Graphite colloid[a,d] without filament	1.5	11.6
Graphite colloid[a,c] without filament	11.2	3.9
Graphite colloid[a,c] with 15 wt.% carbon filaments	15.8	2.9
Graphite colloid[a,c] with 20 wt.% carbon filaments	18.9	2.0
Graphite colloid[a,c] with 30 wt.% carbon filaments	19.8	1.8
Graphite colloid[a,c] with 35 wt.% carbon filaments	24.2	1.3
Graphite colloid[b,c] without filaments	24.3	1.3
Graphite colloid[b,c] with 20 wt.% carbon filaments	37.1	0.9
Graphite colloid[b,c] with 30 wt.% carbon filaments	38.0	0.9
Graphite colloid[b,c] with 30 wt.% carbon filaments and PVA	30.0	1.0

[a] From Fuchs Lubricant Co.
[b] From Acheson Colloids Co.
[c] Water-based.
[d] Alcohol-based.

effectiveness at least partly by increasing the reflectivity. This applies to both graphite colloids.

The alcohol-based graphite colloid from Fuchs is much inferior to the water-based graphite colloid from Fuchs, due to the smaller thickness after drying for the former coating. The water-based graphite colloid from Acheson is superior to that from Fuchs for shielding, as shown by a higher attenuation upon transmission and a lower attenuation upon reflection in the absence of carbon filaments. This difference may be related to the binder, which presumably affects the degree of direct contact between adjacent graphite particles in the coating after drying.

The shielding effectiveness increases with carbon filament content up to 35 wt.% for the Fuchs water-based colloid, but up to only 20 wt.% for the Acheson water-based colloid. Nevertheless, the highest shielding effectiveness attained in this work with the help of carbon filaments is greater for the Acheson colloid than the Fuchs colloid. The highest value attained is 38 dB at 1 GHz.

The addition of the PVA binder to the Acheson water-based colloid with 30 wt.% carbon filaments diminishes the shielding effectiveness from 38 to 30 dB. This means that the binder hinders the direct contact between the conductive filaments and particles in the coating. However, the binders help the mechanical integrity, as shown by simple manual bending testing and visual observation of the damage.

The superior performance of the Acheson colloid (whether with or without PVA) compared to the Fuchs colloid, both containing carbon filaments, is probably due to the difference in binder type and quantity and the consequent difference in the degree of direct contact between adjacent filaments in the dried coating. Due to the proprietary nature of these compositions, scientific confirmation of this notion is difficult.

In summary, the EMI shielding effectiveness of colloidal graphite was improved by the combined use of graphite particles and 0.1 μm diameter discontinuous carbon filaments. The addition of 30 wt.% carbon filaments to a commercial graphite colloid increased the shielding effectiveness from 11 to 20 dB for a Fuchs water-based graphite colloid with a starch-type binder, and from 24 to 38 dB for an Acheson water-based graphite colloid without binder. The addition of a PVA binder to the latter decreased the shielding effectiveness from 38 to 30 dB, though it improved the mechanical integrity. The improvement in shielding was at least partly due to an increase in reflectivity. The attenuation upon reflection decreased monotonically with increasing carbon filament content, while the attenuation upon transmission increased monotonically.

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